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Carbon Removal of Organohalides in Drinking Water

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CARBON REMOVAL OF ORGANOHALIDES IN DRINKING WATER

BY

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RESEARCH REPORT

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ABSTRACT

Drinking water samples provided by Orlando Utilities from various locations and from Florida Technological University were analyzed for organohalides. Compounds tentatively identified were 0.0024 mg/l DDT, 0.003 mg/l phosdrin, 0.00036 mg/l BHC, and 0.000095 mg/l endosulfan. These concentrations are well below recommended limits for drinking water.

Two water samples were mixed with 10 mg/l of 20-40 mesh granular activated carbon, agitated for 2 minutes and then allowed to settle in the flask for 45 minutes. A reduction in the organohalide concentration varied from 25 to 98 percent of the original concentration. Also, a solution of seven common pesticides of 0.1 mg/l each were mixed with 1, 5, 10, 25, and 50 mg/l of carbon. The results indicate a reduction of 99 percent or better for all pesticides with 5 ppm carbon concentration.

Director of Research Report

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CHAPTER I

INTRODUCTION

National news media reports of potentially harmful chlorinated hydrocarbons in drinking water have caused a lot of concern during the last several years. The United States Environmental Protection Agency (EPA) has documented the harmful effects of many of these compounds in their List of Publications (U.S. Environmental Protection Agency, 1975) compiled by the Office of Pesticide Programs. This has caused some worry as to what the extent of occurrence of these compounds is and what the effects of the chlorinated hydrocarbons in drinking water are on human health.

Several studies have been made linking these chemicals to the cancer rate in the New Orleans area (Epstein, 1974; Vermeij, 1974) and one report (Dowty, et al., 1975) showed that some of the chlorinated compounds found in the New Orleans drinking water were being concentrated in the blood of New Orleans' residents. Besides the possibility of being carcinogens the ingestion of most of these compounds results in poisoning symptoms that are similar in nature but differ in

severity. These symptoms can range from headaches, dizziness, gastrointestinal disturbances, numbness and weakness of the extremities, apprehension, and hyperirritability for mild cases to muscular fasciculations followed by muscle spasms which can lead to convulsions and death for more severe cases. The severity of the symptoms appears to be a direct consequence of the concentration of the chlorinated compounds in the nervous system and primarily in the brain (Dale et al., 1963).

However, to date, there has been no conclusive experimental data to support claims that the chlorinated organics at the levels present in drinking water are harmful (Morris, 1975). It has even been suggested that this class of compounds is suspect because the technology that has developed with gas chromatography is able to detect them at very low concentrations. Thus they can be detected while other potentially harmful chemicals, though possibly present at equal concentrations, are not detected. However, a hazard might exist since many of these compounds are not metabolized by the body but are accumulated in the fatty tissues and thus concentrated.

It should also be noted that there are other constant sources of these materials in the environment besides drinking water. Seiber, Woodrow, Shafik, and Enos (1974) have reported recent increases in pesticide

levels in the air at remote locations of three to one hundred times the previously measured levels. Also, pesticide residue levels in soil have been increasing (Crockett et al., 1974). Due to plant uptake of these chlorinated substances they may be finding their way to the dinner table in vegetables and meat. The concentration of these compounds and their residues through accumulation plus the alternate sources of exposure are extremely important and must be taken into account when establishing safe, pesticide concentration limits for drinking water.

It appears that there are four possible sources of chlorinated compounds in drinking water. These consist of the chlorination of sewage effluents, the chlorination of drinking water, industrial pollution, and non-point sources such as rainfall containing the constituents of atmospheric pollution and runoff containing pesticides and other agricultural chemicals.

The chlorination of sewage effluents and drinking water may result in the chlorination of any organic materials that may be present. In the case of sewage effluents it should be recognized that it is quite possible for treated effluents to find their way into drinking water sources and is not at all an uncommon

occurrence. Currently, drinking water chlorination is known only to cause the formation of chlorophenols and chlorinated methanes such as chloroform. However, Bellar, Lichtenberg, and Kroner (1974) of the EPA are currently researching this subject and they report that since there are an almost infinite number of organic compounds, it is readily possible that many of these may, under water treatment conditions, react with the free chlorine that is introduced during chlorination. Their research indicates that these compounds do not constitute an immediate threat to public health but that research into what the long term effects of these compounds are on human health is needed.

For municipalities located along the major rivers of the United States, industrial pollution is considered to be the major source of chlorinated hydrocarbons in drinking water. Both accidental spillages and intentional discharges contribute heavily to this class of pollution. The Federal Water Pollution Control Act (Public Law 92-500), which now requires issuance of new source National Pollutant Discharge Elimination System (NPDES) permits, should check this type of pollution and eventually greatly reduce it.

The ability of activated carbon to absorb organic materials has made it useful in removing tastes and odors

of organic origin in the treatment of drinking water. It has been used in drinking water treatment systems with taste and odor problems since 1930 (Fair, Geyer, and Okum, 1971), but it has never received widespread usage beyond that particular application in the treatment of drinking water. It has, however, been successfully used for removing small amounts of organic material from secondary wastewaters undergoing tertiary treatment (Slechta and Culp, 1967; Culp, 1968).

To date, very little work has been done specifically on the removal of pesticides or other chlorinated organics from drinking water by the use of activated carbon. Moergeli (1972) investigated the removal of the pesticide lindane by various water treatment processes and found that ozonation and rapid sand filtration had little effect on the lindane concentration. However, he found that activated carbon was able to suitably remove the lindane and showed that removal characteristics varied with the type of activated carbon used.

An earlier study by Robeck, Dostal, Cohen, and Kreissl (1965) investigated the removal of several common pesticides from drinking water by coagulation, oxidation with chlorine, chlorine dioxide, ozone, and potassium permanganate, and by activated carbon. Their results show that coagulation with iron salts or alum was

effective only in removing DDT and that while ozone and chlorine dioxide were able to oxidize some of the pesticides, the products of oxidation were in some cases more toxic than the pesticides oxidized. The work with activated carbon showed that it was effective in reducing the concentrations of all of the pesticides tested, but that the dosages required for a 90 percent removal of the pesticides varied somewhat with the pesticide being tested.

On the basis of this data plus some obtained from similar testing, Sigworth (1965) concluded that a carbon dosage of about 10 ppm would effect a 90 percent removal of most of the common pesticides. For percent removals greater than 90 percent, Sigworth predicts that high and possibly massive dosages of activated carbon would be necessary.

Gas chromatography using an electron capture detector has been very successful in detecting these trace concentrations of chlorinated hydrocarbons. It also detects and measures other compounds but is much more sensitive to halogenated compounds due to the nature of the electron capture detector. This detector sets up an electron flux across a cell located at the outlet of the gas chromatography column and the instrument records changes in this flux which are proportional to the

concentrations of the materials leaving the column. Electron deficient compounds such as those that contain halogen atoms are highly capturing and thus readily change the electron flux even at very low concentrations (for many chlorinated compounds only a fraction of a picogram is necessary for detection).

The separation of the compounds present in a sample is done in the chromatography column on the basis of their affinity for two different states. In the gas chromatography column the two states or phases are gas and liquid. The carrier gas flows over a solid support (the column packing) that is coated with a liquid that constantly absorbs and desorbs the components of the sample. Each component has a unique partitioning coefficient and is thus carried along the column at a unique velocity under a given set of conditions. As a result of this the components elute from the column as distinct, separate bands (provided the values of the partitioning coefficients differ by a reasonable amount) and the detector measures the amount of each component as it elutes. This is represented graphically on a chromatogram which plots changes in the electron flux against time.

Objectives

The experimental work for this project was done in two stages in order to accomplish two major, independent objectives.

The first objective was to determine the occurrence of organohalides in the drinking water of the Orlando, Florida area. In order to do this nine water samples, eight of them provided by Orlando Utilities from various locations and one sample of the drinking water at Florida Technological University, were analyzed by gas chromatography for chlorinated organics using a technique designed for this (EPA, 1974). This analysis was done to provide the number of compounds of this nature present, an indication of their relative concentrations, and to allow tentative identification of a few of the compounds by comparing their relative retention times (relative to aldrin) with those of a set of standards that have been run on the FTU gas chromatograph.

The second part of the experiment was done to determine the effects of treating waters containing organohalides with activated carbon. To do this a sample of distilled water was spiked with several pesticides (chlorinated hydrocarbons) and then treated with varying amounts of activated carbon under identical conditions. Also the two samples of Orlando drinking water with the highest

organohalide concentrations were treated with a reasonable dosage of activated carbon. For this a batch treatment process was chosen. The process was designed to simulate the conditions of flash mixing and subsequent sedimentation and filtration in an actual water treatment plant.

CHAPTER II

EXPERIMENTAL PROCEDURE

The method used for determining the presence of chlorinated hydrocarbons and other organohalides consisted of extraction of the organic compounds from the water into hexane, evaporation of the hexane to increase the concentration of the organic contaminants, and detection of the extracted compounds using gas chromatography.

Extraction of Hydrocarbon

The following procedure was used for the eight Orlando Utilities samples, which consisted of seven tap water samples and one well water sample, and the FTU environmental laboratory tap sample.

The extraction of the hydrocarbon contaminants into hexane was accomplished by shaking 2000 ml of each sample with 150 ml of a hexane-methylene chloride mixture (the methylene chloride was added to enhance the solubility of some organohalides in hexane). The mixture used was 15 percent methylene chloride by volume. Each sample was shaken for 10 minutes on an electric shaker and then the hexane was separated from the water by using a separatory

funnel. Between 10 and 15 minutes were allowed for each separation. This process was carried out three times so that a total of 450 ml of the hexane mixture were collected for each sample. The hexane mixture was then dried by pouring it through a sodium sulfate filter. The sodium sulfate filters were regenerated by drying them overnight in an oven at 103 degrees centigrade.

The hexane-methylene chloride mixture was evaporated in a Kuderna-Danish apparatus utilizing a Snyder column. Boiling water was used as a heat source. This method would not evaporate to less than about 15 ml. Upon reaching this point the hexane mixture was further evaporated to between 3 and 10 ml by blowing dry nitrogen across its surface. At this time the samples were transferred to clean sample tubes, sealed, and then frozen until it was time to run them through the gas chromatograph.

Calibration and Detection

The samples were run on a Hewlett Packard model 5750, research gas chromatograph using a five foot, glass column with an inside diameter of 2mm. The column used was a 3 percent DC-200, 100/120 Chrom Q type. This column was used in conjunction with a tritium electron capture detector using a pulse interval of 150 microseconds.

A gas mixture of 95 percent argon and 5 percent methane was used as the carrier gas. The carrier gas was fed into the chromatograph at pressures of 40 to 50 psi and a flow through the column of approximately 22.7 ml per minute was maintained. Temperatures used were 228-229 degrees centigrade for the injection port, 199 degrees centigrade for the column oven, and 200-210 degrees centigrade for the electron capture detector. The size of the samples injected into the gas chromatograph varied from 4 to 5 microliters. Forty minutes were allowed for the elution of each sample.

Each time the gas chromatograph was used a calibration run with a known amount of aldrin was made along with a run on the solvent to check for impurities. Also, a sample of distilled water was extracted and analyzed as a control sample.

Carbon Adsorption

Two sets of samples were run to determine the effects of activated carbon treatment. The treatment used consisted of vigorously shaking a measured dosage of activated carbon with the sample in a closed container for two minutes and then allowing it to settle out for forty-five minutes. The sample was then separated from the activated carbon by filtering.

The first set of samples, which was run to determine the effects of activated carbon treatment on actual drinking water from the central Florida area, consisted of two of the Orlando Utilities samples (Kuhl and Kirkman tap samples). Each of these samples were divided into two 1000 ml samples, one of which was treated with 10 ppm of activated carbon while the other was not treated at all with activated carbon. All of these samples were then extracted with 150 ml of hexane three times.

The second set of samples were taken from a mixture prepared by dissolving 0.0002 grams each of heptachlor, chlordane alpha, chlordane gamma, o'p'-DDT, p'p'-DDT, endrin, and methoxychlor in 2 liters of distilled water to give 0.1 ppm of each. From these two liters six sampleas of 200 ml apiece were drawn and treated with dosages of 0, 1, 5, 10, 25, and 50 ppm of 20-40 mesh, granular, activated carbon. After treatment, 100 ml of each sample was extracted three times using 50 ml of hexane for each extraction.

All of the samples dealing with carbon adsorption were evaporated as previously described to less than 5 ml and then brought up to 5 ml by the addition of clean hexane. Five microliters of each sample were run on the same gas chromatograph and column described earlier. The

same settings were used except for the following differences. The column oven temperature range was 192-195 degrees centigrade, the injection port temperature was 220-221 degrees centigrade, and the electron capture detector temperature range was 205-208 degrees centigrade. The carrier gas inlet pressure was maintained at 50 psi.

Two other deviations from the procedure used for the Orlando Utilities samples were that all glassware was rinsed with chromic acid before being used instead of being rinsed with clean hexane and the sodium sulfate filters were not reused after being regenerated. Another distilled water control sample was run to check the effects of these changes on laboratory contamination.

CHAPTER III

EXPERIMENTAL RESULTS

The collected and calculated data is tabulated on the following pages. Along with the tables, reproductions of chromatograms obtained from this experiment are included in this section. Peaks numbered in the tables are labeled accordingly in the illustrations.

The chromatograms of the samples used to determine the occurrence of organohalides (Orlando Utilities samples and the FTU environmental lab tap sample) were reproduced at sensitivity settings that would allow all peaks to remain on scale. These settings are given above the accompanying data tables. The chromatograms reproduced for the samples run to determine the effects of activated carbon treatment, however, are all shown at a sensitivity setting of 10^2 x 8 so that they can be easily compared with each other. Peak heights for off scale peaks in this section were obtained by rerunning the samples at less sensitive machine settings and then multiplying the heights obtained to make them consistent with a setting of 10^2 x 8.

A chart speed of 0.25 inches per minute was used

for all of the chromatograms and the left hand border of each of the illustrated chromatograms is equal to time zero. The chromatograms then proceed from left to right. Because of their length, most of the chromatograms are divided into two parts with the second half being located above the first half and to the right side of the illustration. The Martain tap sample chromatogram had to be broken into three parts due to rezeroing the pen to prevent it from going off scale in the negative direction. However, except for the break occurring at 1.5 inches into the run, it is read in the same manner as the other chromatograms.

Each data table given is also accompanied by a concentration factor. The first number given is the volume of the water sample used for the extraction and the second number is the volume of the extract after evaporation. Thus a factor listed as 2000 ml/4.0 ml would mean that the organics extracted from a 2000 ml water sample were contained in 4.0 ml of hexane and that theoretically the concentration of the organics in the original sample had been increased in the extract by a factor of 2000/4 or 500.

Aldrin was used to calibrate the chromatograms and all relative retention times are based on the retention time of aldrin.

Abbreviations used in the tables are explained in Appendix 1.

TABLE 1: Kuhl Tap Data

Sample Size: 4 ul

Concentration Factor: 2000 ml/5.4 ml

Sensitivity Setting: 10^2 x 32

Calibration: Aldrin (5 ul) RT--336.84 sec.

Ht--211 mm per 200 pg at 10^2 x 32

Peak	RT (sec)	RRT	Ht (mm)
1	49.69	0.148	31
2	78.20	0.232	39
3	185.24	0.550	19
4	379.12	1.126	219
5	1029.62	3.244	4
6	1470.18	4.365	-3
7	2289.82	6.798	24

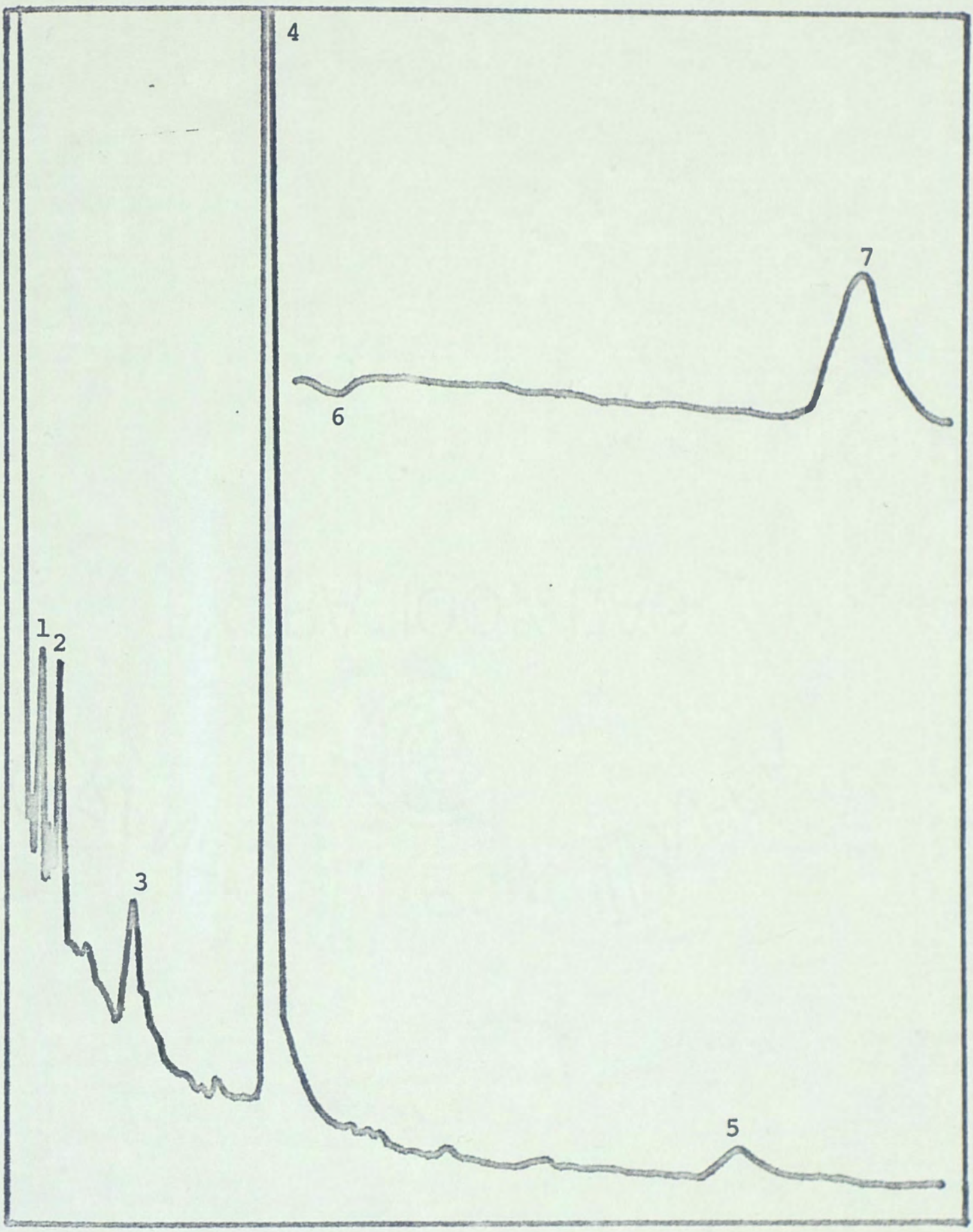

Figure 1. Chromatogram of Kuhl Tap Sample

TABLE 2: Kirkman Tap Data

Sample Size: 4 ul

Concentration Factor: 2000 ml/3.9 ml

Sensitivity Setting: 10^2 x 32

Calibration: Aldrin (5 ul) RT--345.03 sec

Ht--214 mm per 50 pg at 10^2 x 8

Peak	RT (sec)	RRT	Ht (mm)
1	119.21	0.346	39
2	144.00	0.417	17
3	200.05	0.580	33
4	225.93	0.655	78
5	312.22	0.905	34
6	382.58	1.109	159
7	525.00	1.522	7
8	792.55	2.297	5
9	933.00	2.704	4
10	1093.95	3.171	4
11	1459.98	4.231	-5
12	2289.85	6.637	4

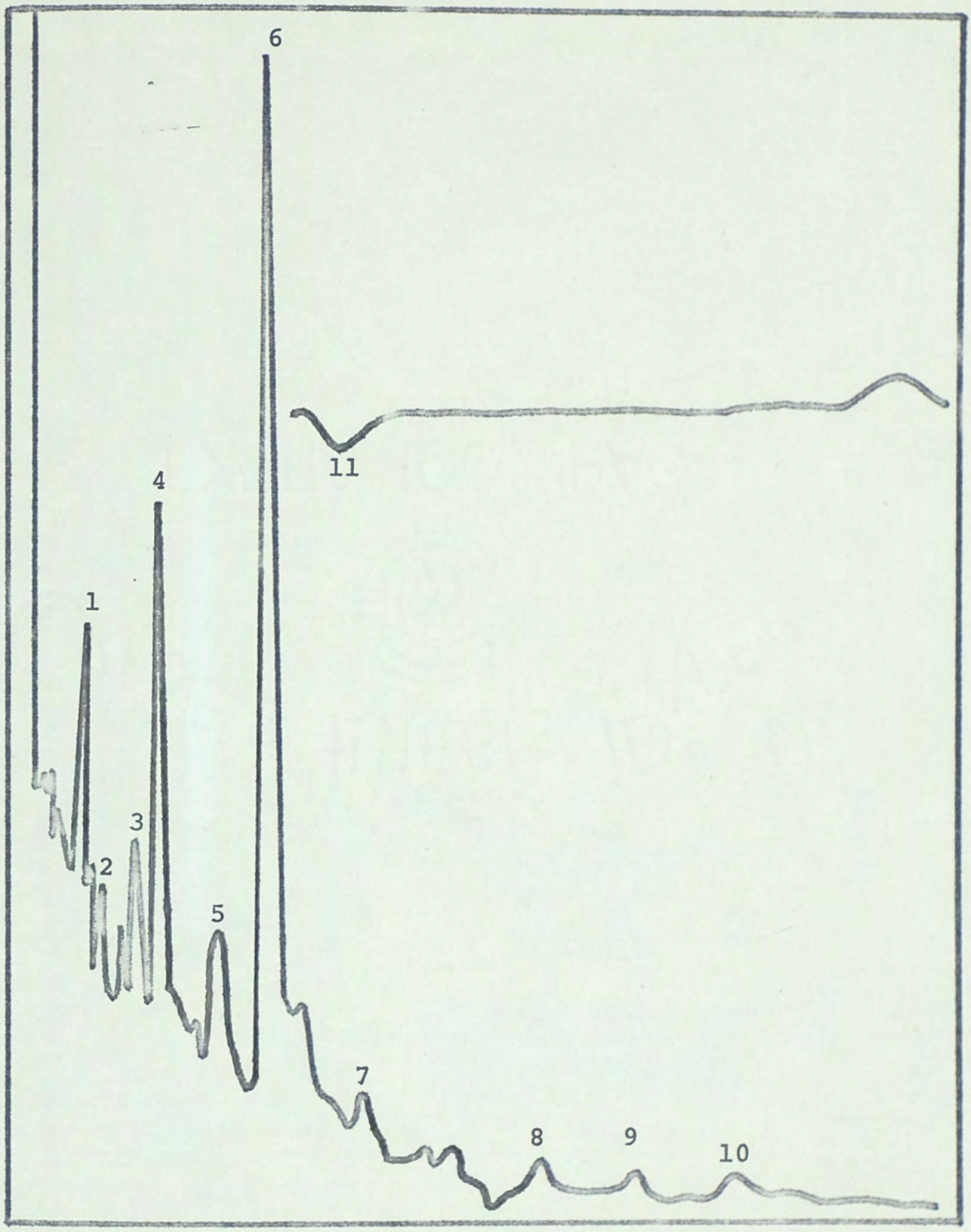

Figure 2. Chromatogram of Kirkman Tap Sample

TABLE 3: Highland Tap Data

Sample Size: 4 ul

Concentration Factor: 2000 ml/6.6 ml

Sensitivity Setting: 10^2 x 8

Calibration: Aldrin (5 ul) RT--345.03 sec

Ht--205 mm per 50 pg at 10^2 x 8

Peak	RT (sec)	RRT	Ht (mm)
1	60.06	0.174	71
2	108.00	0.313	19
3	122.00	0.356	16
4	150.00	0.435	26
5	204.65	0.593	35
6	233.10	0.676	60
7	310.93	0.901	14
8	449.23	1.302	18
9	537.57	1.558	18
10	795.00	2.304	10
11	952.90	2.762	8
12	1118.40	3,241	9
13	1490.85	4.321	-20
14	2665.05	7.724	20

Figure 3. Chromatogram of Highland Tap Sample

TABLE 4: Conway Tap Data

Sample Size: 5 ul

Concentration Factor: 2000 ml/5.1 ml

Sensitivity Setting: 10^2 x 8

Calibration: Aldrin (5 ul) RT--359.52 sec

Ht--184 mm per 50 pg at 10^2 x 8

Peak	RT (sec)	RRT	Ht (mm)
1	45.22	0.126	124
2	59.00	0.164	91
3	108.98	0.303	79
4	145.56	0.405	43
5	164.85	0.459	77
6	201.00	0.559	18
7	236.84	0.659	36
8	303.75	0.845	11
9	380.99	1.060	18
10	445.28	1.239	38
11	533.95	1.485	38
12	639.33	1.778	21
13	642.00	1.786	20
14	798.60	2.221	22
15	951.80	2.647	17
16	1122.80	3.123	13
17	1498.00	4.167	-22
18	2366.00	6.581	6

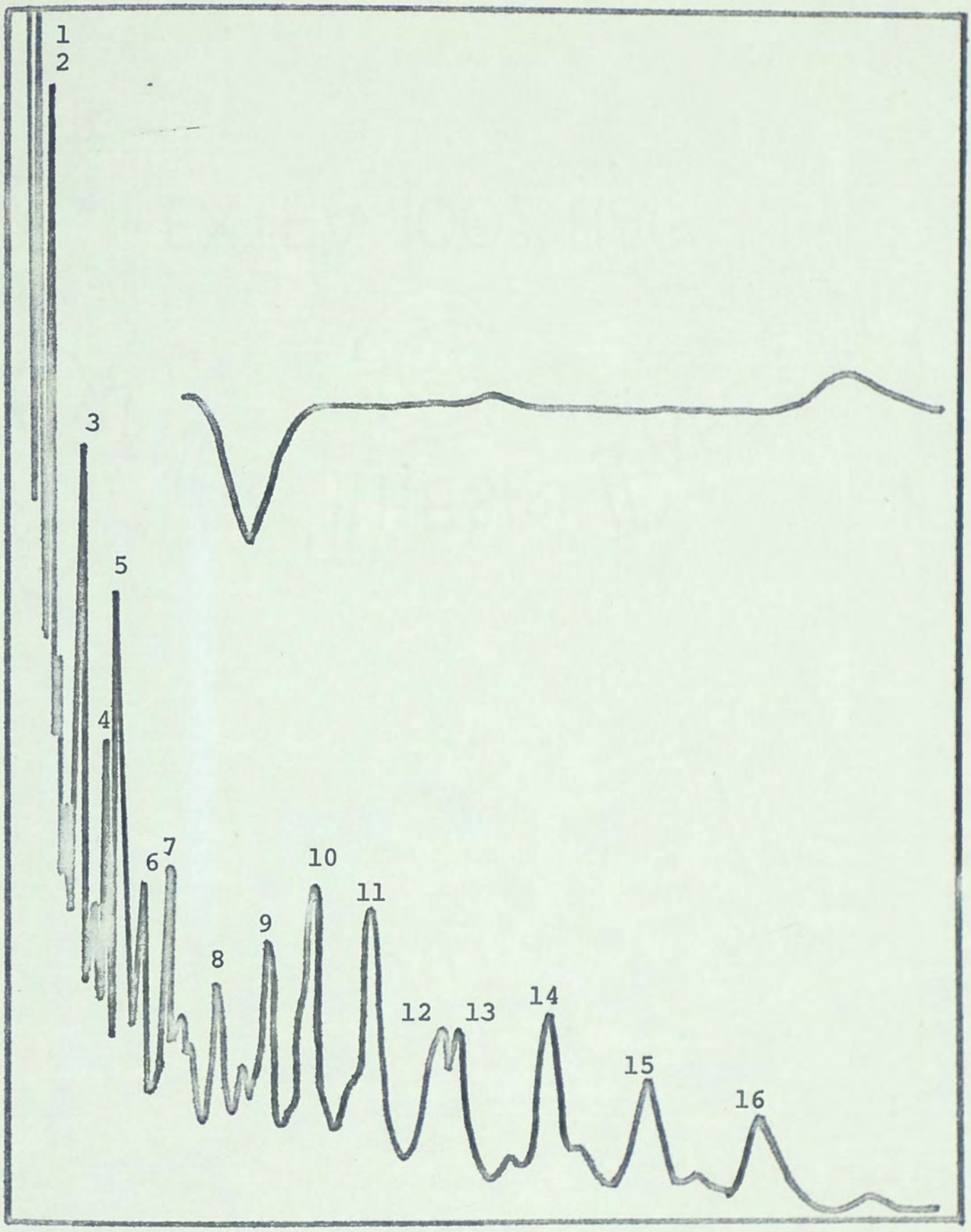

Figure 4. Chromatogram of Conway Tap Sample

TABLE 5: Primrose Tap Data

Sample Size: 5 ul

Concentration Factor: 2000 ml/5.8 ml

Sensitivity Setting: 10^2 x 8

Calibration: Aldrin (5 ul) RT--359.52 sec

Ht--184 mm per 50 pg at 10^2 x 8

Peak	RT (sec)	RRT	Ht (mm)
1	59.26	0.165	74
2	109.00	0.303	20
3	132.00	0.367	17
4	148.00	0.412	19
5	167.91	0.467	37
6	239.21	0.665	28
7	306.42	0.852	18
8	382.87	1.065	113
9	445.33	1.239	22
10	536.30	1.492	23
11	671.13	1.867	12
12	745.60	2.074	-8
13	801.31	2.229	14
14	952.50	2.649	11
15	1118.50	3.111	9
16	1494.20	4.156	33
17	2329.00	6.478	4

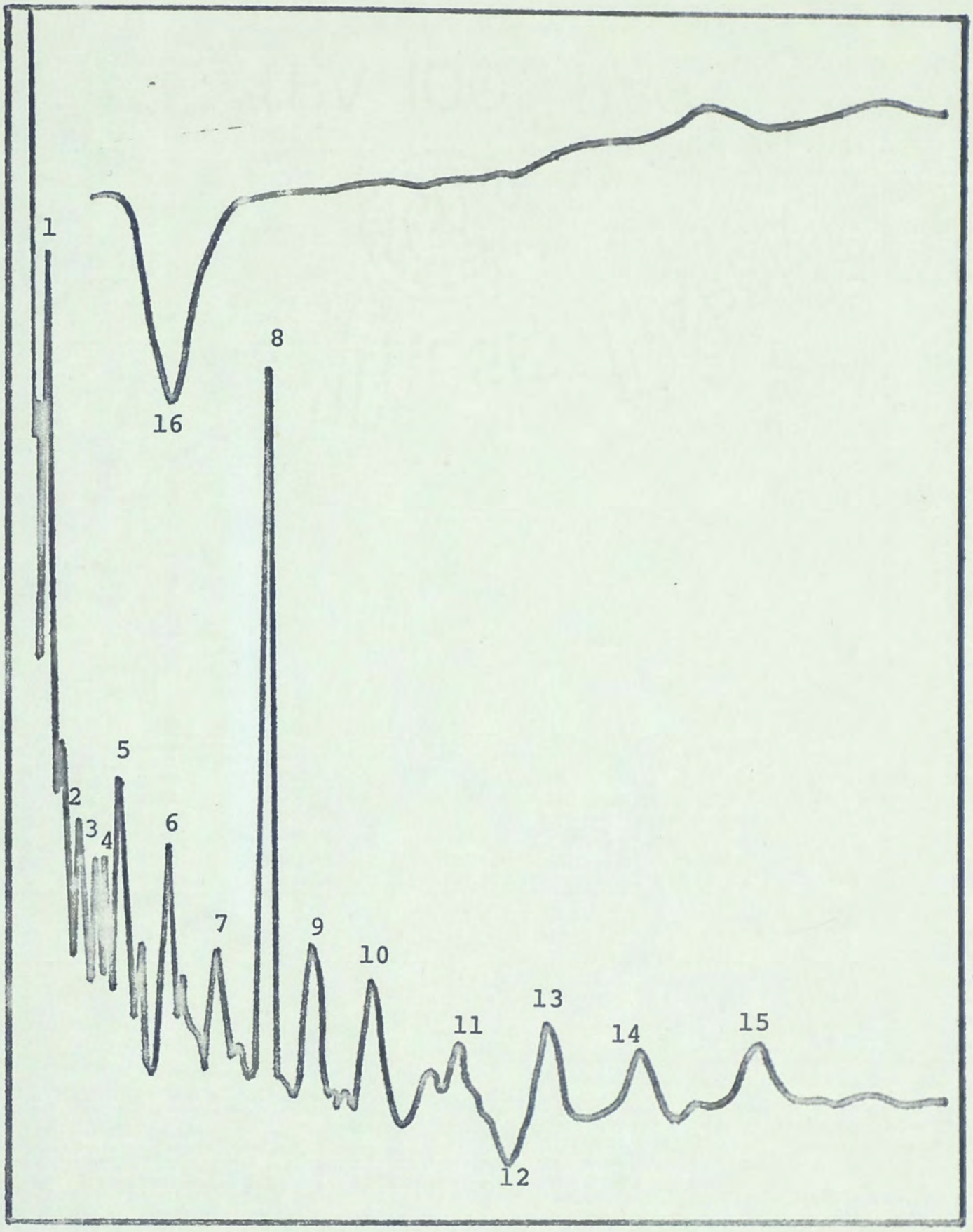

Figure 5. Chromatogram of Primrose Tap Sample

TABLE 6: Highland Plant Well No. 3 Data

Sample Size: 5 ul

Concentration Factor: 2000 ml/5.5 ml

Sensitivity Setting: 10^2 x 8

Calibration: Aldrin (5 ul) RT--359.52 sec

Ht--184 mm per 50 pg at 10^2 x 8

Peak	RT (sec)	RRT	Ht (mm)
1	45.00	0.125	100+
2	59.00	0.164	106
3	82.82	0.230	54
4	109.65	0.305	121
5	165.04	0.459	58
6	234.20	0.651	32
7	295.00	0.821	13
8	375.54	1.045	22
9	436.81	1.215	24
10	524.14	1.458	17
11	654.35	1.820	12
12	783.41	2.179	15
13	924.45	2.571	11
14	1094.60	3.045	10
15	1461.00	4.064	-30
16	2289.61	6.369	4

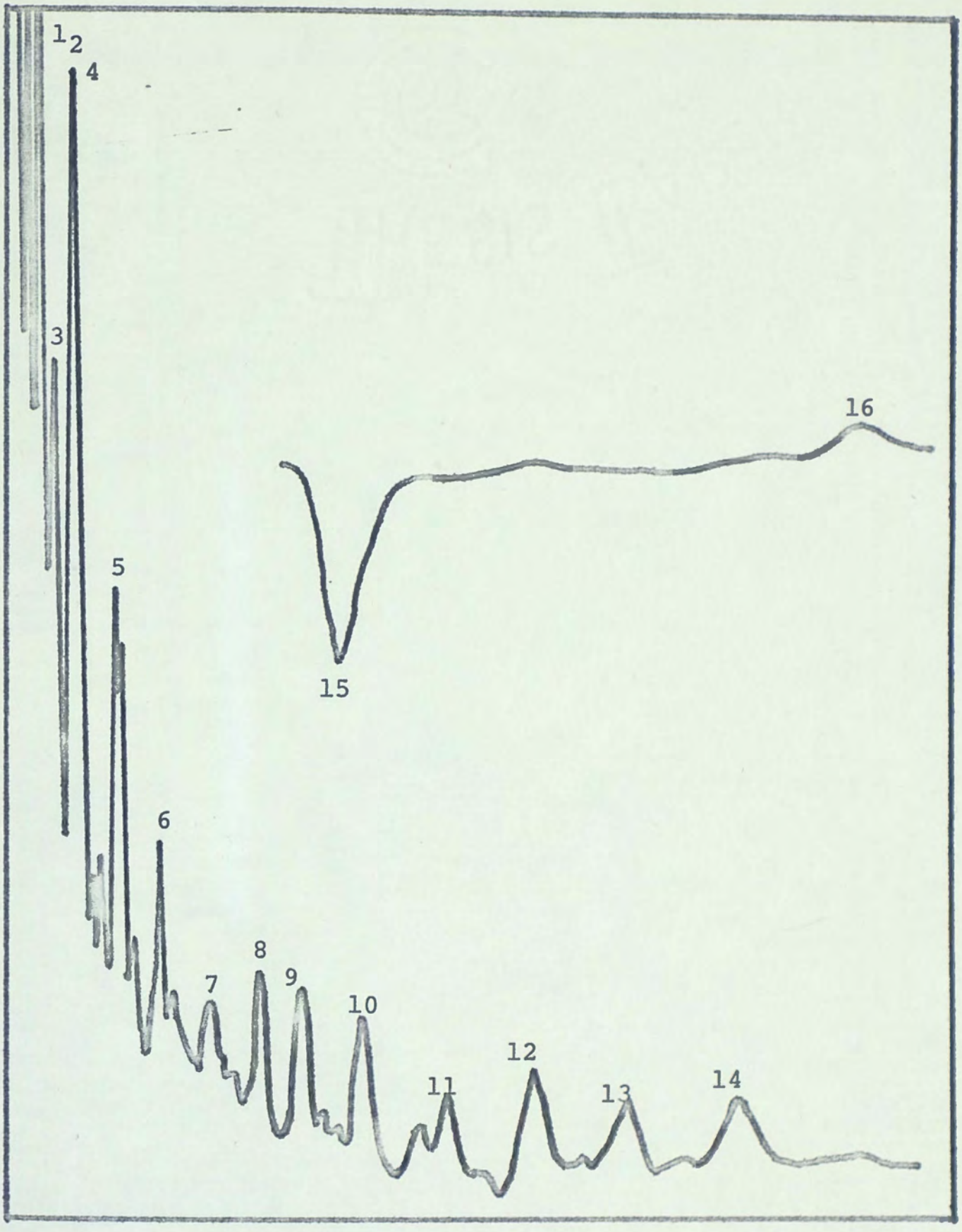

Figure 6. Chromatogram of Highland Plant Well No. 3 Sample

TABLE 7: Martin Tap Data

Sample Size: 5 ul

Concentration Factor: 2000 ml/3.4 ml

Sensitivity Setting: 10^2 x 4

Calibration: Aldrin (5 ul) RT--333.00 sec

Ht--208 mm per 50 pg at 10^2 x 4

Peak	RT (sec)	RRT	Ht (mm)
1	56.4	0.170	57
2	66.0	0.198	90
3	90.0	0.271	78
4	102.0	0.307	92
5	124.8	0.375	34
6	139.2	0.418	75
7	158.4	0.476	31
8	192.0	0.577	75
9	214.2	0.644	132
10	295.2	0.887	45
11	420.0	1.26	36
12	504.0	1.51	36
13	625.2	1.88	20
14	750.0	2.25	15
15	888.0	2.67	17
16	1047.0	3.15	17
17	2162.4	6.50	10

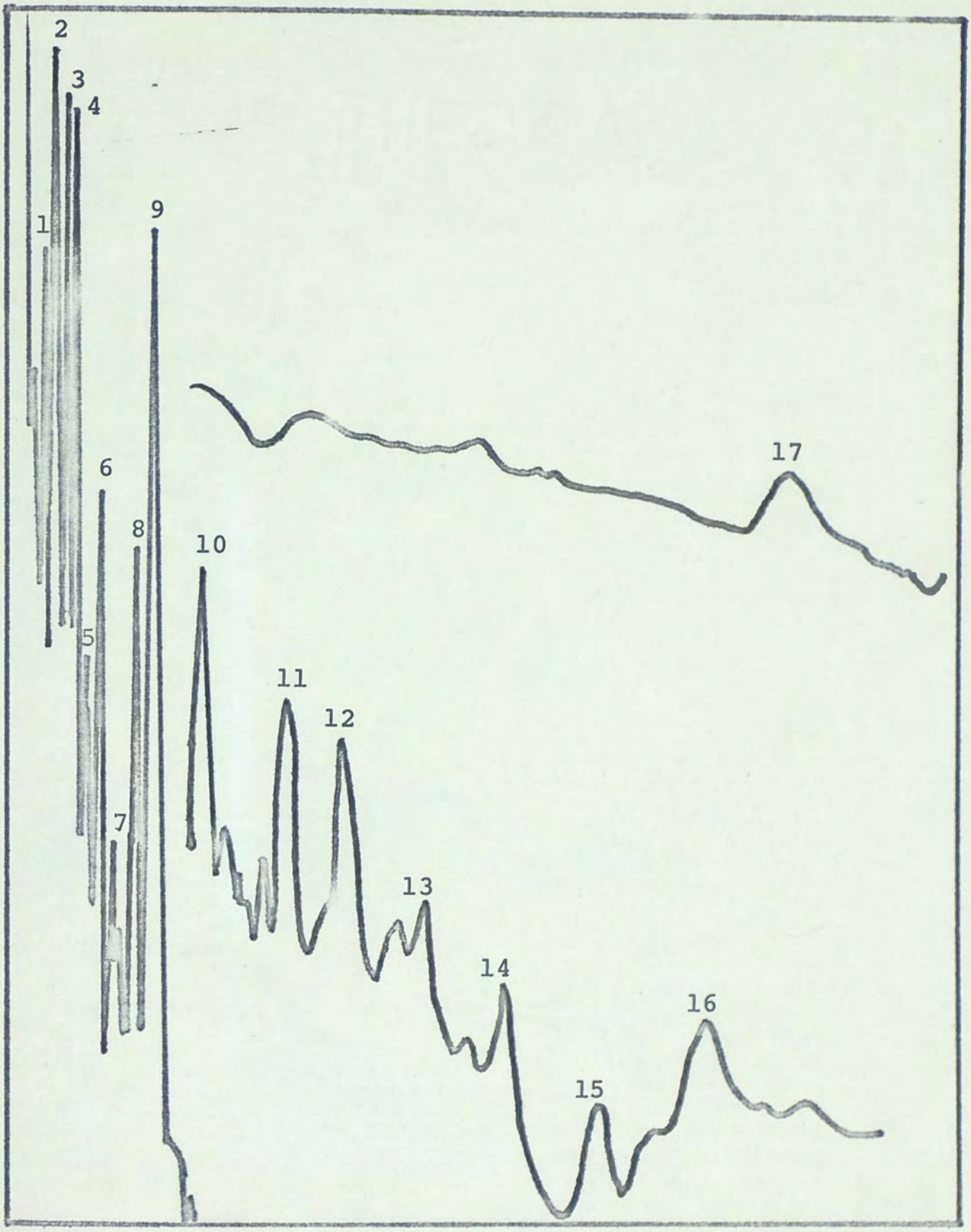

Figure 7. Chromatogram of Martin Tap Sample

TABLE 8: Pine Hills Tap Data

Sample Size: 5 ul

Concentration Factor: 2000 ml/3.6 ml

Sensitivity Setting: 10^2 x 4

Calibration: Aldrin (5 ul) RT--333.0 sec.

Ht--208 mm per 50 pg at 10^2 x 4

Peak	RT (sec)	RRT	Ht (mm)
1	57.6	0.173	42
2	78.6	0.236	22
3	107.4	0.323	45
4	140.4	0.422	61
5	160.8	0.483	65
6	191.4	0.575	24
7	228.6	0.687	30
8	287.4	0.857	26
9	366.6	1.102	31
10	424.8	1.277	28
11	508.8	1.529	30
12	603.6	1.814	14
13	633.0	1.903	16
14	756.0	2.272	15
15	907.2	2.724	10
16	914.4	2.746	-35
17	1060.8	3.188	6
18	1408.8	4.234	-14

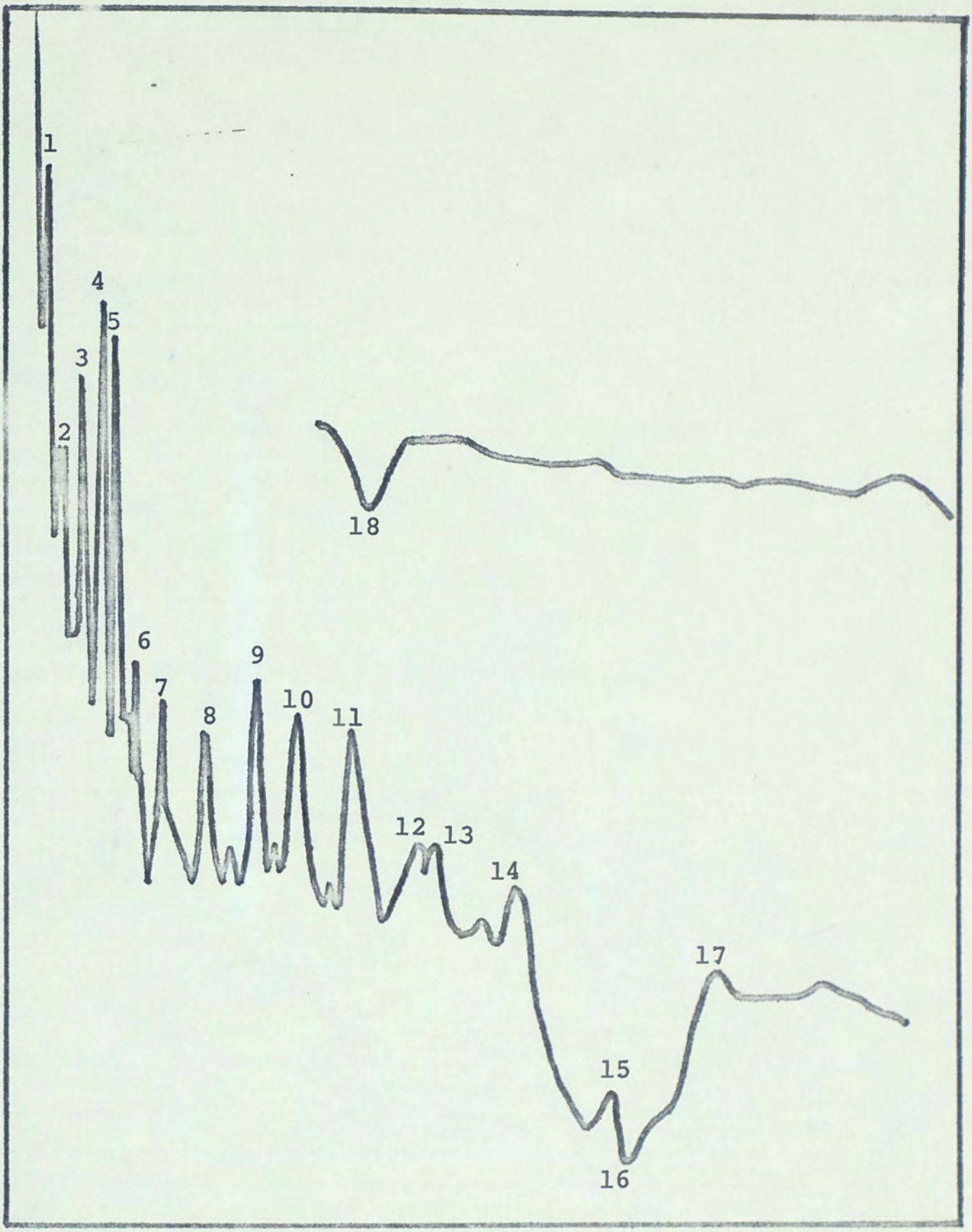

Figure 8. Chromatogram of Pine Hills Tap Sample

TABLE 9: FTU Environmental Lab Tap Data

Sample Size: 5 ul

Concentration Factor: 2000 ml/5.1 ml

Sensitivity Setting: 10^2 x 8

Calibration: Aldrin (5 ul) RT--342.66 sec

Ht--217 mm per 50 pg at 10^2 x 8

Peak	RT (sec)	RRT	Ht (mm)
1	61.73	0.180	45
2	85.00	0.248	31
3	164.80	0.481	28
4	235.66	0.688	12
5	302.87	0.884	11
6	436.75	1.275	14
7	528.00	1.541	15
8	659.65	1.925	52
9	785.98	2.294	15
10	926.86	2.705	9
11	1098.60	3.206	12
12	1540.00	4.494	13
13	2302.00	6.710	4

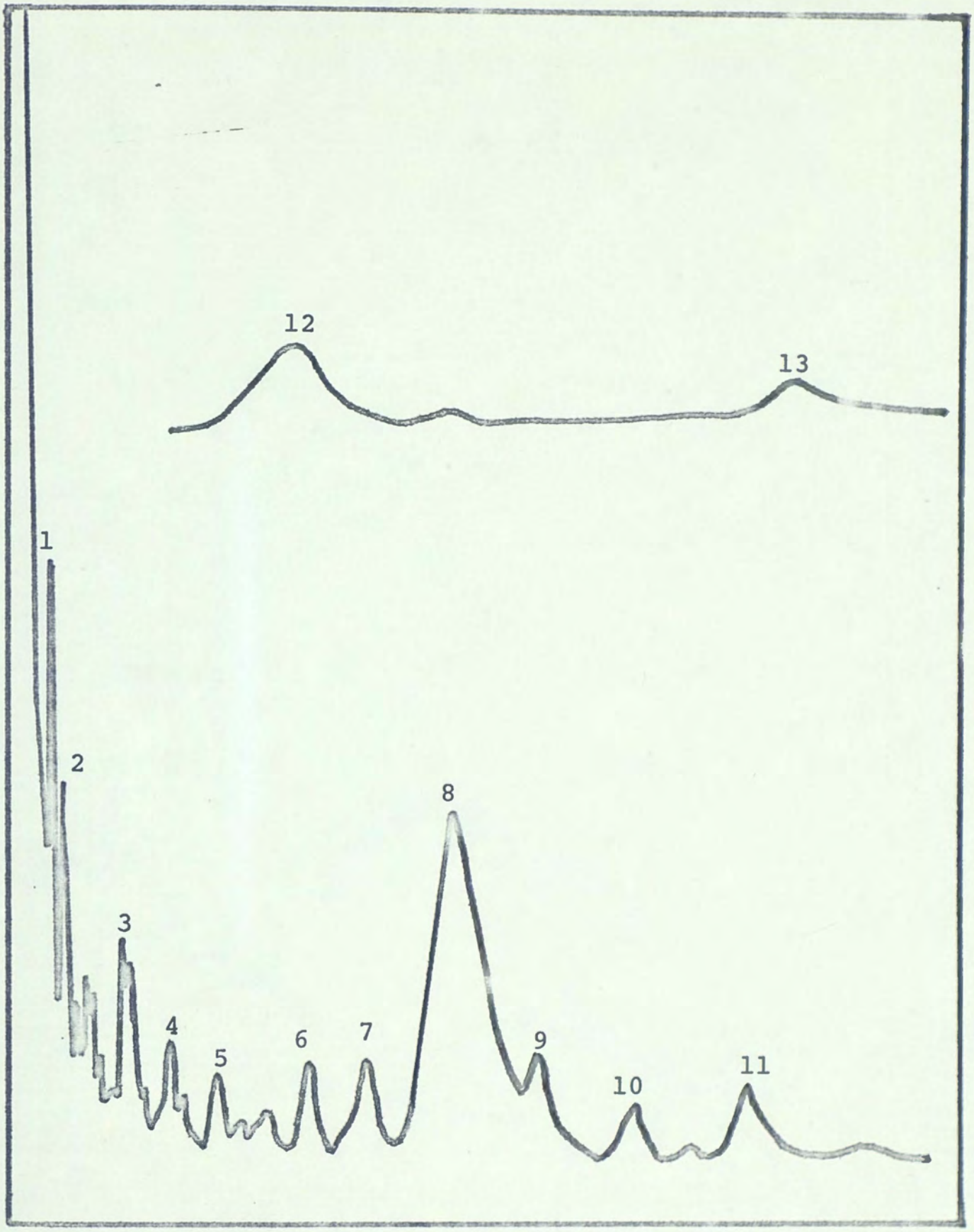

Figure 9. Chromatogram of FTU Environmental Lab Tap Sample

TABLE 10: Comparison of Data from Untreated and 10 ppm Treated Kuhl Tap Samples

Volume of Samples Injected: 5 ul

Concentration Factors: 1000 ml/5.0 ml

Sensitivity Settings: 10^2 x 8

Calibration: Aldrin (5 ul)

RT--308.81 sec

Peak	RT (sec)	RRT	Ht (mm) untreated	Ht (mm) treated	% Reduced
1	73.8	0.239	43	7	83.7
2	94.2	0.305	24	6	75.0
3	105.6	0.342	65	9	86.2
4	129.6	0.420	95	28	70.5
5	149.4	0.484	28	9	67.9
6	178.2	0.577	30	3	90.0
7	196.2	0.635	397	8	98.0
8	270.0	0.874	209	12	94.3
9	395.4	1.280	23	9	60.9
10	478.8	1.551	16	12	25.0

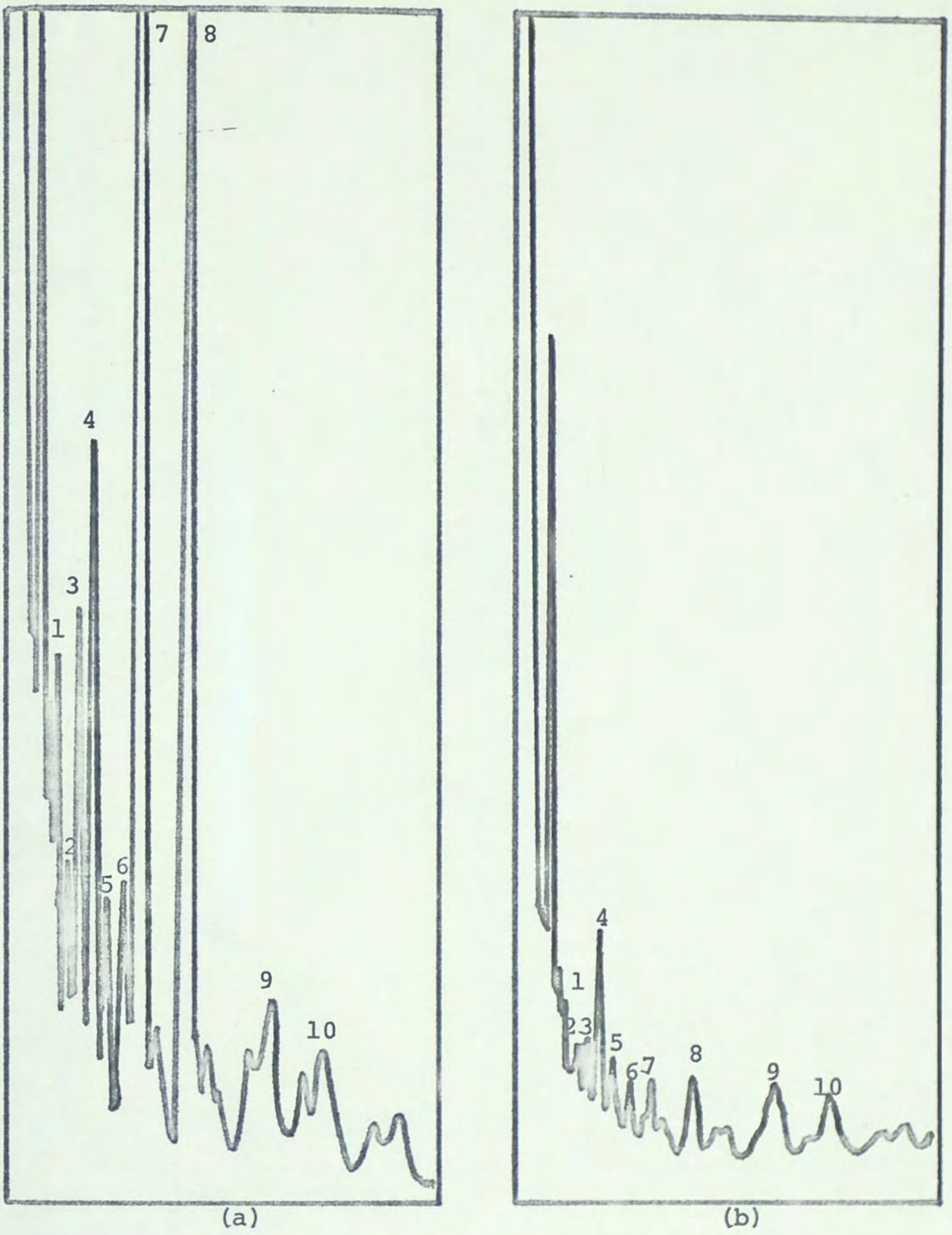

Figure 10. Chromatograms of Supplemental Kuhl Tap Samples (a) without treatment and (b) with treatment

TABLE 11: Comparison of Data from Untreated and 10 ppm Carbon Treated Kirkman Tap Samples

Volume of Samples Injected: 5 ul

Concentration Factors: 1000 ml/5.0 ml

Sensitivity Settings: 10^2 x 8

Calibration: Aldrin 5 (ul)

RT--308.81 sec

Peak	RT (sec)	RRT	Ht (mm) untreated	Ht(mm) treated	% Reduced
1	93.6	0.303	23	11	52.2
2	105.0	0.340	61	22	63.9
3	127.8	0.414	95	44	53.7
4	135.3	0.438	30	13	56.7
5	175.2	0.567	31	14	54.8
6	265.2	0.859	43	21	51.2
7	389.4	1.261	16	23	43.8

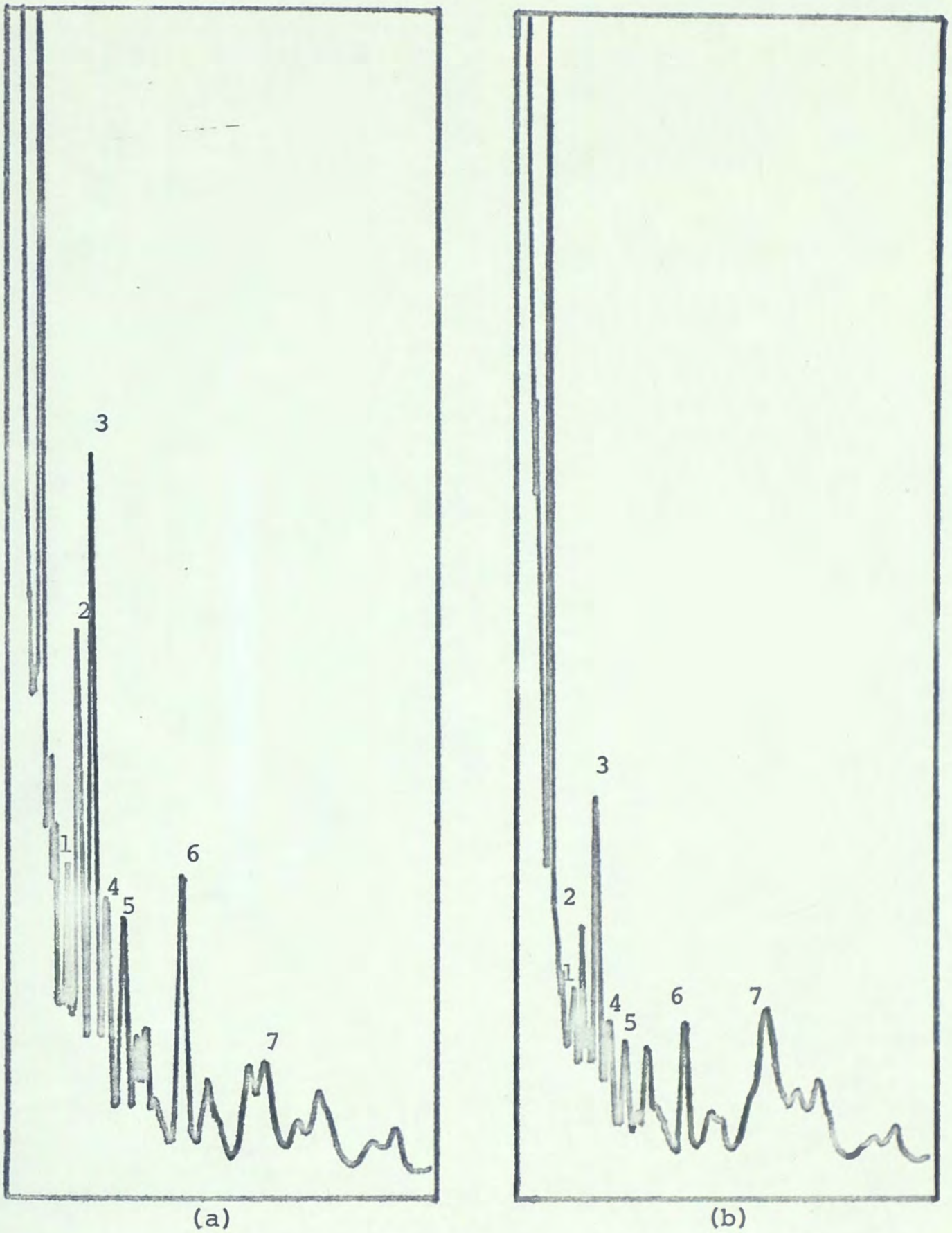

Figure 11. Chromatograms of Supplemental Kirkman Tap Samples (a) without treatment and (b) with treatment

TABLE 12: Peak Height Data for the Pesticide Mixture Sample

Sample Size Injected: 5 ul

Concentration Factors: 100 ml/5.0 ml

Sensitivity Settings: 10^2 x 8

Calibration: Aldrin (5 ul) RT--318.0 sec

Concentration of Each Pesticide: 0.1 ppm

Peak	Compound	Height of peaks after being treated with the following activated carbon dosages: 0 ppm	1 ppm	5 ppm	50 ppm
1	heptachlor	4500	11	10	11
2	chlordane alpha	2900	436	4	4
3	chlordane gamma	10700	2	1	1
4	endrine	4000	1	2	3
5	o'p'-DDT	6000	6	6	3
6	p'p'-DDT	900	0	0	0
7	methoxychlor	1100	17	11	6

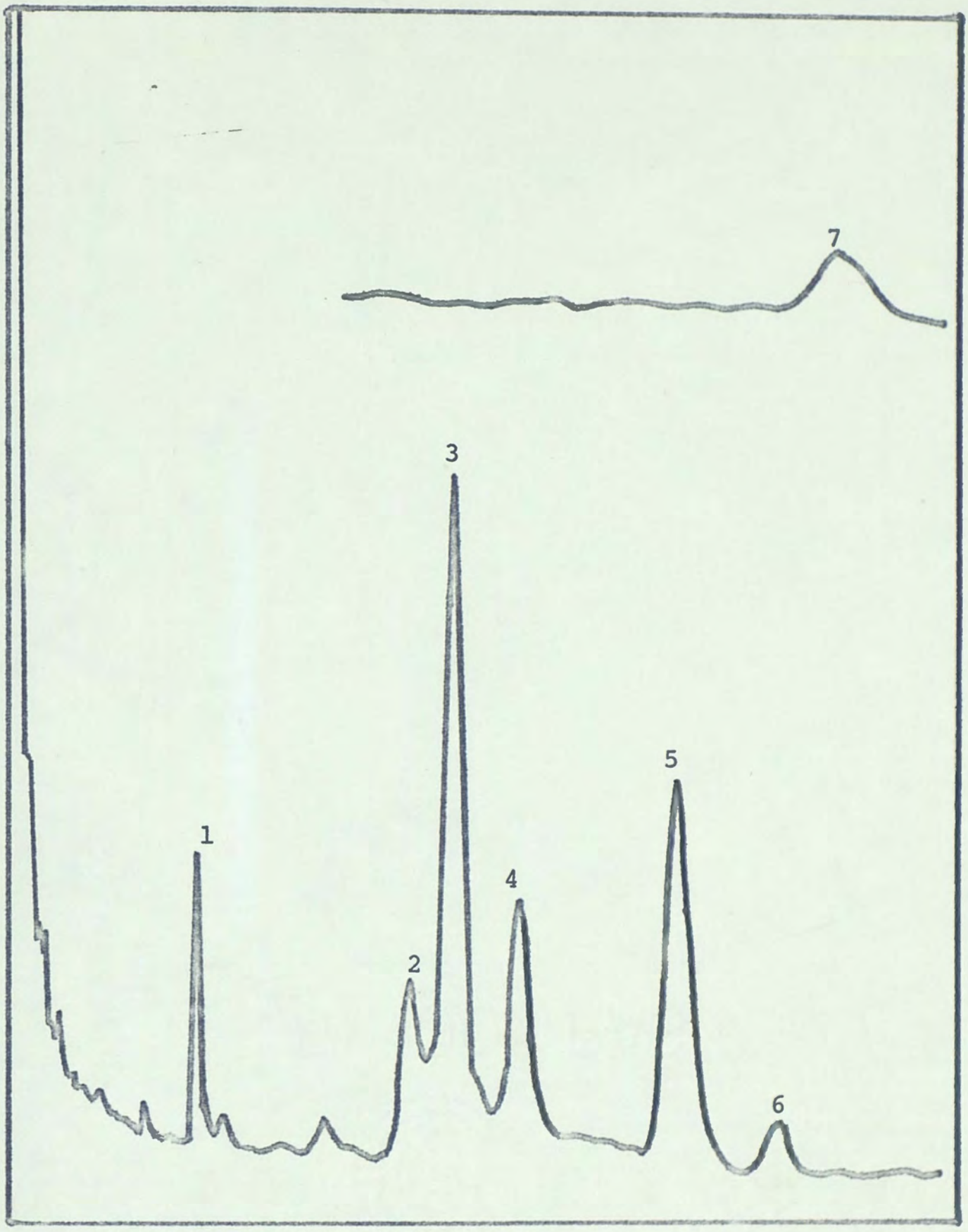

Figure 12. Chromatogram of the Pesticide Mixture (A 1 to 100 dilution of the sample was used so the actual concentrations of each pesticide is 0.001 mg/l.)

TABLE 13: Percent Reduction in Peak Heights of the Pesticide Mixture Samples

Peak	Compound	% Reduction by dosages 1 ppm	5 ppm	50 ppm
1	heptachlor	99.76	99.78	99.76
2	chlordane alpha	84.97	99.86	99.86
3	chlordane gamma	99.98	99.99	99.99
4	endrine	99.98	99.95	99.93
5	o',p' DDT	99.90	99.90	99.95
6	p',p' DDT	100.00	100.00	100.00
7	methoxychlor	98.45	99.00	99.45

TABEL 14: Maximum Possible Concentrations* of the Pesticide in the Pesticide Mixture Samples

Peak	Compound	Concentrations (mg/l) after treatment with the following dosages of activated carbon: 0 ppm	1 ppm	5 ppm	50 ppm
1	heptachlor	0.10	0.00024	0.00022	0.00024
2	chlordane alpha	0.10	0.015	0.00014	0.00014
3	chlordane gamma	0.10	0.00002	0.00001	0.00001
4	endrine	0.10	0.00002	0.00005	0.00007
5	o'p'-DDT	0.10	0.00010	0.00010	0.00005
6	p'p'-DDT	0.10	0.0	0.0	0.0
7	methoxychlor	0.10	0.0016	0.0010	0.00055

*The pesticide mixture stock solution was made by adding 0.10 mg of each pesticide per liter of water, but not all of the pesticides added dissolved completely. Because the actual concentrations of those that did not dissolve entirely are not known, their maximum possible concentrations of 0.1 mg/l are used and the subsequent concentrations of the treated samples are based on these.

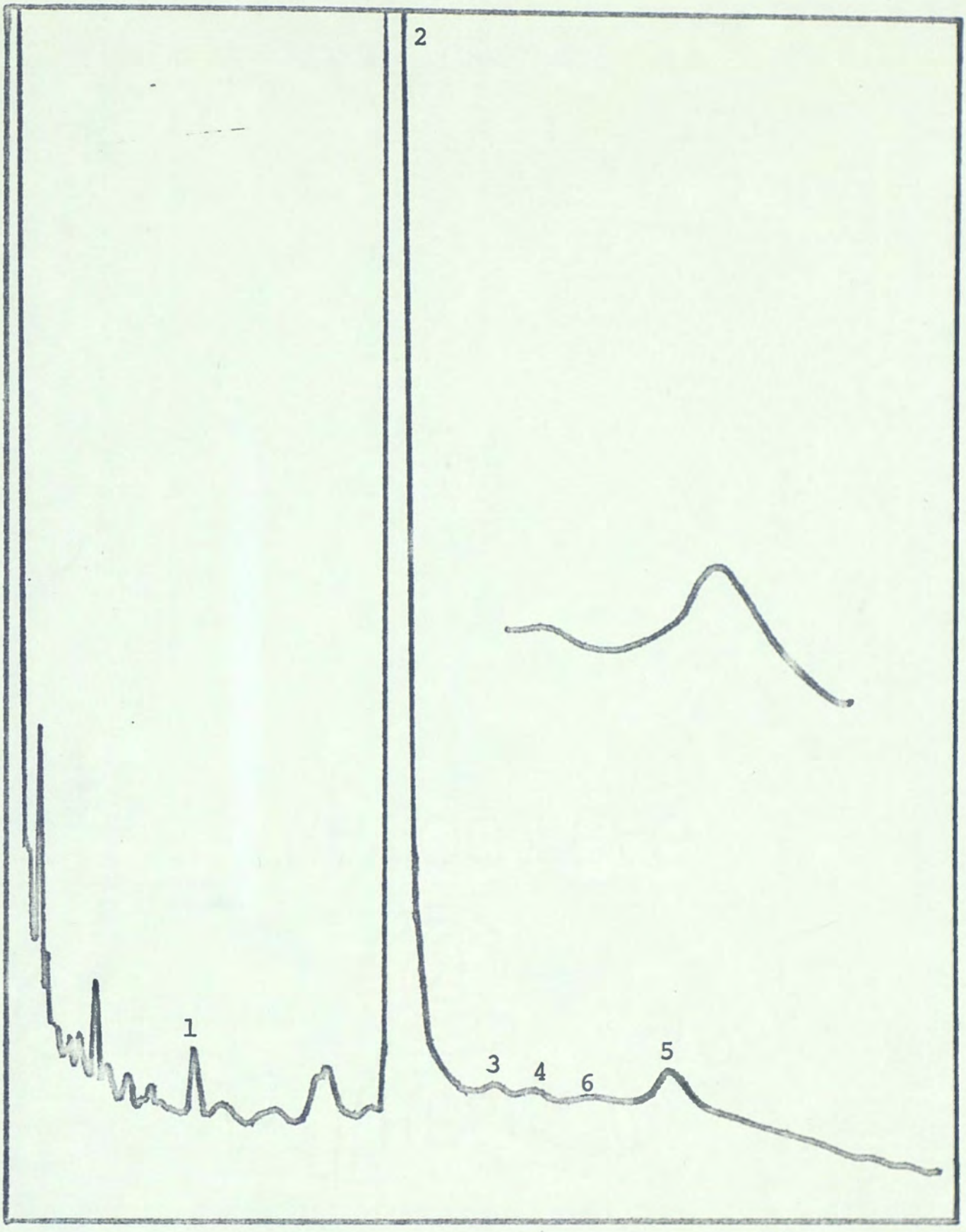

Figure 13. Chromatogram of the pesticide mixture after treatment with 1 ppm of activated carbon

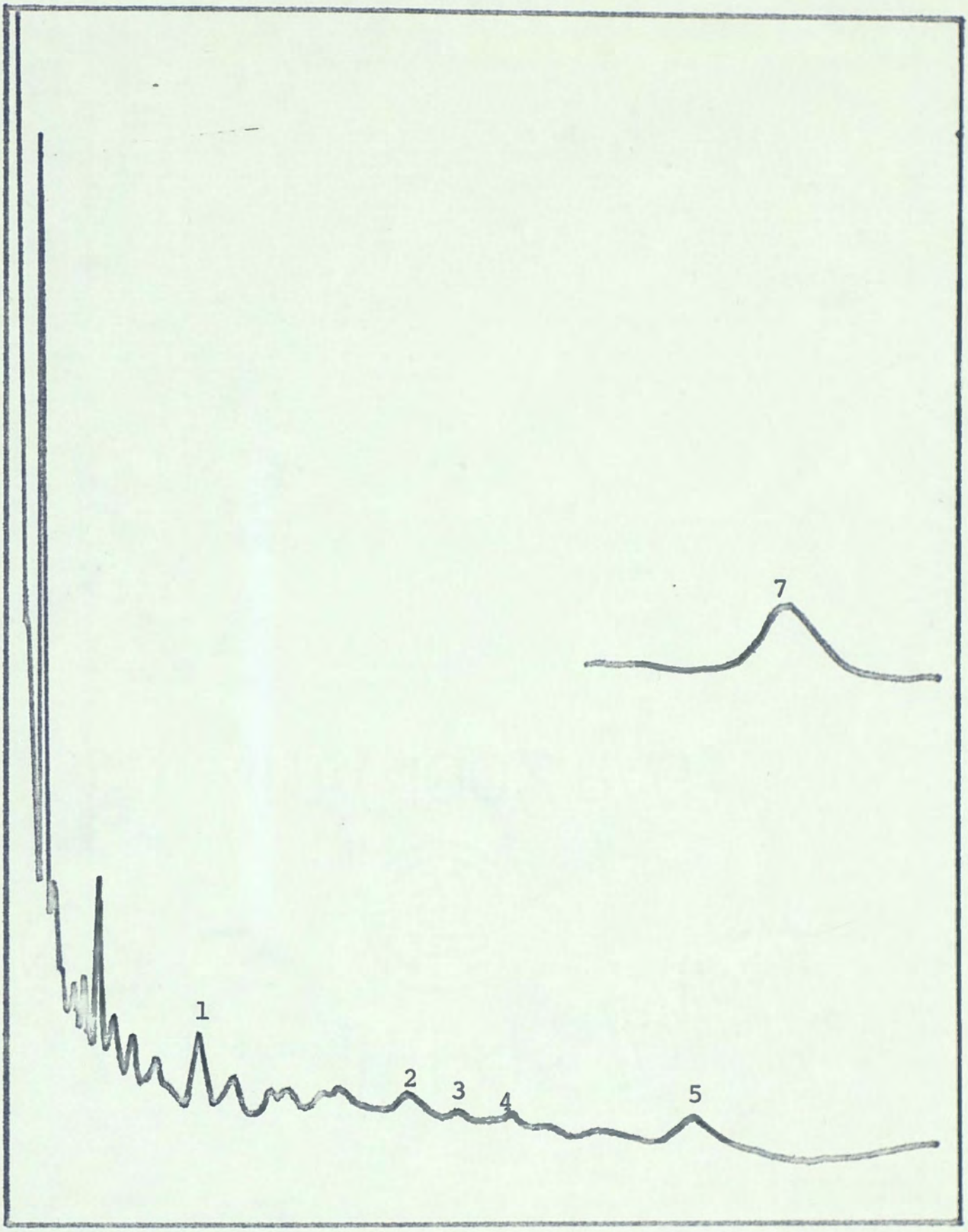

Figure 14. Chromatogram of the pesticide mixture after treatment with 5 ppm of activated carbon

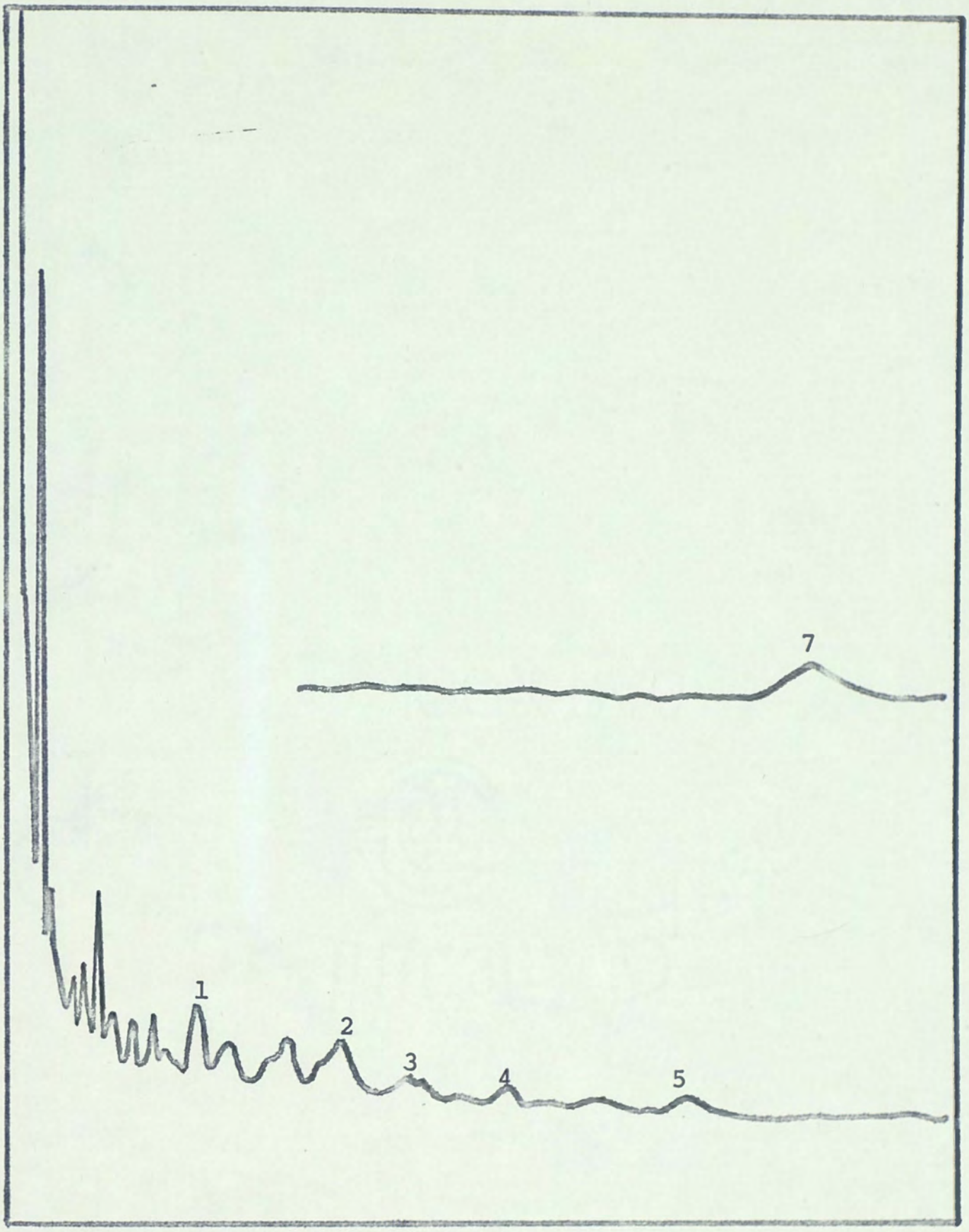

Figure 15. Chromatogram of the pesticide mixture after treatment with 50 ppm of activated carbon

CHAPTER IV

DISCUSSION OF RESULTS

Organohalides in Drinking Water

At this point it is only possible to determine the number of organohalide contaminants present and an approximation of their relative concentrations. This is because all of the separations were done on the same chromatography column. There are a large number of chlorinated hydrocarbons known today and many have relative retention times that overlap enough to make positive identification impossible by gas chromatography when using a single separating column. This problem can be overcome by using two dissimilar columns so that each compound has two characteristic relative retention times. However, for this project using two columns was not feasible for several reasons. First, the chromatograph that was used contains only one electron capture detector and second, the number of standards that have been run on this machine and column is too small to permit identification of more than a small handful of compounds, so that unless we were looking for a particular compound this would be impractical.

However, the peaks obtained were compared with the chlorinated pesticide and herbacide standards that have been run at FTU and tentative peak assignments have been made where possible. These assignments were made if the relative retention time was within 0.01 units of that of the standard. For the peaks that could be tentatively identified in this manner, the concentrations were estimated by correlating the peak height of the standard (given in mm/ng) to that of the peak under consideration.

It should be noted that a distilled water blank was run which produced a series of peaks at a sensitivity setting of 10^2 x 8. The origin of these peaks is not known, but they seem to appear regularly in the chromatograms of water samples being analyzed for pesticides at FTU with sensitivity settings of 10^2 x 8 or higher. Because of this it is reasonable to assume that these peaks are due to contamination from the glassware or from the technique used in the preparation of the samples. The relative retention times of these peaks are as follows:

RRT	comments
0.17	
0.43	
0.59	
0.69	very small peak
0.86	very small peak
1.27	
1.51	
2.24	
2.65	
3.13	negative peak
6.40	
7.38	negative peak

Also, a double peak that was not listed occurred with a relative retention time that varied between 1.78 and 1.90. These peaks when found on the chromatograms in this relative order were not considered as constituents of the sample. From the peak heights and the sensitivity settings used, their approximate concentrations would for the most part be less than 0.010 ppb.

Before considering the chromatograms of the samples there are two more observations that should be stated. First, the general variance of relative retention times seems to increase with increasing retention time. This means that for peaks with longer retention times the

random error in relative retention time values increases somewhat. Repetitive runs of standards show a variance of about two percent for compounds with relative retention times of 1 or less and a variance of up to 10 percent for relative retention times of about 6. Second, some negative peaks were encountered. In order for a negative peak to occur, the compound being eluted would have to cause an increase in the electron flux in the electron capture detector. Some amines have been identified to give negative peaks by other researchers when using an electron capture detector but it is not known if these amines are responsible in this case.

In the following paragraphs tentative peak assignments will be made where possible on the basis of comparing relative retention times of the peaks to those of the standards run on our column. The peaks minus the contaminant peaks mentioned above will be listed in an approximate order of relative concentration based on peak heights. This is only an approximate order since peak height varies not only with concentration but also with the compound being detected. It should also be noted that peak height to concentration relationships are not always linear. The concentration is directly proportional to the area under a peak and not the peak height which is indirectly related to the area of the peak. However, for

this experiment it is felt that the peak height is adequate for the approximation of concentrations and the concentrations of the tentatively assigned peaks are based on the height of the peak of a known concentration of the standard.

The Kuhl tap sample, because of the relatively high organohalide concentrations, showed none of the contaminants found in the distilled water sample. The concentrations of the components of this sample were about 40 times those found in most of the samples. The major peaks are as follows:

Peak	RRT
4	1.126
2	0.232
7	6.798
1	0.148
3	0.550

The Kirkman tap sample also showed higher concentrations than the other samples. The contaminants in this sample appear to be about 4 times as concentrated as most of the other samples. The major peaks are:

Peak	RRT
6	1.109
4	0.655
1	0.346
5	0.905

Peak number 1 has a relative retention time that is very close to one found for a component of DDT (0.342). If it is DDT the concentration of DDT in the original sample would be about 2.4 ug/l (0.0024 mg/l). This concentration is well below the U.S. Environmental Protection Agency's (EPA) recommended limit for DDT concentration in drinking water of 0.05 mg/l.

For the Highland tap sample the major peaks are:

Peak	RRT
6	0.676
2	0.313
3	0.356
7	0.901
14	7.724

The major peaks of the Conway tap sample in order of magnitude are:

Peak	RRT
1	0.126
2	0.164
3	0.303
5	0.459
4	0.405
7	0.659
9	1.060
8	0.845

The major peaks of the Primrose tap sample are:

Peak	RRT
8	1.065
1	0.165
5	0.467
6	0.665
2	0.303
3	0.367
11	1.867

Peak number 1 has a relative retention time that is characteristic of phosdrin (0.163). If it is indeed phosdrin its concentration would be approximately 3.0 ug/l (0.003 mg/l) in the original water sample. The limit recommended by the EPA for organophosphorous pesticides is 0.1 mg/l (EPA, 1974), thus the concentration found for phosdrin is only 3 percent of the limit.

For the Highland Plant Well No. 3 samples the major peaks are:

Peak	RRT
1	0.125
4	0.305
2	0.164
5	0.459
3	0.230
6	0.651
9	1.215

Peak	RRT
8	1.045
10	1.458
12	2.179
7	0.821

Peak number 5 has a relative retention time close to that of BHC (0.45) and peak number 12 has a relative retention time that is close to that of endosulfan (2.18). If this is correct their concentrations in the actual sample would be approximately as follows:

BHC--0.36 ug/l (0.00036 mg/l)

endosulfan--0.095 ug/l (0.000095 mg/l)

No EPA recommended limits for BHC or endosulfan in drinking water were found, but these exceedingly low concentrations indicate that this water sample poses no threat to human health.

The major peaks of the Martin tap sample are:

Peak	RRT
9	0.644
4	0.307
2	0.198
3	0.271
6	0.418
8	0.577
10	0.887

Peak	RRT
5	0.375
7	0.476

For the Pine Hills tap sample the major peaks are:

Peak	RRT
5	0.483
4	0.422
3	0.323
9	1.102
6	0.575
2	0.236

The major FTU environmental lab tap sample peaks in order are:

Peak	RRT
8	1.925
2	0.248
3	0.481
7	1.541
9	2.294
12	4.494

The total number of significant compounds found in each sample are:

Kuhl tap	5
Kirkman tap	4
Highland tap	5
Conway tap	8
Primrose tap	7
Highland Plant Well No. 3	11
Martin tap	9
Pine Hills tap	6
FTU environmental lab tap	6

Three peaks were repeated fairly often on the chromatograms. One (relative retention time of approximately 0.30) was found in four of the samples and the other two (relative retention times of 1.05 and 1.10) were found in three and two of the samples respectively.

Carbon Adsorption

As mentioned in the experimental section of this report, the preparation of this set of samples varied in two respects from the preparation of the previous samples. These two changes in technique were adopted to reduce laboratory contamination of the samples. The control samples were prepared by using distilled water and showed no measurable peaks at a sensitivity setting of 10^2 x 8 which indicates that all of the peaks detected at this setting are valid.

There were two distinct differences in the chromatograms of the untreated Kuhl and Kirkman tap samples run earlier and the untreated samples run to compare with the carbon treated samples. There were more peaks in the later chromatograms and when considering the difference in sensitivity settings, a reduction in peak heights was noticeable. The reduction in peak heights was probably due to decomposition of the organohalide contaminants with time (about 2 months elapsed between the preparation of the two sets of samples which were prepared from the same stock). The increase in the number of peaks is probably the result of lighter fractioned compounds resulting from the decomposition products of the original compounds and from a change in sensitivity settings that allowed peaks to be seen that were previously obscured.

On the chromatograms of the pesticide mixture there are a number of small peaks concentrated on the left side of the chromatograms which are also probably due to the decomposition of the primary pesticides being investigated. Other observations that should be noted when considering these chromatograms is that all of the pesticides did not dissolve completely and that the extraction efficiency varies somewhat with the compound and therefore the concentrations of the pesticides vary.

It should also be noted that in each of the

chromatograms that there is a sizable peak with a relative retention time of 0.168 (retention time of about 53.4 sec) that is not numbered. Because of its regularity it is assumed to be due to the methyl chloride in the solvent.

The Kuhl and Kirkman tap samples were chosen for activated carbon treatment because they are the two samples that would benefit the most from such treatment due to their high concentrations (high compared to the other samples) of organohalides. The dosage of 10 ppm of activated carbon was based on the dosage used by a water treatment plant in a neighboring county (Melbourne, Florida water treatment plant) to control taste and odor problems and on Sigworth's (1965) conclusion that about 90 percent of the pesticide concentration of a drinking water sample would be removed when using this dosage.

The batch process, carbon treatment of these samples resulted in the peak heights that were selected for measurement being reduced by 25 to 98 percent for the Kuhl tap sample and by 51 to 64 percent for the Kirkman tap sample except for one peak that increased by 44 percent. The reason for the 44 percent increase in height of one peak while all of the other peaks decreased in height is not known, but it could be due to experimental error or laboratory contamination. There was a similar

peak (one that increased in height after the carbon treatment) in the Kuhl tap sample chromatogram; however, because of its location it was not pictured in Figure 10 and was not chosen for measurement. But it is mentioned here because if this occurred in both samples then the possibility of it being the result of random laboratory contamination or experimental error is greatly reduced. The reason for these increases requires further investigation.

From a comparison of the two Kuhl tap chromatograms of Figure 10 a strong relationship between the original contaminant concentrations and the percent removed by carbon treatment can be seen. As the concentration increases the percent reduction in concentration increases. This relationship is not as clear when considering the Kirkman tap sample because the concentrations of its contaminants are lower and are grouped closer together.

The chromatograms of the pesticide mixture (Figures 12-15) and the accompanying data tables show some interesting results. Originally it was hoped to determine the differences in the effects of activated carbon on the different pesticides by describing the effects on each graphically using the Freundlich Equation. However, this approach was found to be unusable because all the pesti-

pesticides did not behave independently. There is a strong indication from comparing Figures 12, 13 and 14 that when the adsorption surface becomes limited that the pesticides compete for attachment sites. This would be possible only if an equilibrium exists between the molecules on the adsorption surface and those in solution that would allow molecules with a higher affinity for the carbon surface to replace those with a lower affinity.

Another interesting result is that the dosages beyond 5 ppm of activated carbon did not further reduce significantly the concentrations of most of the pesticides. Because of this only the chromatograms of the 1, 5, and 50 ppm dosages are shown and discussed. Those of the 10 and 25 ppm dosages show the same random, statistical deviations in concentrations as shown in the chromatograms of the 5 and 50 ppm dosage samples. Possible reasons for these semi-static concentrations could be related to the equilibrium between the adsorbed state and the solution state or due to a low statistical probability of contact of the pesticide molecules with the carbon surface at very low concentrations. However, the equilibrium would be expected to shift somewhat (as it appears to for the methoxychlor) and the statistical probability of contact would be expected to increase for increasing carbon dosages. Because of this it is possible that the reason

behind a low, static, nonremovable concentration of these pesticides after treatment is due to a statistical proportion of the molecules not having the correct energy requirements for attachment to the carbon surface. Since the attachment of a molecule to a surface is dependent on the potential energy of the molecule, the proportion of the molecules not meeting the energy requirements should be dependent on the reaction time and the temperature for a liquid sample. Work done by Booth, English, and McDermott (1965) also shows the presence of a low and seemingly nonremovable concentration of organics after carbon treatment. Their work also shows a slight dependence on reaction time but this dependence may not be as high as what would be expected if energy requirements were the only factor responsible for activated carbon's inability to significantly reduce this concentration.

If in fact a residual pesticide concentration that is possibly dependent on time and temperature, but is independent of the carbon dosage is reached, then it implies that the empirically derived Freundlich Equation is unsatisfactory for describing adsorption when treating very low concentrations of organics.

It is already known that this equation is unsatisfactory when considering very high concentrations because it implies that adsorption increases indefinitely with

their concentrations, with the exception of a few, appear to be insignificant.

2. Samples collected from the Kuhl tap and Kirkman tap showed higher concentrations of halogenated hydrocarbons, as compared to other water samples tested. However, those high concentrations were far below permissible concentration limits in drinking water and do not constitute a known health hazard.

3. Compounds tentatively identified by characteristic relative retention times from the Orlando Utilities samples are 0.0024 mg/l DDT, 0.0030 mg/l phosdrin, 0.00036 mg/l BHC (component with RRT of 0.45), and 0.000095 mg/l endosulfan. The concentrations found for DDT and phosdrin are both less than 5 percent of the limits recommended by the U.S. Environmental Protection Agency (EPA) for drinking water. No recommended limits were found for BHC or endosulfan.

4. Other unidentifiable organohalides were detected in the water samples tested.

5. The carbon adsorption data obtained from the Kuhl and Kirkman tap samples show that the percent removal of an organohalide at a given carbon dosage is dependent on the initial concentration of the compound. The data from the pesticide mixture samples (confirmed) reinforces this conclusion.

Treatment with 1 ppm of activated carbon effected a removal of better than 98 percent of all of the pesticides except for the chlordane alpha component of chlordane which was reduced by about 85 percent. After treatment with a dosage of 5 ppm of activated carbon all of the pesticides were reduced in concentration by 99 percent or better and all of the concentrations except that for heptachlor were well below the recommended limits. (A check on the heptachlor concentration was made by recalculating its concentration from the peak heights using the data obtained with known concentrations of the pesticide standards as was done for the peaks identified in the Orlando Utilities samples. This check showed that the concentration of heptachlor in all of the treated samples was above the recommended limits.)

As mentioned earlier, treatment with higher carbon dosages did not appear to effect any additional reduction in concentration, though small random deviations in the concentration are noted.

Conclusions

1. Measurable concentrations of halogenated organics were found in all of the water samples collected from various locations in the Orlando area. The number of compounds found in each sample varied from 5 to 11 and

their concentrations, with the exception of a few, appear to be insignificant.

2. Samples collected from the Kuhl tap and Kirhman tap showed higher concentrations of hydrocarbons, as compared to other water samples tested. However, those high concentrations are far below permissible concentrations in drinking water and will not constitute a health hazard.

3. Compounds tentatively identified by characteristic relative retention times from the Orlando Utilities samples are 0.0024 mg/l DDT, 0.0030 mg/l phosdrin, 0.0030 mg/l phosdrin, 0.00036 mg/l BHC, and 0.000095 mg/l endosulfan. The concentrations found for DDT and phosdrin are both less than 5 percent of the limits recommended by the U.S. Environmental Protection Agency (EPA) for drinking water. No recommended limits were found for BHC or endosulfan.

4. Other unidentifiable organohalides were detected in the water samples tested.

5. The carbon adsorption data obtained from the Kuhl and Kirhman tap samples show that the percent removal of an organohalide at a given carbon dosage is dependent on the initial concentration of the compound. The data from the pesticide mixture samples reinforces.

6. The results show that carbon treatment by a

6. The results show that carbon treatment by a batch process is effective in reducing organohalide concentrations. The Kuhl and Kirkman tap samples showed reductions in the concentrations of halogenated organics ranging from 25 to 98 percent after treatment with 10 ppm of carbon.

7. There was no significant difference in percent removal of organohalides by activated carbon of concentrations 5, 10, 25 and 50 mg/l. The mixture of seven different pesticides was reduced by 99 percent of the initial concentration after treatment with 5 mg/l activated carbon.

Appendix 1. Explanation of abbreviations

l	liter
mg	milligram
ml	milliliter
mm	millimeter
ng	nanogram
pg	picogram
ppm	parts per million
RRT	retention time relative to aldrin
RT	retention time relative to the solvent front
sec	second
ug	micrograms
ul	microliter

Appendix 2. U.S. EPA pesticide standards run on the same column and gas chromatograph as used in this experiment

Standard	RRT (based on aldrin)
Organic phosphorous pesticides	
phosdrin (mevinphos)	0.163
dimethoate	0.506
methyl parathion	0.702
malathion	0.925
ethion	2.707
Chlorinated herbacides	
2,4,5-T acid	1.600
o,p' DDE	1.542
p,p' DDE	1.920
DDD	2.496
2,4-DB acid	3.354
2,4-D acid	3.502
Chlorinated pesticides	
heptachlor	0.791
dieldrin	1.847
endosulfan	2.182
endrin	2.170
mirex	6.121

Standard	RRT (based on aldrin)
Multi-peaked pesticides	
BHC	0.364
	0.449
	0.637
DDT mix	0.342
	2.613
	3.298
Dowpon	1.431
	1.595
	1.842
Chlordane	0.12
	0.21
	0.34
	0.45
	0.61
	0.70
	0.80
	0.96
	1.16
	1.37
	1.46
	1.62
	1.72
	1.87

Standard	RRT (based on aldrin)
	2.58
	3.20

Appendix 3. List of chemicals used

Hexane, nanograde. Mallinckrodt Chemical Works.

Methylene chloride (dichloromethane), pesticide grade. Fisher Scientific Company.

Sodium sulfate (anhydrous), Certified A.C.S. Fisher Scientific Company.

Activated charcoal, Darco G-60 20-40 mesh, granular. Matheson, Coleman, and Bell.

The following are EPA pesticide standards obtained from the EPA research facilities at Research Triangle Park, North Carolina.

Aldrin

Chlordane alpha

Chlordane gamma

Endrine

Heptachlor

Methoxychlor

o',p' DDT

p',p' DDT

Appendix 4. Sample calculation of a pesticide concentration in drinking water.

The calculation of the approximate concentration of phosdrin in the Primrose tap sample is illustrated below. Data from standards run on the FTU gas chromatograph indicates that peaks due to phosdrin are 0.813 inches high per nanogram of phosdrin injected at a sensitivity setting of 10^2 x 8. The peak height in the Primrose tap sample was 7.4 cm. The concentration of the phosdrin in the hexane extract would then be:

(1 ng/0.813 inches)(1 inch/2.54 cm)(7.4 cm/5 ul)=

0.717 ng/ul. The concentration of phosdrin in the original sample would then be:

$$(0.717 \text{ ng/ul})(5.8 \text{ ml}/2000 \text{ ml})(10^6 \text{ ul}/1)(1 \text{ mg}/10^6 \text{ ng})\left(\frac{1}{0.7}\right)$$

0.00297 mg/l.

The 1/0.7 is an estimated coefficient of extraction efficiency.

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