

DDT Residues in Mountain Stream Water as Influenced by Treatment Practices¹

ALFRED R. GRZENDA,² H. PAGE NICHOLSON,² JOHN I. TEASLEY,² and JAMES H. PATRIC³

ABSTRACT

During 1961 and 1962, a mountainous 4000-acre oak-hickory forest watershed was sprayed with DDT to control the elm spanworm, *Ennomos subsignarius* (Hübner). The sprayings were made over the entire basin by fixed-winged aircraft in 1961. The next year sprayings were made by helicopter and were restricted to 2000 acres of upper slopes and ridges.

DDT residues were noted in stream water when the entire basin was sprayed in 1961. The highest concentration of DDT recovered (0.346 parts per billion) was observed

in a sample taken during treatment. The minimum concentration (0.005 parts per billion) was noted 2 months after application, in the last sample collected. The following year, when only 49% of the basin was sprayed, no DDT residues were noted in stream water and suspended sediment samples collected over a 7-month period. The results of this study and other investigations indicate that the probability of DDT occurring as stream contaminant is greatly reduced by its use in controlled spot-applications.

The Coweeta Hydrologic Laboratory is a 4000-acre oak-hickory forest watershed maintained by the U. S. Forest Service for the purpose of hydrological research. It is situated in the Nantahala Mountains near Franklin, North Carolina. The watershed perimeter is characterized by sharply rising slopes where the elevation drops as much as 1500 ft in a horizontal distance of about 1.25 miles.

In 1960 an egg-mass survey indicated that an infestation of the elm spanworm, *Ennomos subsignarius* (Hübner), a hardwood defoliating insect, was a serious threat to the following year's foliage. To provide for the continuity of forest hydrological investigations spanning almost 3 decades, the Forest Service initiated a control program.

MATERIALS AND METHODS.—Control Practices.—In 1961 fixed-winged aircraft treated the entire watershed with a 12% DDT-oil solution (No. 2 fuel) discharged at a rate of 0.89 lb technical per acre. The applications were made on May 28, 29, and 31. On June 19 a helicopter sprayed a 30-acre unit previously missed. It was treated with a 6% DDT-oil solution at a rate of 0.5 lb technical per acre. In 1962 helicopters applied a 6% DDT-oil solution at 0.5 lb technical per acre over 2000 acres. Sprayings were restricted to the ridges and upper slopes and were made from May 16–20. Actual rates of deposition on the forest canopy and floor were not determined. The areas sprayed and the watershed drainage patterns are shown in Fig. 1. The miles of streams present in the treated areas are given in Table 1.

Sample Collection.—Coweeta Creek, which receives drainage from the entire Coweeta Laboratory, was sampled at a point just outside the downstream boundary of the sprayed area. Stream water was sam-

pled by the carbon adsorption method described by Rosen and Middleton (1959). This procedure involves the passage of a large quantity of water through a 3×18-in. column packed with 400(±5) g of activated carbon. Subsequently, the carbon is air dried and then extracted for 24-hr in a Soxhlet apparatus. The extract is purified by column chromatography through florisil prior to analysis. The specifics of these procedures are given by Nicholson et al. (1964).

In 1961 carbon adsorption samples were collected at a flow rate of 1/2 gallons per minute (gpm), and sample sizes varied from 1296 to 6515 gal. Within sampling periods the collecting device was permitted to operate continuously during the 3- to 8-day period required to obtain a sample. Although stream turbidity seldom exceeded 24 Jackson Candle units,⁴ the sampling unit frequently became clogged with near-colloidal detritus. By August 1961, the problem became so acute that sampling was halted for the year.

In 1962 the sampling device was modified to avoid difficulties experienced the previous year. The flow rate was reduced to 1/4 gpm. During the first 5 sampling periods, as in 1961, the sampling device was operated continuously. Thereafter it was in operation for three 180-min intervals each day (5–8 AM, 1–4 PM, 9 PM–12 AM) until the desired gallonage was obtained. A semipermanent sand filter normally found on the water line leading to the carbon column was removed and replaced with a Cuno wool filter designed to remove particles larger than 25μ. The Cuno filter, depending upon the detrital content of the water, was changed from 1 to 3 times per sampling period. The filters used during each sampling period were pooled, ground, and then extracted with a mixture of petroleum ether and acetonitrile. The extract was analyzed for DDT to investigate possibility of in-

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² U. S. Department of Health, Education and Welfare, Public Health Service, Division of Water Supply and Pollution Control, Southeast Water Laboratory, Athens, Georgia.

³ U. S. Department of Agriculture, Forest Service, Coweeta Hydrologic Laboratory, Dillard, Georgia.

⁴ A Jackson candle unit is an arbitrary unit associated with the Jackson Turbidometer. The units are based on the depth of a water column required to make the image of the flame from a standard candle disappear when viewed vertically (Welch 1948). Candle units values of 25 or less are associated with natural waters of low turbidity.

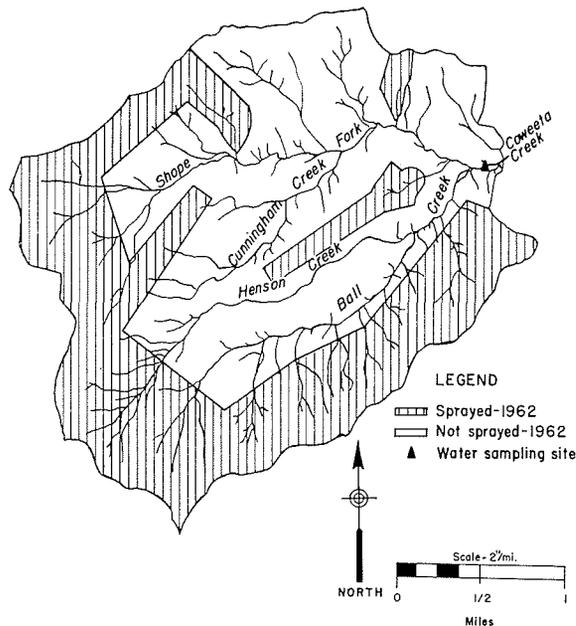


FIG. 1.—The drainage pattern of the Coweeta Laboratory showing the area sprayed in 1962. The entire basin was sprayed in 1961.

secticide transport associated with suspended detritus. The pooled samples, with the exception of 2 (about 2500 gal), represented the detritus removed from 816 to 1625 gal of stream water.

The sampling technic in 1962 also differed in that 2 carbon adsorption columns were attached in series to determine if 1 carbon column, such as used in 1961, was adequate to achieve the removal of detectable quantities of DDT.

Analytical Techniques.—Initial analysis in 1961 utilized infrared spectroscopy, paper chromatography (Mitchell 1957), and fish bioassay using the fathead minnow (*Pimephales promelas*). The presence of DDT was indicated only by bioassay as evidenced by the death and response of fish in water solutions containing sample extract. Early in 1962 an IR instrument of substantially greater sensitivity than that used in 1961 was obtained. The threshold of DDT detectability for this instrument is estimated at about 50 μ g. Later that year a microcoulometric gas chro-

Table 1.—The drainage characteristics of the treated and untreated areas of the Coweeta Hydrologic Laboratory.

Year	Area (square miles)		Miles of streams		Stream density (miles/square mile)	
	Treated	Untreated	Treated area	Untreated area	Treated area	Untreated area
1961	6.3	0 ^a	38.0	—	6.1	—
1962	3.1	3.2	14.5	23.5	4.7	7.1

^a The entire basin was sprayed in 1961.

matograph capable of detecting as little as 50 nanograms of DDT was acquired. All residues remaining from 1961 and early 1962 were re-analyzed by this method. The samples collected after mid-June 1962 were analyzed by gas chromatography only. A general discussion of microcoulometric gas chromatography is given by Cassil (1962) and the specific techniques and instrumentation used in this study are reported by Nicholson et al. (1964).

RESULTS.—Carbon Adsorption Samples.—In 1961, the year the entire watershed was sprayed, all the carbon adsorption samples collected from May 28 to August 1 contained DDT residue (Table 2). The highest concentration recovered (0.346 ppb) was noted during the spraying period. Subsequent samples contained consistently lower quantities of DDT. The minimum concentration recovered (0.005 ppb) was observed in a pooled sample collected from July 19 to August 1. The sampling device was not operating continuously during these dates because of clogging by suspended detritus. This necessitated the use of 2 carbon columns. These were extracted and the residues pooled for DDT analysis.

A log-log plot of the data (DDT recovery versus accumulative discharge) shown in Table 2 for 1961

Table 2.—The recovery of DDT from carbon adsorption samples collected from Coweeta Creek, North Carolina.

Collection period	Stream discharge, millions of gallons		DDT recovered
	For period	Accumulative total	Parts Per billion
1961			
May 28-31	34.2	34.2	0.346
May 31-June 4	33.0	67.2	.217
June 4-8	37.5	104.7	.080
June 8-19	116.2	220.9	.033
June 19-23	108.1	329.0	.020
June 23-July 3	63.8	392.8	—
July 3-10	64.4	457.2	.019
July 10-18	75.7	532.9	.010
July 18-19	3.1	536.0	—
July 19-Aug. 1	192.4	728.4	.005
1962 ^b			
May 16-17	15.4	15.4	0 ^a
May 17-19	21.3	36.7	0 ^a
May 19-21	20.3	57.0	0
May 21-23	20.0	77.0	0
May 23-26	30.1	107.1	0
May 26-June 1	55.8	162.9	0
June 1-8	79.1	242.0	0 ^a
June 8-15	83.8	325.8	0 ^a
June 15-22	61.5	387.3	0
June 27-July 5	55.1	442.4	0
July 5-12	49.3	491.7	0
July 12-19	38.4	530.1	0
July 19-26	33.7	563.8	0
July 26-Aug. 2	33.4	597.2	0
Aug. 2-Nov. 23 ^c	57.1-118.1 ^d	1,084.8	0

^a Determinations made by infrared analysis only. Other data are the results of microcoulometric gas chromatography.

^b The analytical results indicated for 1962 are the results of individual analyses made on 2 carbon columns attached in series for each sampling period.

^c Nine carbon adsorption samples were collected during this period. Microcoulometric gas chromatography indicated the absence of DDT in all samples.

^d These data represent the range in discharge noted for the 9 individual collection periods made during the indicated time span.

results in a straight line. Fitting the line by visual inspection and computing the slope the equation for the regression becomes:

$$Y = 46,000 X^{-1.34}$$

where Y = DDT recovery as indicated by the carbon adsorption method (parts per trillion)
X = Accumulative discharge (millions of gal)

However, this equation should not be used for accumulative discharge measurements less than 34 million gal because this portion of the regression was constructed by extrapolation to estimate the intercept on the Y-axis.

In 1962, the year of controlled spot-spraying, sampling was carried on from mid-May to approximately 1 month after the fall of leaves from deciduous hardwoods (mid-November). Two standard carbon columns were linked in series to the line delivering the stream water. As shown in Table 2 neither the proximal (in relation to the direction of water flow) nor the distal carbon column for any sampling period contained detectable quantities of DDT.

Both spray concentration and method of application contributed to DDT recovery in stream water during 1961. The Coweeta basin narrows and drains from west to east (Fig. 1). As the spray plane flew from west to east at higher-than-planned altitudes, the flights tended to converge over the narrow east side. Post-flight examination of oil-sensitive cards showed that the widest streams nearest the water sampling unit were sometimes sprayed up to 3 times with the more concentrated DDT (1 lb technical/gal). In contrast, during 1962 less concentrated DDT (0.5 lb technical/gal) was placed evenly on the ridges by low-flying helicopters. These headwater streams were both narrower and less dense, exposing far less water surface to spray.

DDT Recovery from Carbon Adsorption Samples.—Laboratory experiments were conducted to estimate the overall recovery of DDT from carbon adsorption samples. Batch dosing of water stored in vessels was judged unsatisfactory because Bowman et al. (1959) reported that a large proportion of DDT added to water in glass or metal containers is lost by sorption within minutes after introduction. Therefore, a micro-pump was used to inject an acetone solution containing 1 µg of DDT/ml into a line delivering tap water to a carbon column at the rate of 1/2 gpm. The injection point was located 6 in. from the carbon column. A total of 100 µg of DDT was allowed to reach the carbon column at a constant rate over a 100-min period.

This was repeated with 3 carbon columns and the recoveries indicated by gas chromatography after extraction and clean-up were as follows: 83, 86, and 106 µg of DDT. Gallon grab samples were taken from the carbon column effluent at the start and the end of each trial. All grab samples were negative for DDT. The minimum level of detectability for the grab samples was about 0.050 ppb.

Wool Filters.—Gas chromatography showed that unused filters (the controls), as obtained from the manufacturer, commonly contained dieldrin (26–280 µg). This fact is not surprising, since the filters are made of reprocessed wool of various origin and woolen products frequently contain dieldrin residues (Coulson 1962). However, the dieldrin residues did not in-

terfere with the field use of the filters or in subsequent analysis for DDT.

The collection periods for the wool filter samples are the same as those indicated for the carbon adsorption samples in 1962 (Table 2). The filters collected from May 16–26 (5 sampling periods) and June 1–8 were analyzed by IR spectrophotometry only. Two samples collected from 26 May–1 June and June 8–15 were analyzed by the IR technique and gas chromatography. The remaining determinations were made by gas chromatography only. None of the samples contained detectable quantities of DDT.

DISCUSSION.—The 1961–62 Coweeta sprayings show that the potential of DDT as a stream contaminant is greatly reduced by its use in controlled spot-applications. Other investigations indicate that, in the case of spot applications, DDT is considerably less likely to occur as a stream contaminant than toxaphene or benzene hexachloride. Nicholson et al. (1964), in a study of a 400-square-mile watershed, found that toxaphene, DDT, and benzene hexachloride (in that order) were the most commonly used insecticides for the control of cotton pests. The insecticides were formulated primarily as dusts and applied almost solely by ground equipment. These workers noted toxaphene and benzene hexachloride in all carbon adsorption samples collected more or less continuously from 1959 through 1962 at a site receiving drainage from the entire basin. DDT was not detected, even though it was consistently used in quantities about 7 times as great as gamma benzene hexachloride. In the 1962 spot-treatment of the Coweeta Laboratory a greater proportion of the total watershed area was treated (49%) with DDT than in the agricultural basin (2.8–3.9%). However, in the agricultural basin, applications were made over a longer period (3 months vs. 4 days) and at a higher total dosage rate (3.9–6.8 vs. 0.5 lb technical DDT/acre).

Bowman et al. (1960) reported that the solubility of DDT in water at 25°C is 1.2 ppb or less. In contrast, the solubility of benzene hexachloride, depending upon the isomer, varies from 5 to 10 ppm at 25°C (Slade 1945). Cohen et al. (1960) report that the solubility of toxaphene at 25°C is 0.4 ppm. Bowman et al. (1959) show that DDT is rapidly and strongly sorbed on a variety of substrates. Hence, it would be expected that DDT would have less potential as a run-off contaminant than either benzene hexachloride or toxaphene.

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