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POLYCHLORINATED BIPHENYLS AND DDTs IN SEDIMENTS AND SEWAGE SLUDGE OF THE NEW YORK BIGHT

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CONTENTS

ABSTRACT

Sediment samples taken on a cruise in September, 1973, in the New York Bight Apex were analyzed for polychlorinated biphenyls and DDT's. In addition, several samples of sewage sludge were obtained from treatment plants in the New York Metropolitan area which dispose of their sewage via ocean dumping. Results of the analyses and data reduction are presented in tabular form and some preliminary conclusions stated. It is noted that although sediments close to the Hudson - Raritan outflow contain organics which are richer in PCB's than sediments in the rest of the Bight, the high organic inputs at the sewage sludge dump site result in this area having the major input of PCB's and DDT's to the Bight Apex.

KEY WORDS: MESA, NEW YORK BIGHT, SEDIMENTS, SEWAGE SLUDGE, POLYCHLORINATED BIPHENYLS, DDT's.

INTRODUCTION

One of the goals of the Marine ecosystems Analysis Program (MESA) in the New York Bight is to characterize the organic chemical constituents of sediments as related to the effects of ocean dumping. A study to analyze sediment and sewage sludge samples for synthetic chlorinated hydrocarbons was initiated as a part of the organic geochemistry program.

Polychlorinated biphenyls (PCB's) and DDT's, which are well-known anthropogenic contaminants of the marine ecosystem, were quantified in sediment samples which were collected from a 25-station grid (Figure 11) which extends 50 km south of the Hudson River Estuary.

METHODS

Sediment samples were collected using a Shipek grab sampler aboard the NOAA Ship FERREL. Sample aliquots were immediately placed in Whirlpak bags by using a stainless steel spoon and stored frozen. The samples were returned to the chemistry laboratories at AOML where, after freeze-drying, they were Soxhlet extracted for 18 hours with hexane. Separation of DDT from PCB in the resulting hexane extract was accomplished using FLORISIL and silicic acid column chromatography (Armour and Burke, 1970; Masumoto, 1972). Specifc DDT's and PCB's were then identified and quantified by gas chromatography using a Tracor 550 gas chromatograph equipped with a Ni^{63} electron capture detector interfaced to a Hewlett-Packard 3380A reporting integrator: Glass columns (2m x 2mm i.d.) packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport were used and achieved suitable separation of peaks when operated isothermally at 202° C. The peaks due to DDT and its metabolites were confirmed using a second 2m x 2mm i.d. column packed with 5% OV-210 on 100/120 mesh Supelcoport and programmed isothermally at 170° C.

DDT concentrations were determined by external standard techniques. The PCB concentrations were also measured by external standard techniques; however, the relative contributions from each of the four AROCLORs were calculated by a computerized pattern recognition technique (Zobel, 1974; West, et al, in preparation).

Total PCB's and total DDT's were calculated by summing the individual contributions of each AROCLOR and DDT or DDT metabolite respectively. Typical chromatograms for standards of DDT's and PCB's are presented in Figures 1, 2, 3, 4, 5, and 6. Representative chromatograms of PCB's and DDT's in sewage sludge and in a sediment sample are shown in Figures 7, 8, 9, and 10. Values less than 0.01 parts per billion were not reported.

RESULTS

The station locations and bulk organic geochemical data (total organic carbon and carbohydrates from Hatcher and Keister, 1976) are listed in Table I. Also listed in Table I are the total PCB and total DDT concentrations in parts per billion (ppb) of dry sediment. Total PCB concentrations range from 0.54 ppb to 1500 ppb with the high value being sample 13 located in a mud accumulation of a topographic low in the Bight which is adjacent to the sewage sludge dump site. The total PCB distributions in the Bight Apex are depicted in Figure 12. Total DDT concentrations in the same sediments range from <0.01 ppb to 120 ppb with only two samples containing what can be considered as "appreciable" amounts, i.e., station 6 with 75 ppb and station 13 with 120 ppb. Half of the stations contained less than 1 ppb total DDT. Total DDT distributions are shown in Figure 13. Figures 12 and 13 clearly show that the highest total PCB and DDT concentrations are found in sediments at the sewage sludge dump site which is a clear indication of their origin. Note that the concentration of PCB's at the sewage sludge dump site (station 13) is actually higher than one of the treatment plant sludges (Wards Island, see Table IV).

Each sample, except #14 where no sample was available for analysis, was also analyzed for individual DDT's and individual AROCLORs. The PCB data is presented in Table II. Figures 14, 15, 16, and 17 show the horizontal distributions of each AROCLOR in sediments of the New York Bight. As with the total PCB's (and DDT's) the figures illustrate that the highest concentrations are at the sewage sludge dump site. The concentrations for each individual DDT or DDT metabolite in sediments of the Bight are presented in Table III but are not contoured in figures due to the low concentrations at most stations.

Sewage sludge samples from four treatment plants in New York City were also analyzed for DDT's and PCB's. The total and individual PCB's and DDT's for these are presented in Table IV. In Tables V and VI we have compared the individual AROCLOR distributions in the sewage sludge from the treatment plants to Bight sediment samples where total PCB concentrations exceeded 100 ppb. Bight samples included those from near the sewage sludge dump site (stations 7, 8, 12 and 13) and one station south of the dump site (station 23, see Figure 12). In each of the Tables, individual AROCLORs are normalized to the total PCB concentration. The data in Table V indicate that the AROCLOR distribution in sewage sludge is quite variable. However, we have calculated a mean distribution of AROCLORs in treatment plant sludge using the data and it is included in the Table. Note that the mean ratios have quite high standard deviations. Table VI shows the same display of data for the Bight sediment samples. Since station 23 was somewhat south of the sewage sludge dump site we calculated a mean Bight sediment AROCLOR distribution both with and without the data from that station. A comparison of the mean sewage sludge AROCLOR distributions (Table V) to the mean for the Bight samples (Table VI) reveals that they are statistically the same given the standard deviations for the means. However, a comparison of the data on individual treatment plants and individual Bight samples shows that these distributions are highly variable. It seems that this variability would preclude any specific tagging of sewage sludges by such a simplified comparison.

TABLE I

BULK AND TRACE ORGANIC GEOCHEMICAL DATA FOR SEDIMENTS OF THE NEW YORK BIGHT COLLECTED SEPTEMBER, 1973

STATION #	LOCATION Latitude	Longitude	TOC* (%)	TCH# (%)	TOTAL PCB	TOTAL DDT
1	40°29.82'	73°57.03'	0.062	0.025	0.88	0.42
2	40°31.07'	73°51.60'	0.074	0.041	3.3	0.73
3	40°31.07'	73°47.76'	0.18	0.074	9.9	3.3
4	" 31.51'	" 40.18'	0.074	0.036	6.3	0.99
5	" 32.73'	" 31.98'	0.097	0.055	6.0	0.69
6	" 25.85'	" 57.55'	0.029	0.011	40	25
7	" 26.90'	" 53.12'	1.3	0.56	270	7.0
8	" 28.66'	" 47.78'	1.1	0.53	162	0.45
9	" 27.77'	" 40.46'	0.078	0.037	31	5.6
10	" 28.86'	" 31.98'	0.11	0.059	20	0.26
11	" 21.95'	" 57.06'	0.082	0.032	44	4.8
12	" 22.98'	" 52.20'	0.81	0.26	390	9.0
13	" 23.08'	" 46.82'	2.7	0.94	1500	120
14	" 24.24'	" 39.23'	-	0.021	-	-
15	" 24.77'	" 30.60'	0.082	0.038	7.7	0.63
16	" 17.79'	" 56.19'	0.082	0.035	9.8	1.2
17	" 18.97'	" 52.04'	0.16	0.063	1.1	0.80
18	" 18.88'	" 46.06'	0.16	0.088	8.4	0.05
19	" 19.96'	" 38.01'	0.083	0.018	1.3	0.64
20	" 20.84'	" 28.74'	0.054	0.032	0.54	0.67
21	" 12.76'	" 56.74'	0.18	0.040	2.4	1.7
22	" 13.96'	" 51.56'	0.076	0.032	6.8	2.2
23	" 14.79'	" 45.93'	2.7	1.8	150	8.8
24	" 15.86'	" 36.89'	0.07	0.050	16	<0.01
25	" 17.02'	" 28.00'	0.082	0.054	2.9	0.11

* Total organic carbon as percent dry sediment weight
\# Total carbohydrates as percent dry sediment weight

TABLE II

POLYCHLORINATED BIPHENYLS IN SEDIMENTS
FROM THE NEW YORK BIGHT
(ng/g (ppb) expressed in dry weight)

STATION	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Total PCB
1	0.49	0.06	<0.01	0.33	0.88
2	0.74	0.33	0.49	1.70	3.30
3	5.60	1.40	1.40	1.50	9.90
4	3.20	1.00	1.00	1.10	6.30
5	2.30	1.60	1.60	0.46	6.00
6	10.00	2.60	19.00	8.60	40.00
7	81.00	69.00	98.00	19.00	270.00
8	39.00	26.00	58.00	39.00	160.00
9	20 00	7.20	4.00	<0.01	31.00
10	4.10	7.70	1.80	6.20	20.00
11	24.00	6.90	6.90	5.80	44.00
12	120.00	170.00	50.00	50.00	390.00
13	170.00	610.00	180.00	490.00	1500.00
15	6.00	0.35	0.78	0.52	7.70
16	5.90	1.70	1.70	0.51	9.80
17	0.72	0.17	0.11	0.14	1.10
18	6.20	0.43	0.97	0.81	8.40
19	0.58	0.46	0.15	0.09	1.30
20	0.44	0.04	<0.01	0.06	0.54
21	0.63	0.91	0.23	0.63	2.40
22	5.00	0.52	0.52	0.78	6.80
23	49.00	15.00	6.50	78.00	150.00
24	3.10	3.10	3.10	7.00	16.00
25	0.09	1.00	1.80	0.01	2.90

TABLE III

DDT AND DDT METABOLITES IN
SEDIMENTS OF THE NEW YORK BIGHT
(ng/gm expressed as dry weight)

STATION	O,P'- DDE	P,P'- DDE	O,P'- DDD	P,P'- DDD	O,P'- DDT	P,Q'- DDT	TOTAL DDT
1	*	*	*	0.42	*	*	0.42
2	0.71	*	*	*	*	.02	0.73
3	2.7	*	*	.57	*	*	3.3
4	.93	*	*	.06	*	*	.99
5	.22	*	.34	*	*	*	.56
6	*	*	4.1	10	1.8	9.4	25
7	1.0	*	*	5.9	*	*	6.9
8	.28	*	*	.01	*	.16	.45
9	*	*	3.6	1.6	0.4	*	5.6
10	*	*	.01	.14	*	.11	.26
11	*	*	1.6	3.0	.10	.10	4.8
12	*	*	4.1	5.0	*	*	9.0
13	*	*	63	56	*	*	120.
15	*	.63	*	*	*	*	.63
16	*	1.2	*	*	*	*	1.2
17	.21	.09	.11	.12	.26	.01	0.79
18	*	.05	*	*	*	*	.05
19	.33	*	*	.15	.12	.04	.64
20	*	*	.07	.60	*	*	.67
21	1.1	*	*	.52	*	.05	1.7
22	*	.64	*	.54	.98	*	2.2
23	*	*	2.4	6.4	*	*	8.8
24	*	*	*	*	*	*	<0.01
25	.11	*	*	*	*	*	.11

* < 0.01 ppb

TABLE IV

PCBs AND DDTs IN SEWAGE SLUDGE FROM TREATMENT PLANTS IN THE NEW YORK METROPOLITAN AREA
(ng/g of solid sewage)

	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Total PCB
Wards Island	60	190	680	300	1200
Hunts Point	700	1300	700	1300	4000
Passaic Valley	2600	2200	770	650	6200
Tallmans Island	650	430	980	240	2300

	O,P'-DDE	P,P'-DDE	O,P'-DDD	P,P'-DDD	O,P'-DDT	P,P'-DDT	TOTAL DDT
Wards Island	-	68	110	180	20	-	380
Hunts Point	-	-	22	120	-	-	140
Passaic Valley	110	-	46	-	-	120	280
Tallmans Island	420	1800	60	-	-	-	2300

TABLE V

INDIVIDUAL PCB CONCENTRATIONS FOR SEWAGE SLUDGE FROM TREATMENT PLANTS NORMALIZED TO TOTAL PCB CONCENTRATION

PLANT	AROCLOR 1242	AROCLOR 1248	AROCLOR 1254	AROCLOR 1260
Wards Island	0.05	0.16	0.57	0.25
Hunts Point	0.18	0.33	0.18	0.33
Passaic Valley	0.42	0.35	0.12	0.10
Tallmans Island	0.28	0.19	0.43	0.10
Mean	0.23	0.26	0.33	0.20
Std. Dev.	0.16	0.10	0.21	0.11

TABLE VI

INDIVIDUAL PCB CONCENTRATIONS FOR
NEW YORK BIGHT SEDIMENT SAMPLES
NORMALIZED TO TOTAL PCB CONCENTRATION

(Samples Containing Greater than 100 ppb Total PCB)

STATION	AROCLOR 1242	AROCLOR 1248	AROCLOR 1254	AROCLOR 1260
7	0.30	0.26	0.36	0.07
8	0.24	0.16	0.36	0.24
12	0.31	0.44	0.13	0.13
13	0.11	0.41	0.12	0.33
23	0.33	0.10	0.04	0.52
Mean*	0.24 (0.26)	0.32 (0.27)	0.24 (0.20)	0.19 (0.26)
Std. Dev.*	0.09 (0.09)	0.11 (0.12)	0.14 (0.15)	0.12 (0.18)

*Values in parenthesis include station 23; others exclude it.

Total PCB's and individual AROCLOR concentrations were also normalized to total organic carbon (TOC). These ratios are plotted and contoured in Figures 18 through 22. The distribution of these ratios (PCB/TOC, AROCLOR/TOC) indicate which sediments in the Bight have organic fractions which are relatively enriched in PCB's. The total PCB/TOC contours (Figure 18) show two areas of such enrichment; the Hudson River plume and the dumping areas for sewage, dredge spoil and cellar dirt. A feature of Figure 18 is the high concentration of PCB's in the organic fractions off Sandy Hook and along the New Jersey coastline to the south.

The following observations are pertinent to the plots for individual AROCLOR/TOC ratios:

- AROCLOR 1242/TOC, 1254/TOC and 1260/TOC ratios all show the same high concentrations of AROCLORs in the organic fractions in the Hudson plume as it moves southward along the Jersey coast as did the total PCB/TOC ratios.
- The AROCLOR 1248/TOC ratios indicate that that AROCLOR is high in the organic fraction near the dump sites, but not near any specific site.
- The AROCLOR 1260/TOC ratio is almost as high at the sewage sludge dump site as it is off Sandy Hook. It is also noteworthy that these high 1260/TOC ratios seem confined to the Christiaensen Basin.

Since Figure 17 shows that the high AROCLOR 1260 concentrations are confined to the sewage sludge dump site, there seems to be very little advection of AROCLOR 1260 away from the Christiaensen Basin area.

- The total PCB/TOC and AROCLOR 1260/TOC ratios both share high values in the vicinity of station 24. This, coupled with the high total PCB concentrations at station 23, may indicate some association of PCB's with the head of the Hudson shelf valley.

CONCLUSIONS

Data presented in this report indicate that the organic fraction of bottom sediments in the New York Bight Apex below the Hudson River plume and the various dump sites is enriched in PCB's and individual AROCLORs relative to the rest of the Bight. However, a consideration of un-normalized concentrations of both total PCB's and individual AROCLORs shows that the disposal of sewage sludge (near station 13) is probably the major source of these compounds in the Bight Apex sediments. This sewage contribution appears to be much more extensive than the Hudson River plume contribution. Although PCB concentrations are relatively low in plume sediments, the PCB's in the organic fraction are high as reflected by the high PCB/TOC ratios. Because the organic load of sewage is much higher, the dump site sediments correspondingly have high TOC values and, even though the sewage PCB/TOC ratios are lower when compared to plume sediments, the net input of PCB's is much higher.

A simple analysis of PCB and DDT data from Bight sediments and individual treatment plants does not allow tagging of specific sewage sludges.

Data on DDT's similarly indicates that the sewage sludge dumping is a major source of these compounds in Bight sediments.

RECOMMENDATIONS

The data in Tables V and VI of this report indicate that an extensive portion of the PCB's in the New York Bight Apex sediments are of sewage origin; however, the variability in sediment samples and sewage sludge samples is so high that we cannot state this with a great degree of certainty. This problem should be addressed and efforts made to clearly demonstrate what the origins of the Apex sediment PCB's are. The same should be done with the DDT's using DDT metabolites. OCL intends to do some work along this line as part of the INSTEP experiment and has described the work in the organic geochemistry work unit of the AOML INSTEP proposal. Perhaps the same should be done for the entire Apex area.

The data in this report seems to clearly identify one major source of PCB's and DDT's in the New York Bight Apex; i.e., sewage sludge dumping. However, this may not be the only source; e.g., the high value for total PCB's, PCB/TOC and 1260/TOC at stations 23 and 24, south of the sewage sludge dump, are of interest in this regard as are the high PCB/TOC and AROCLOR/TOC ratios below the Hudson River plume. The extent of all other inputs, possibly small, should be investigated; e.g., transport of outer shelf sediments to the Apex, transfer across the air/sea interface, inputs through the Hudson-Raritan Estuary, etc. Some of these sources will be investigated as part of the INSTEP program. Other sources can probably be studied in the proposed Air/Sea Interface and the Estuarine Interaction studies.

ACKNOWLEDGEMENTS

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LIST OF FIGURES

Figure 21. Aroclor 1254/TOC in New York Bight Sediments.

Figure 22. Aroclor 1260/TOC in New York Bight Sediments.

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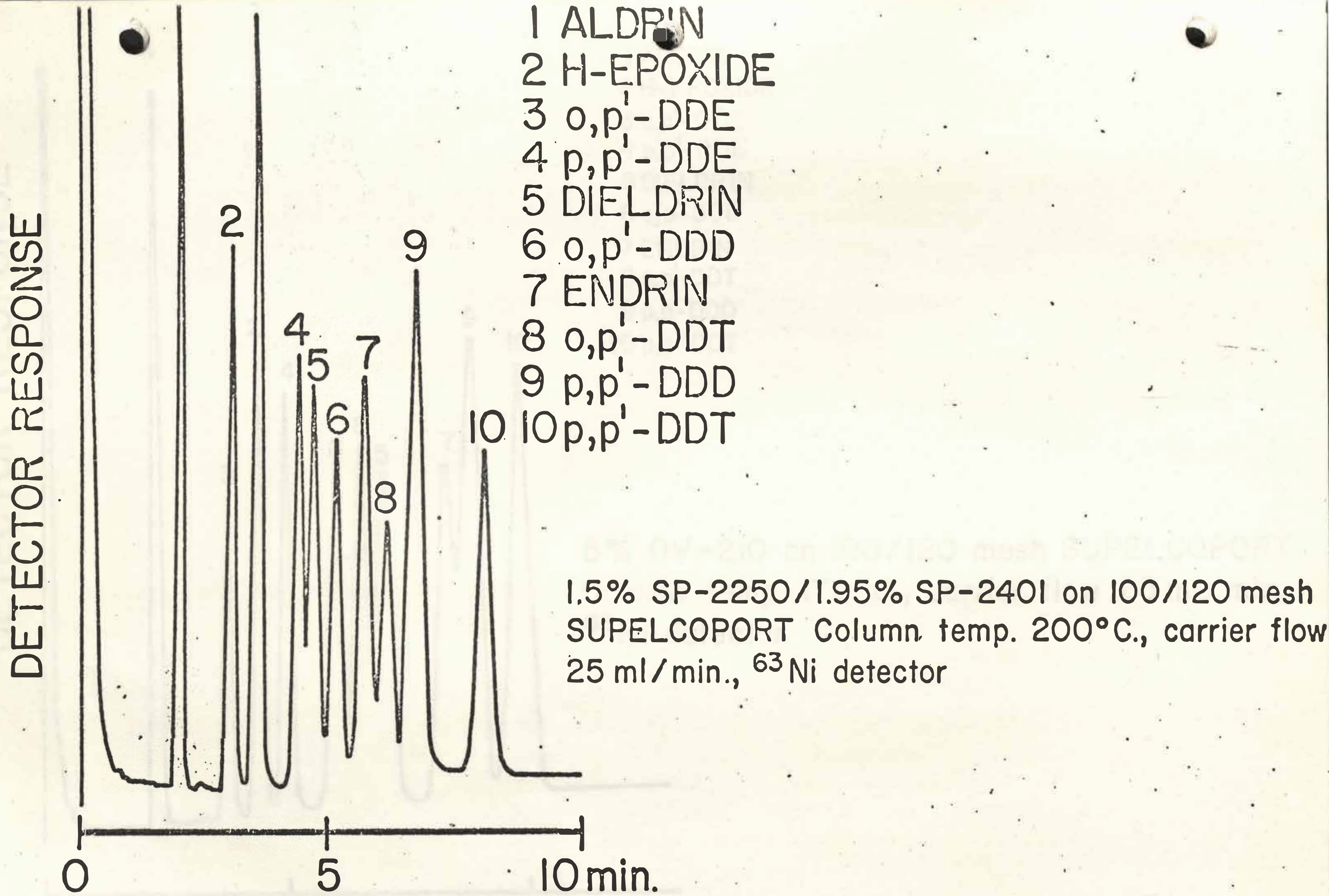

Figure 1. Gas Chromatogram of DDT and pesticide standards on a column of 1.5% SP-2250/1.95% SP-2401.

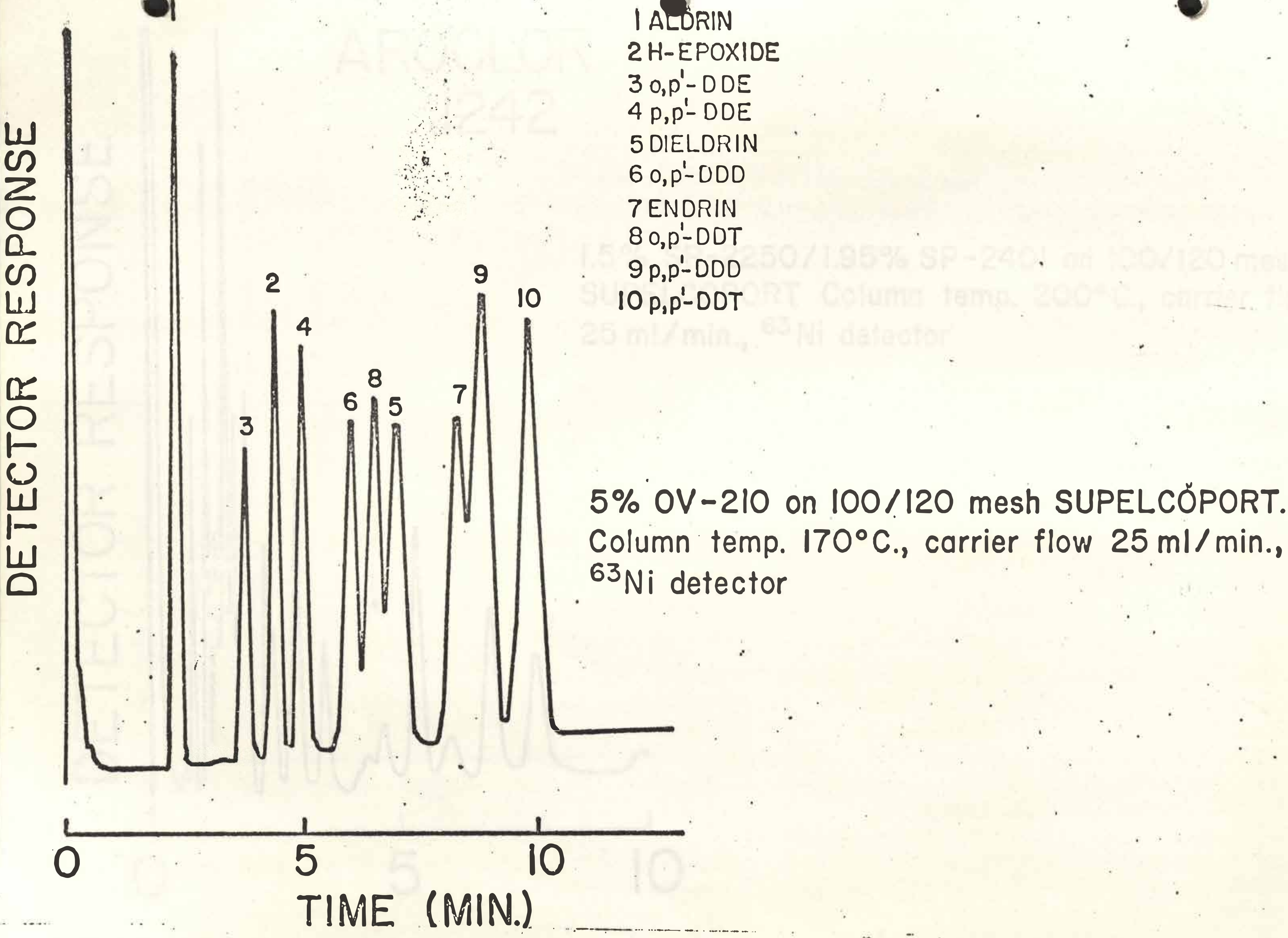

Figure 2. Gas Chromatogram of DDT and pesticide standards on a column of 5% OV-210.

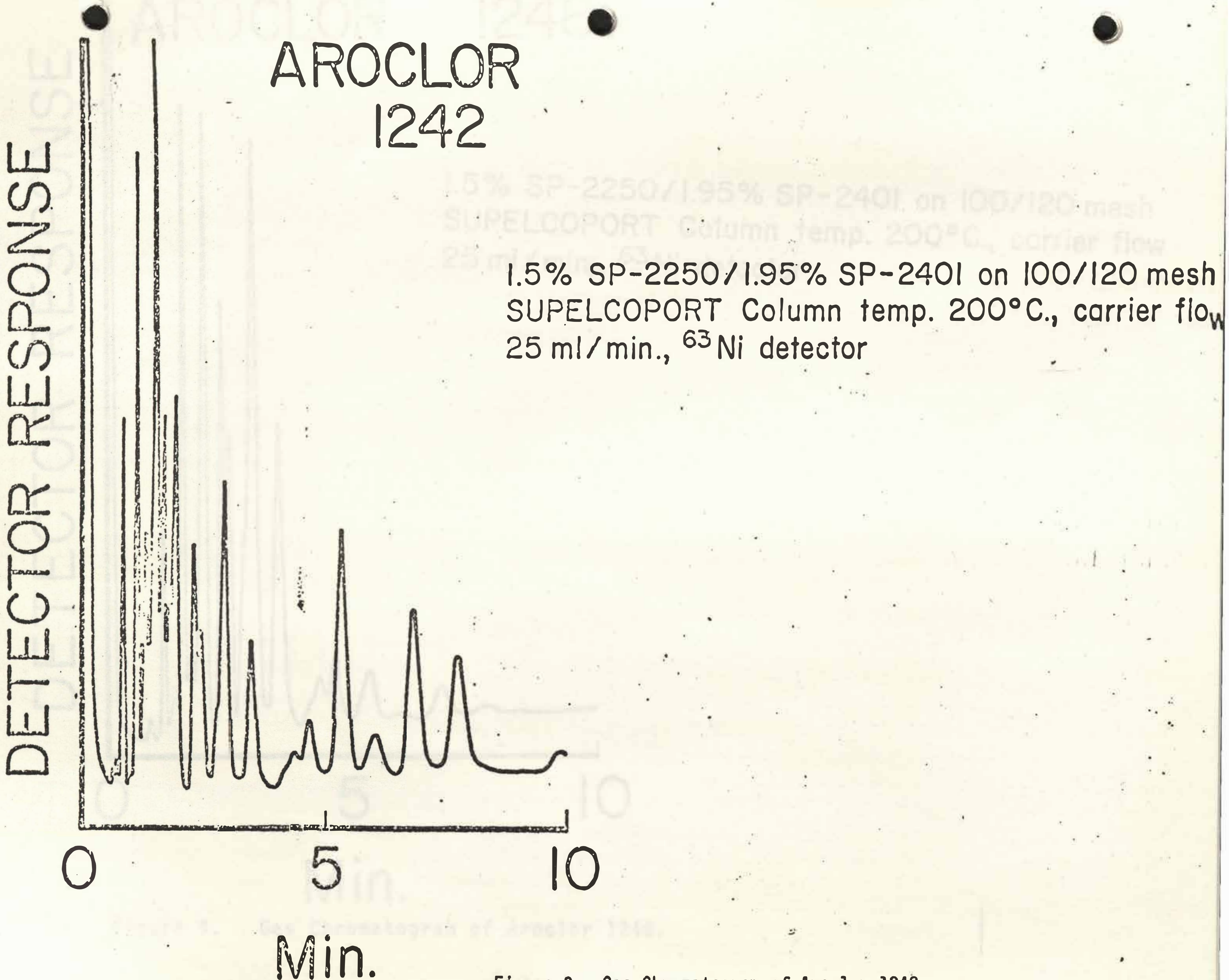

Figure 3. Gas Chromatogram of Aroclor 1242.

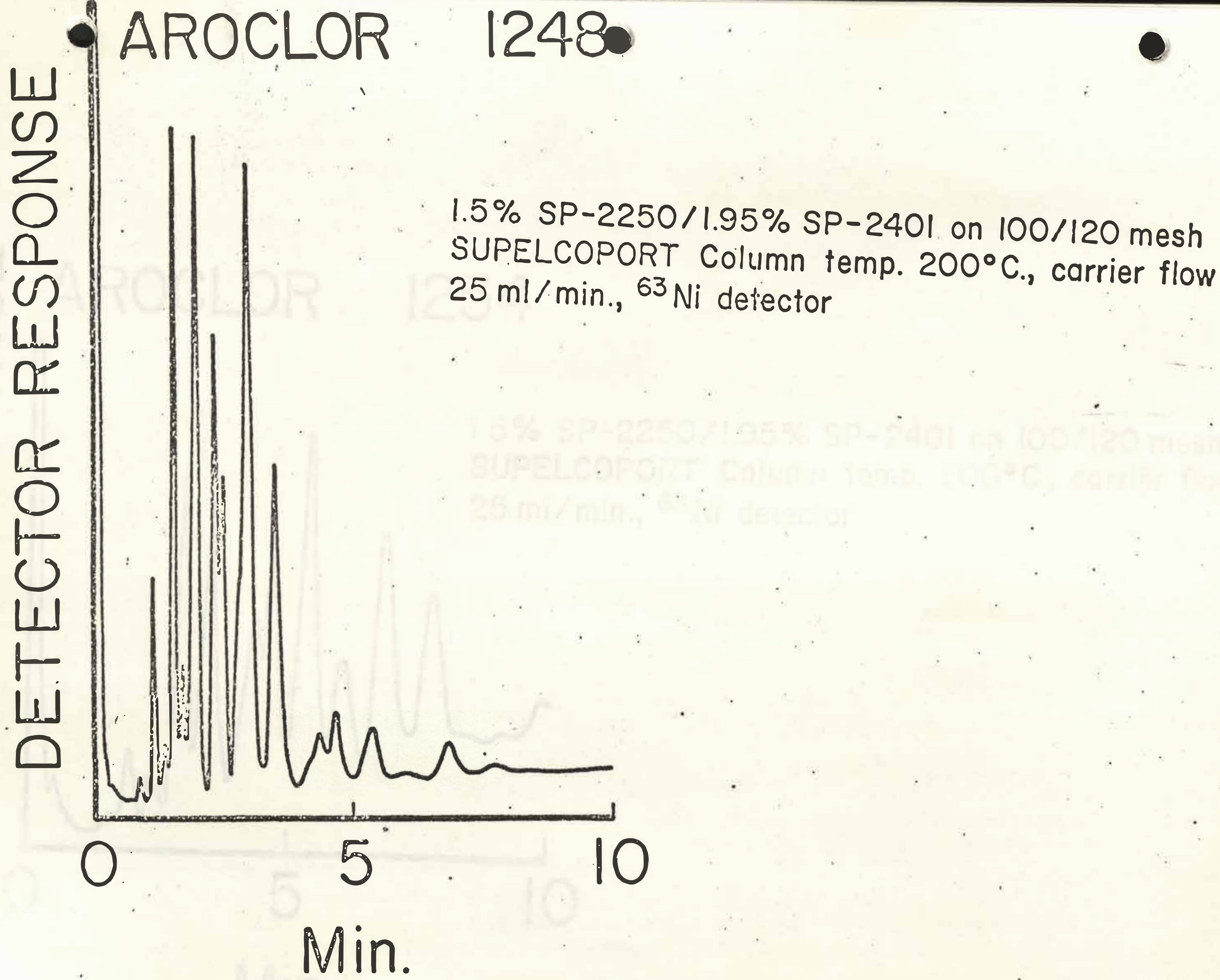

Figure 4. Gas Chromatogram of Aroclor 1248.

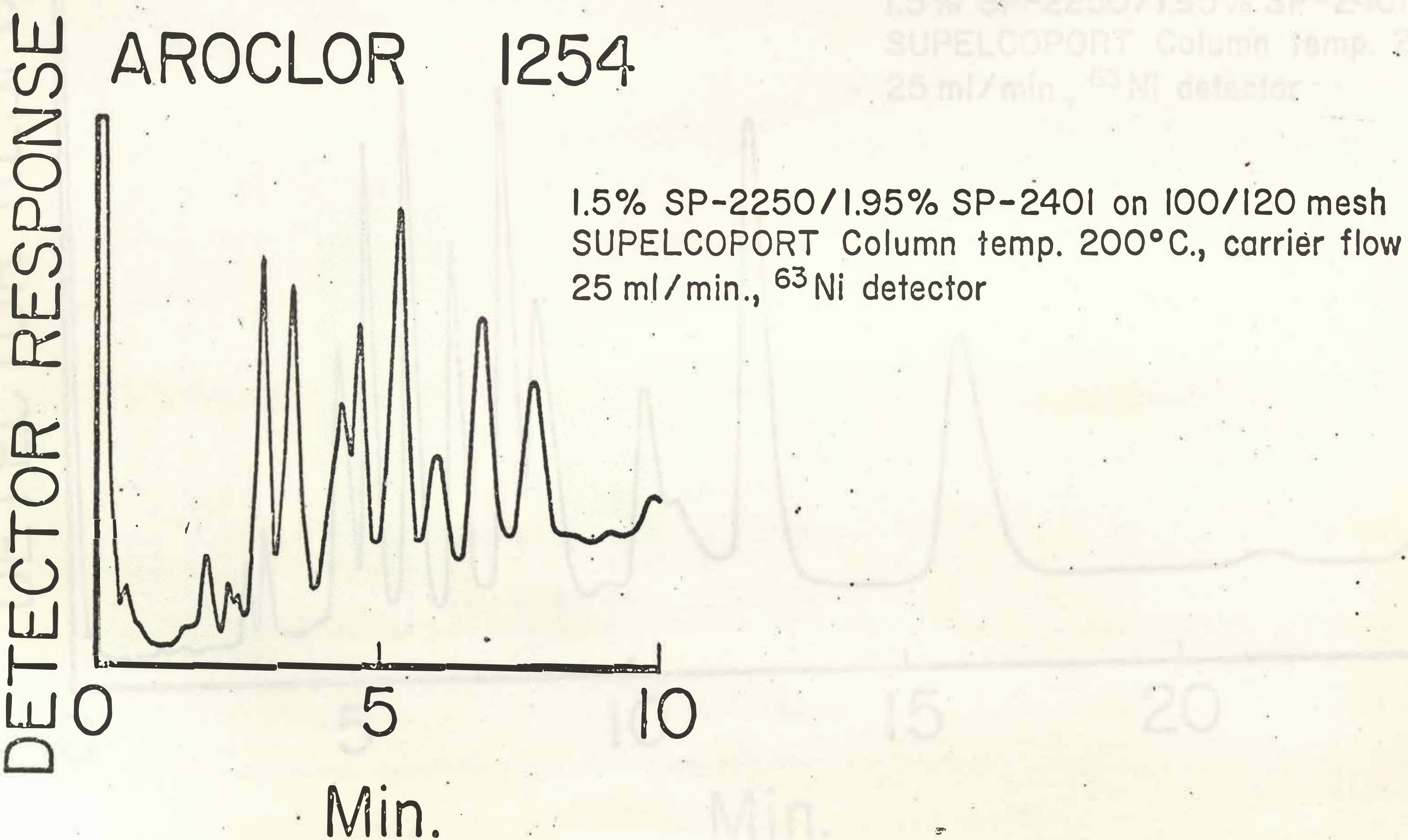

Figure 5. Gas Chromatogram of Aroclor 1254.

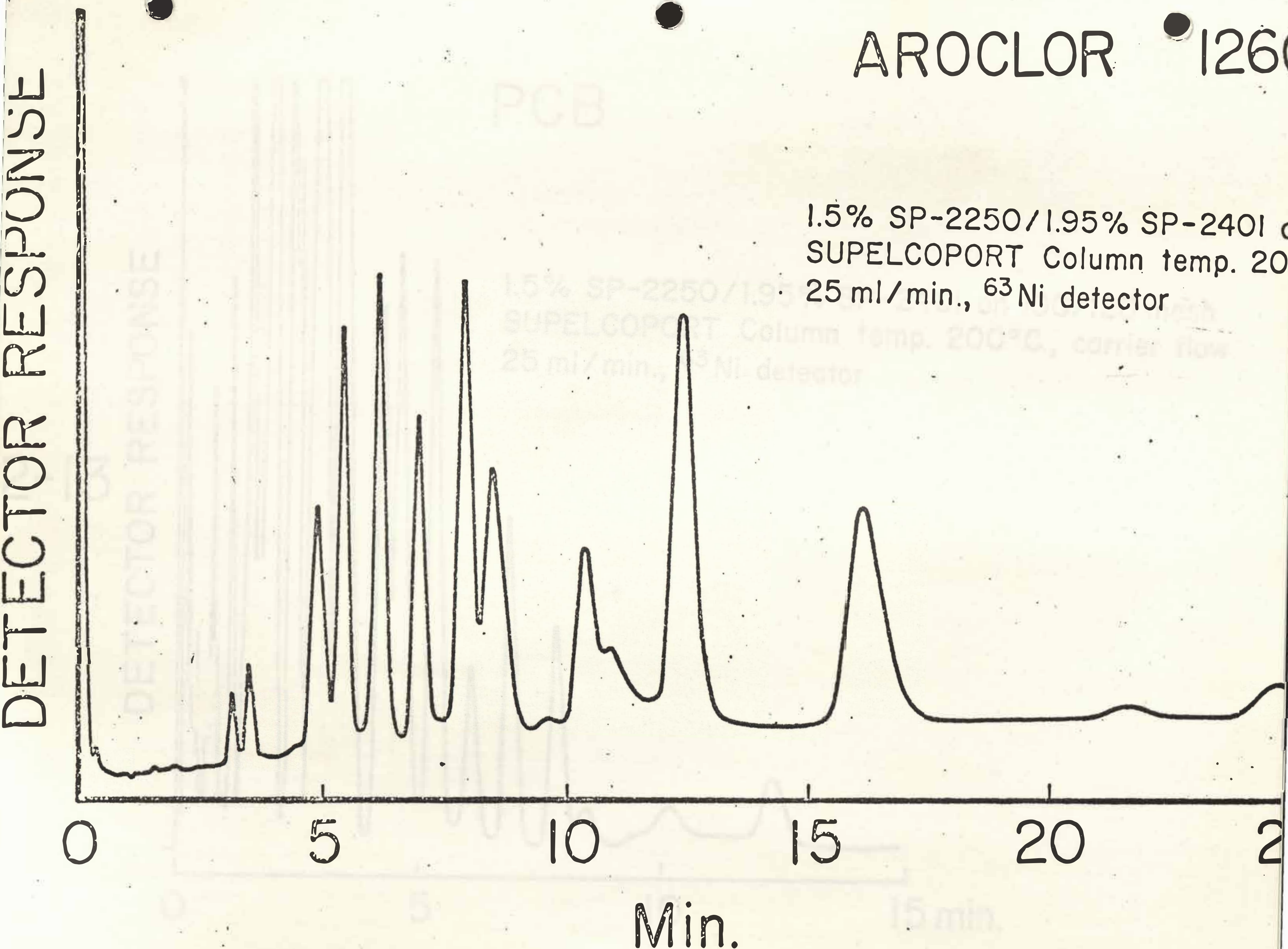

Figure 6. Gas Chromatogram of Aroclor 1260.

2-13

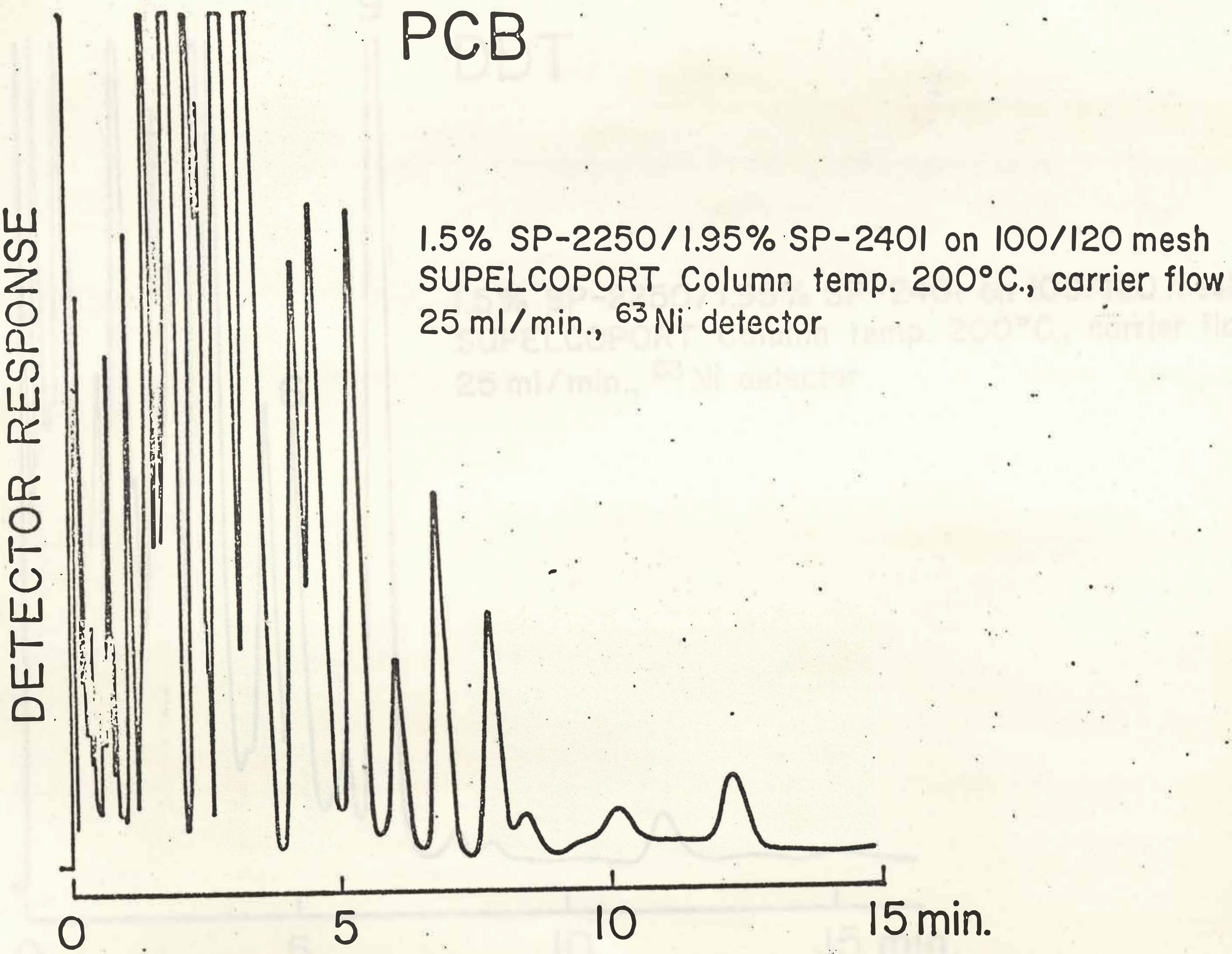

Figure 7. Gas Chromatogram of PCB at station 13.

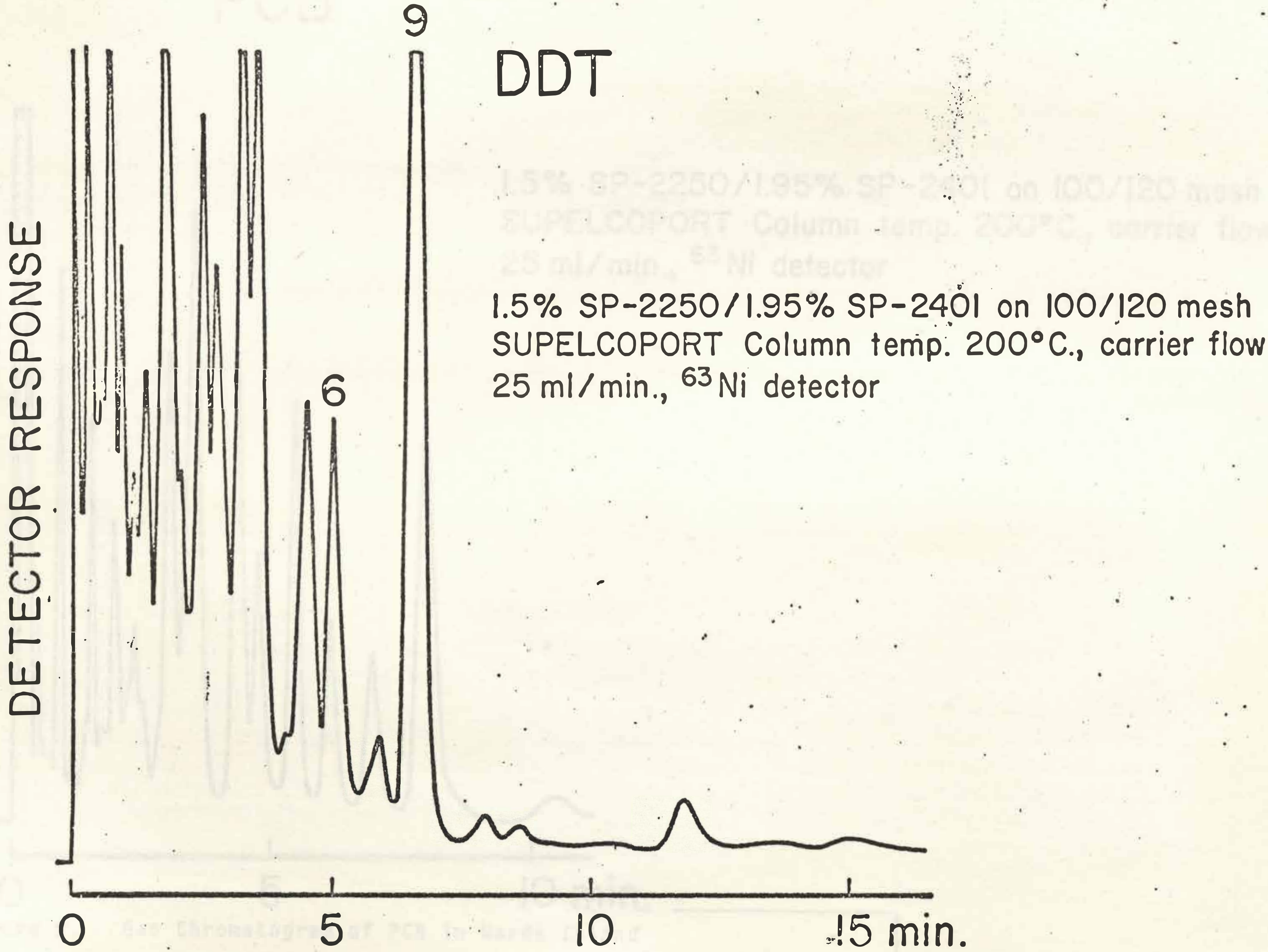

Figure 8. Gas Chromatogram of DDT at station 13.

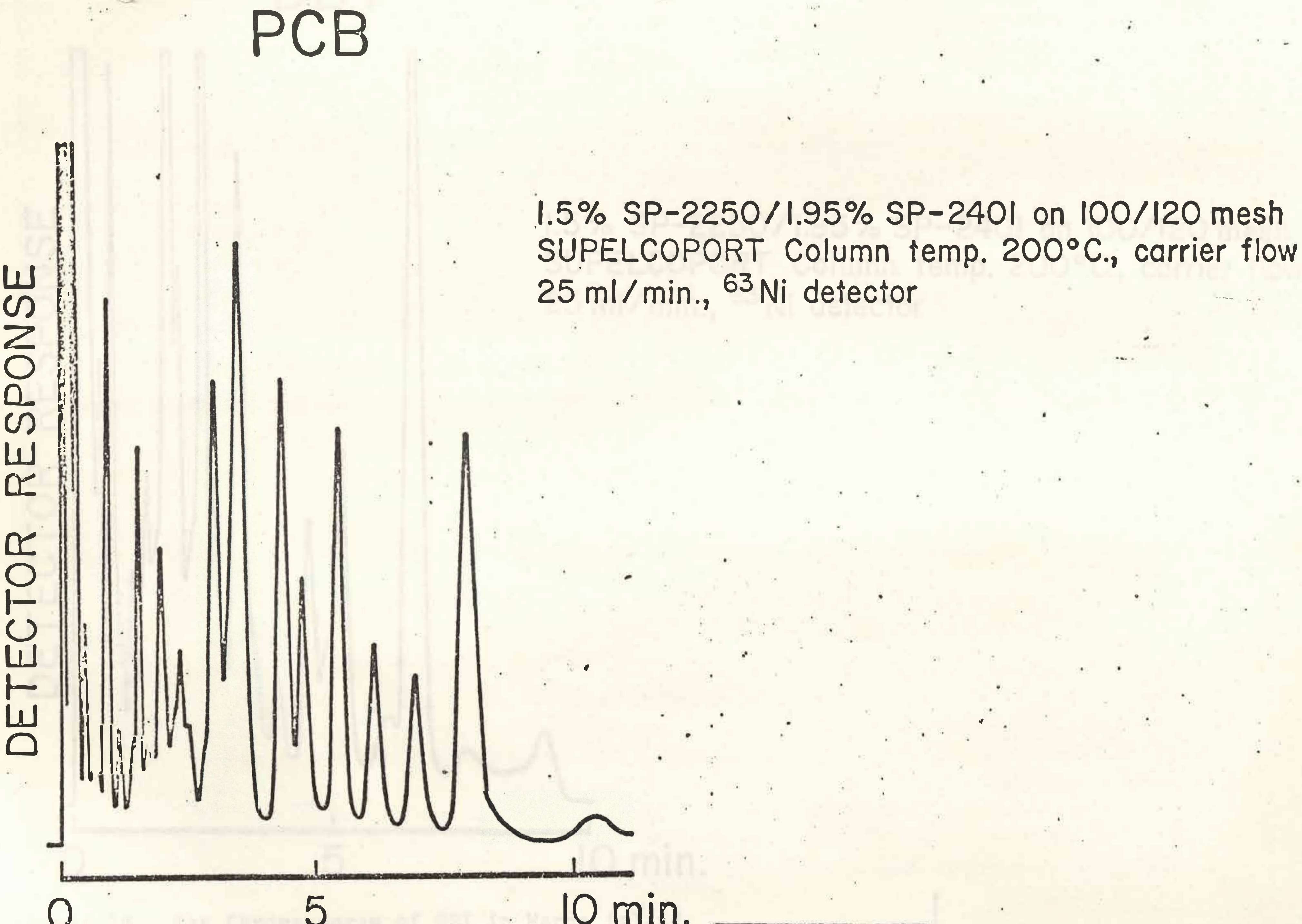

Figure 9. Gas Chromatogram of PCB in Wards Island sewage sludge.

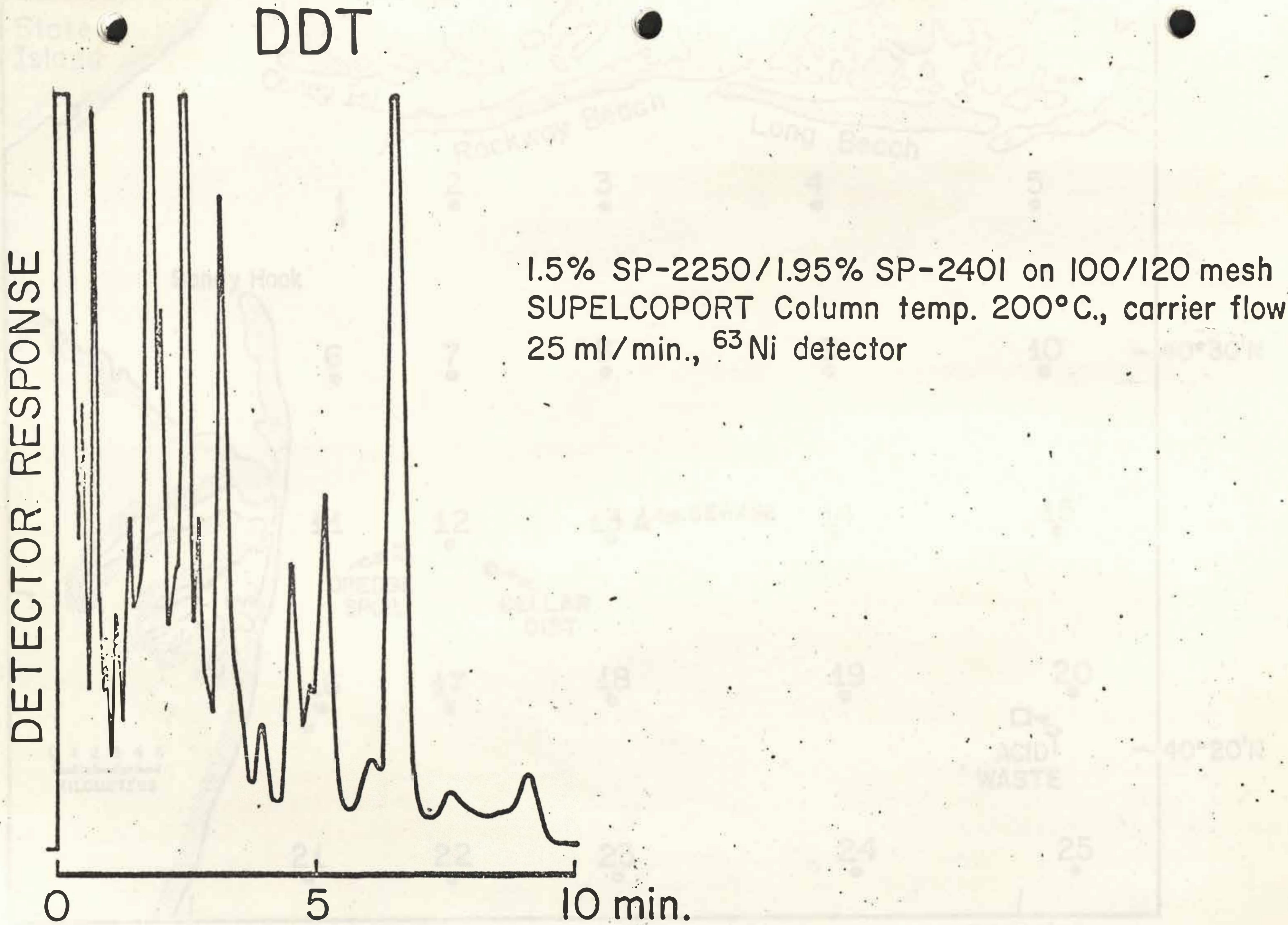

Figure 10. Gas Chromatogram of DDT in Wards Island sewage sludge.

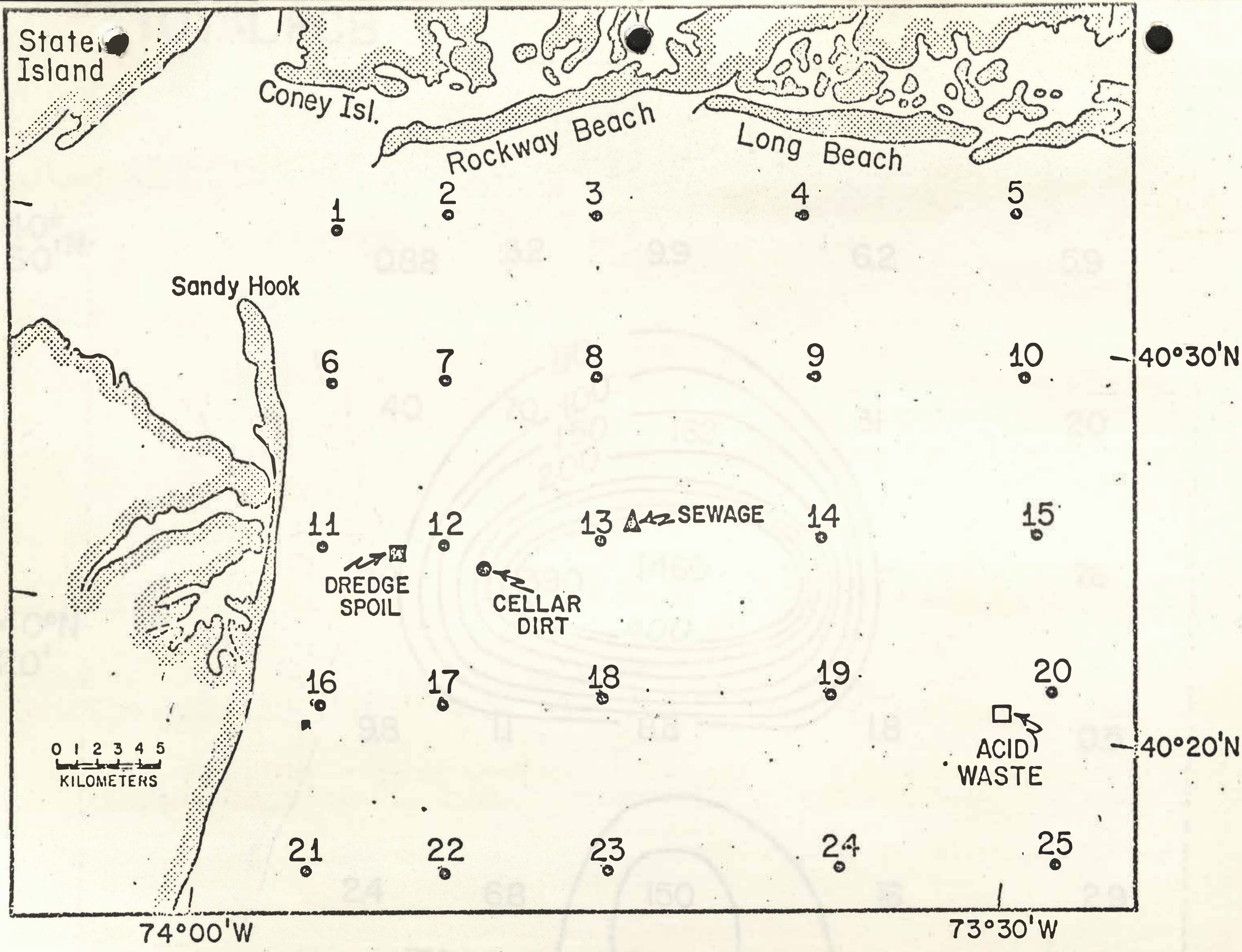

Figure 11. Station locations in the New York Bight Apex.

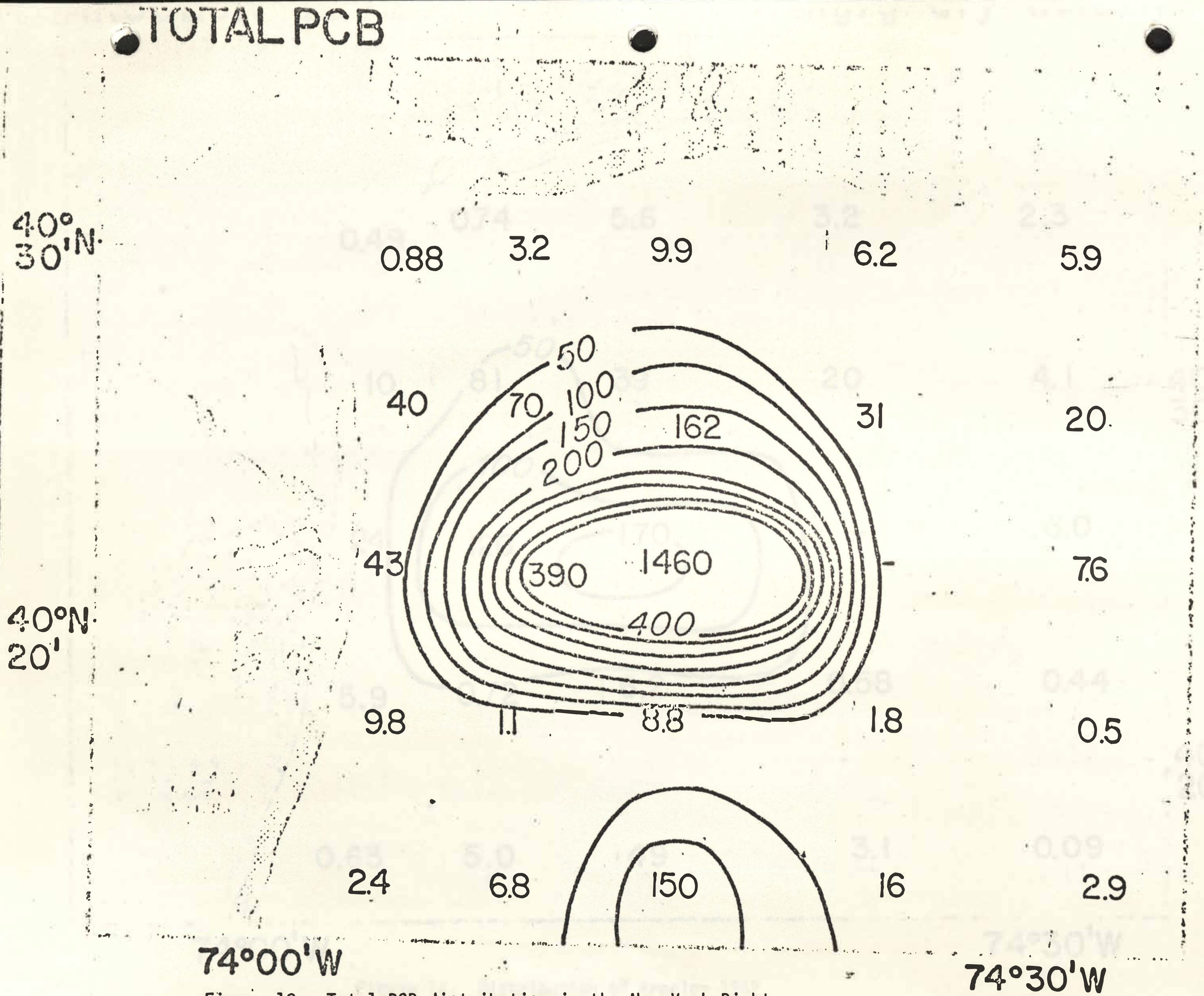

Figure 12. Total PCB distribution in the New York Bight.

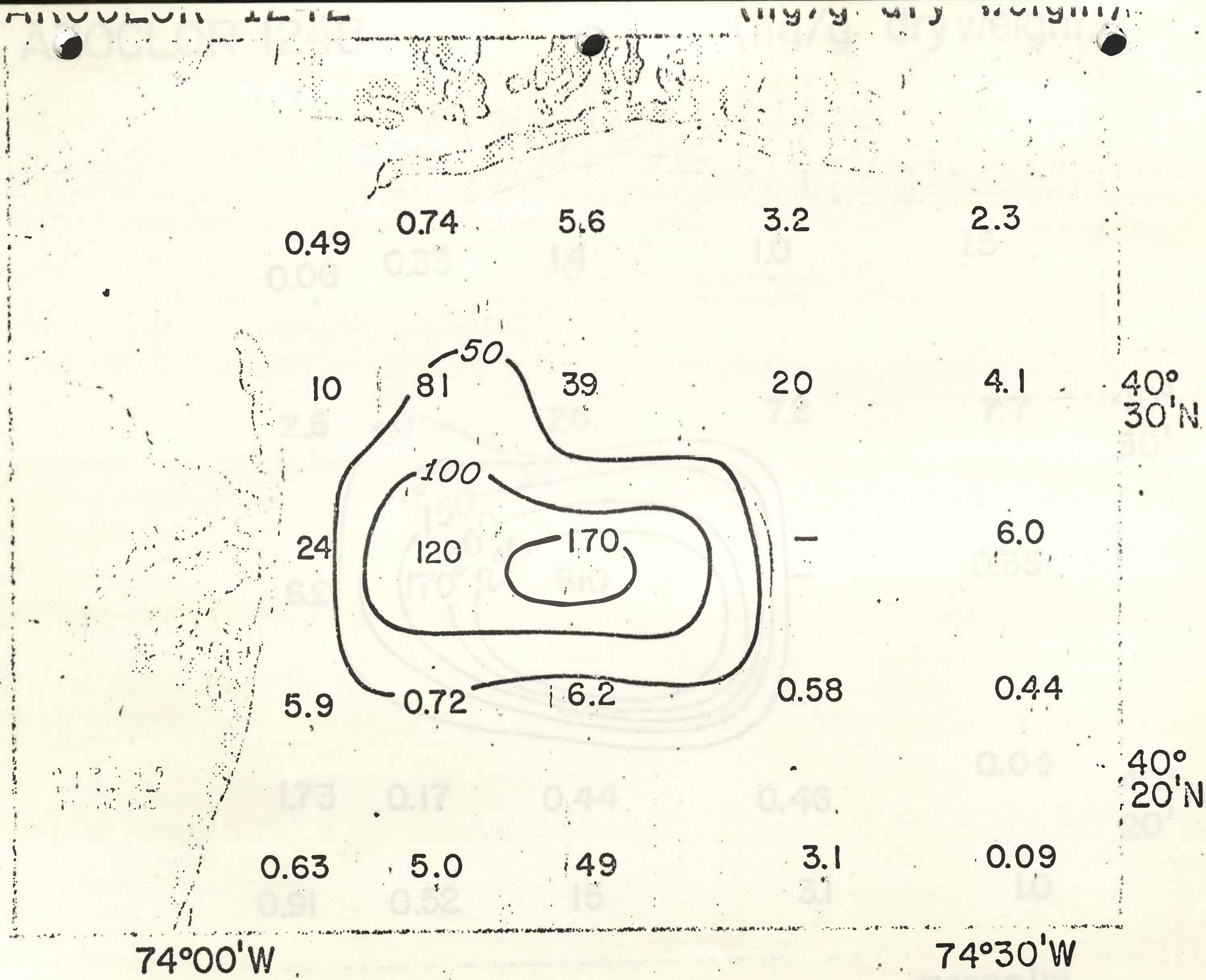

Figure 14. Distribution of Aroclor 1242.

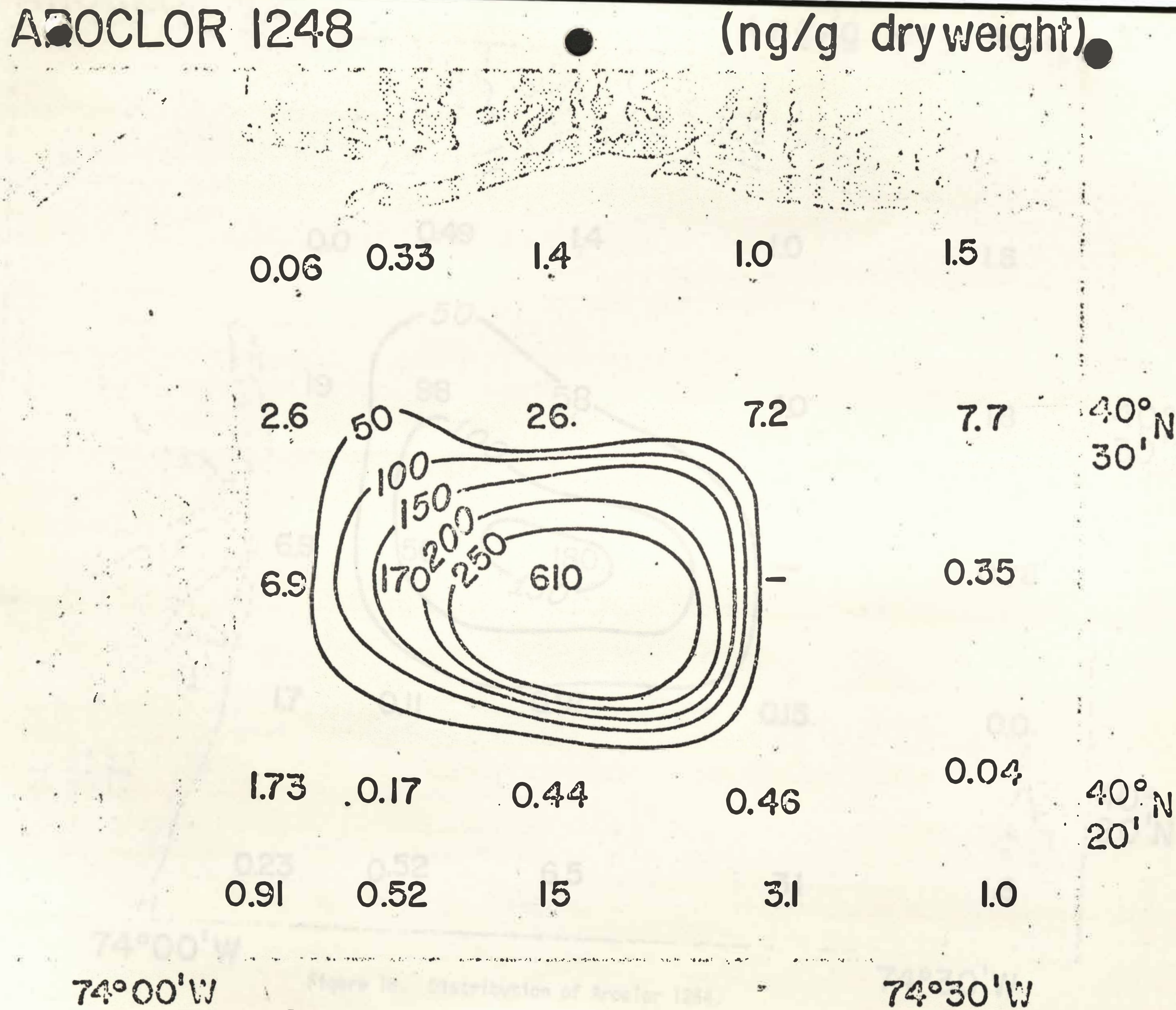

Figure 15. Distribution of Aroclor 1248.

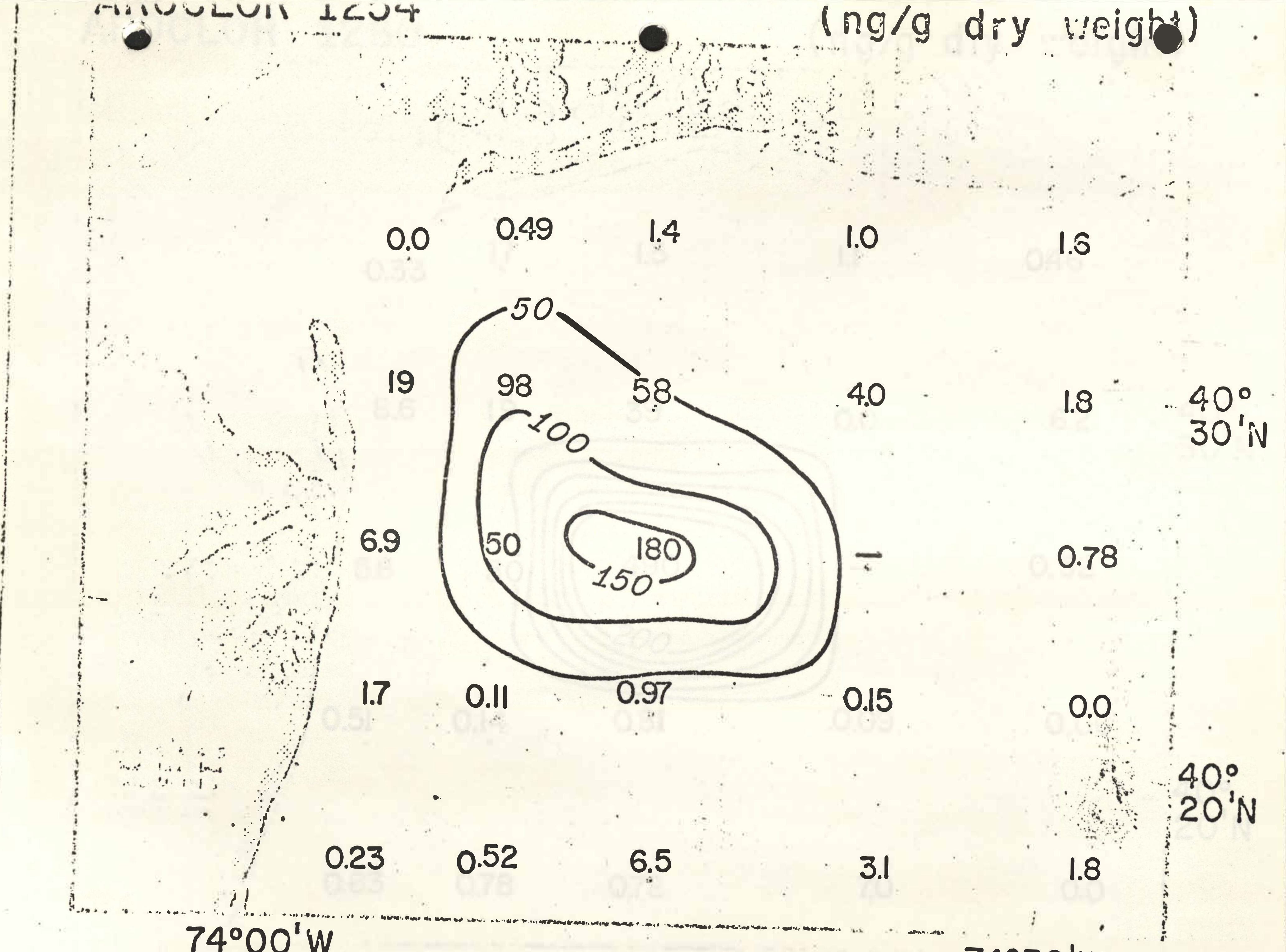

Figure 16. Distribution of Aroclor 1254.

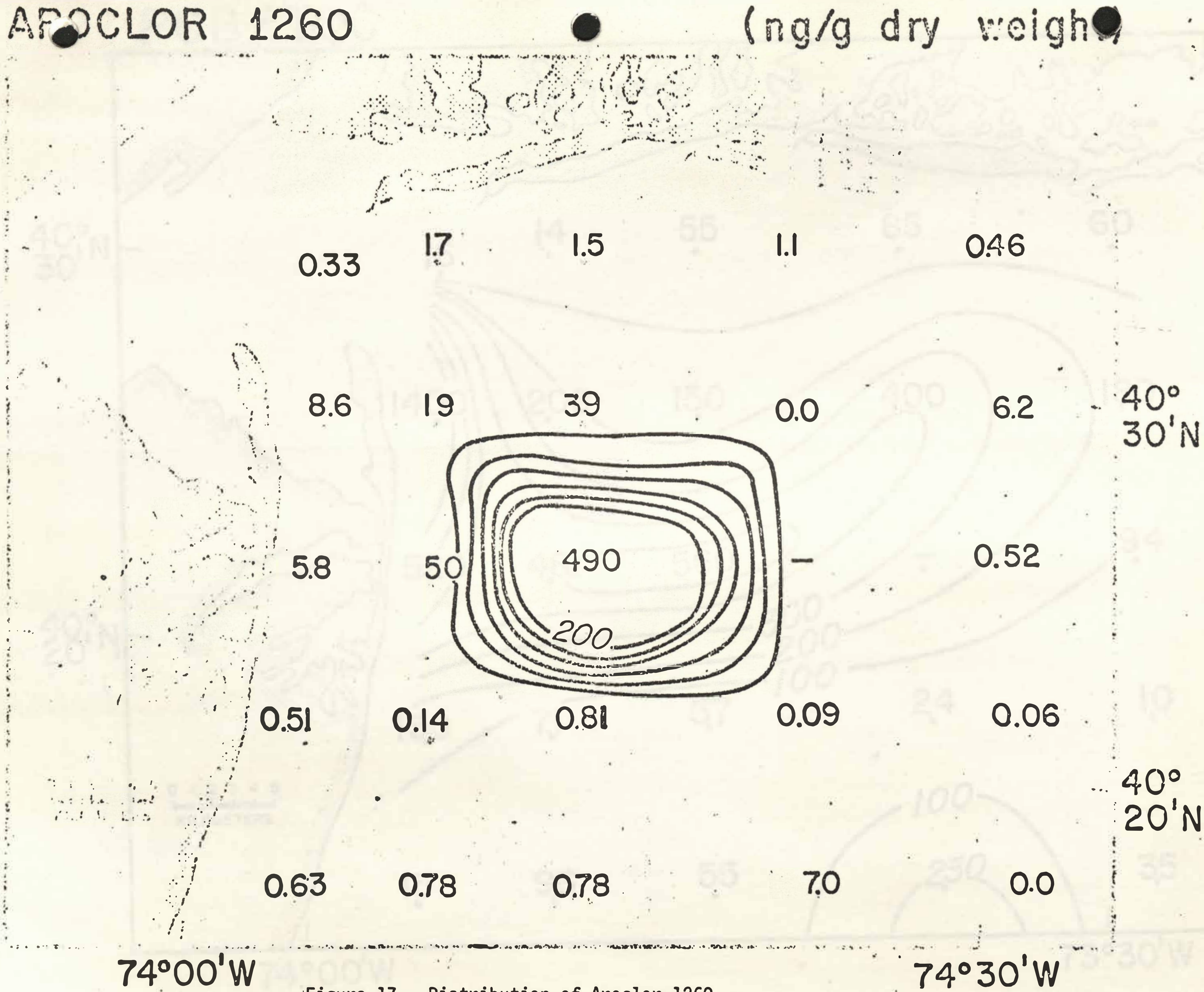

Figure 17. Distribution of Aroclor 1260.

PCB/TOC

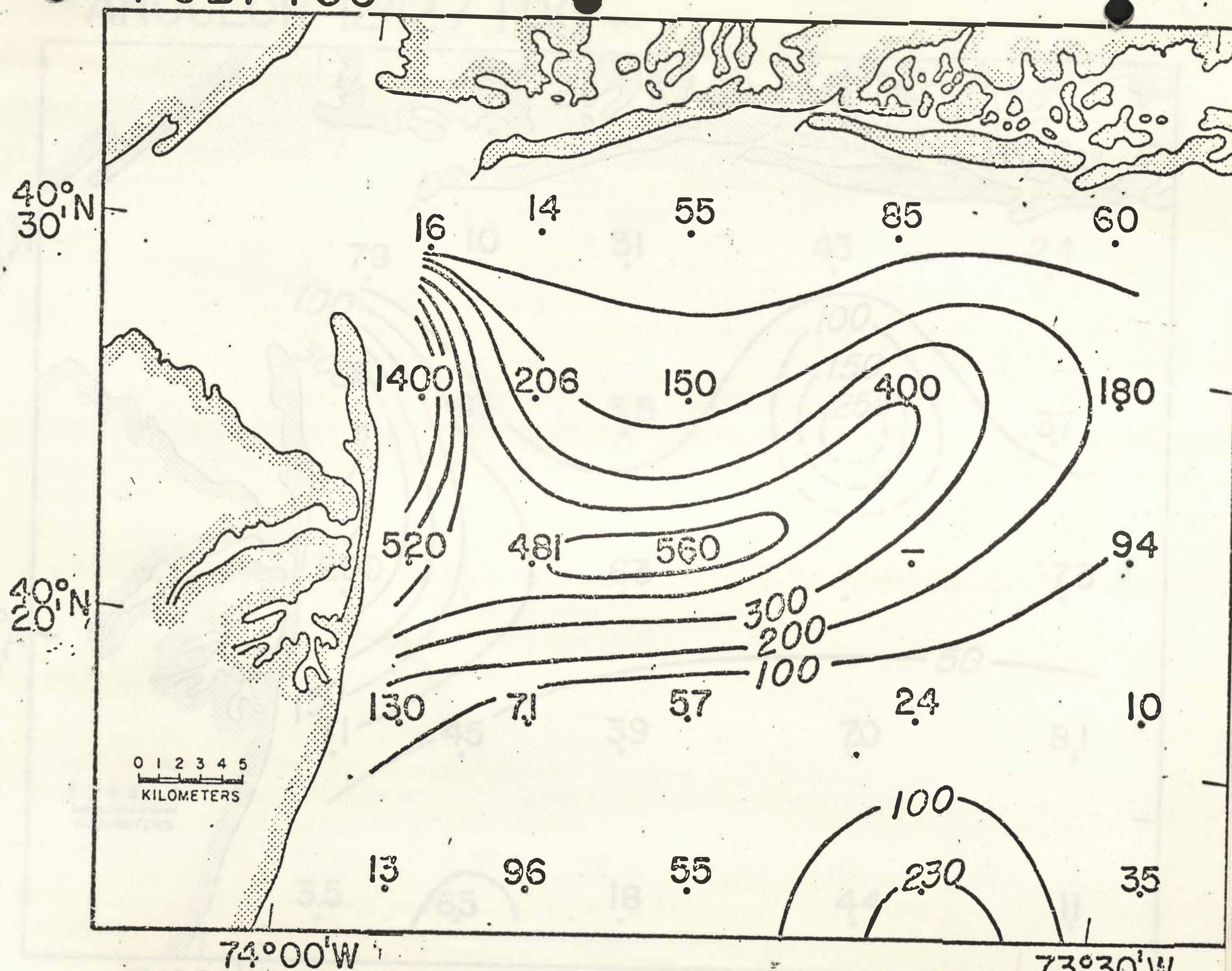

Figure 18. Total PCB/TOC in New York Bight Sediments.

AROCLOR 1242/TOC

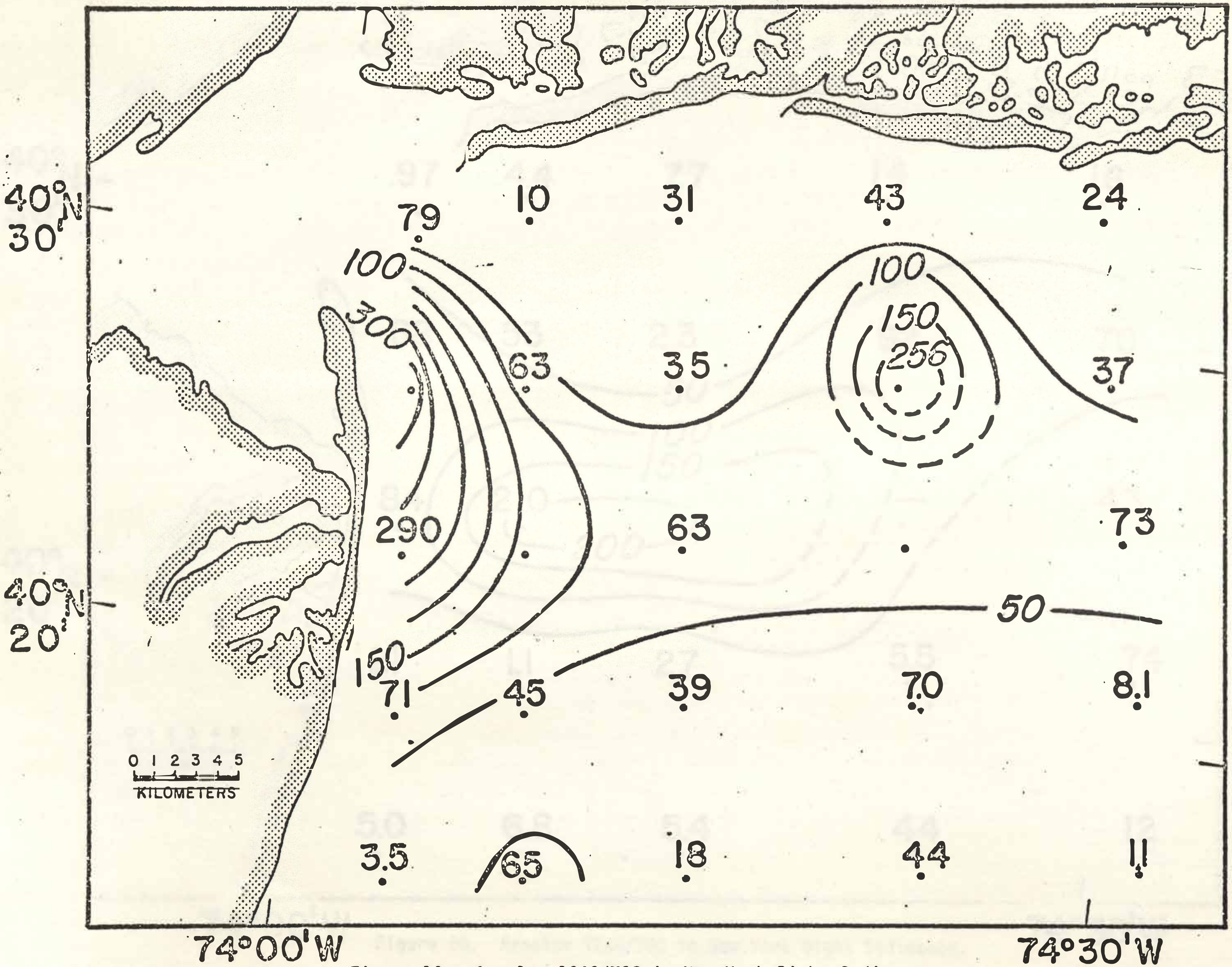

Figure 19. Aroclor 1242/TOC in New York Bight Sediments.

AROCLOR 1248/TOC

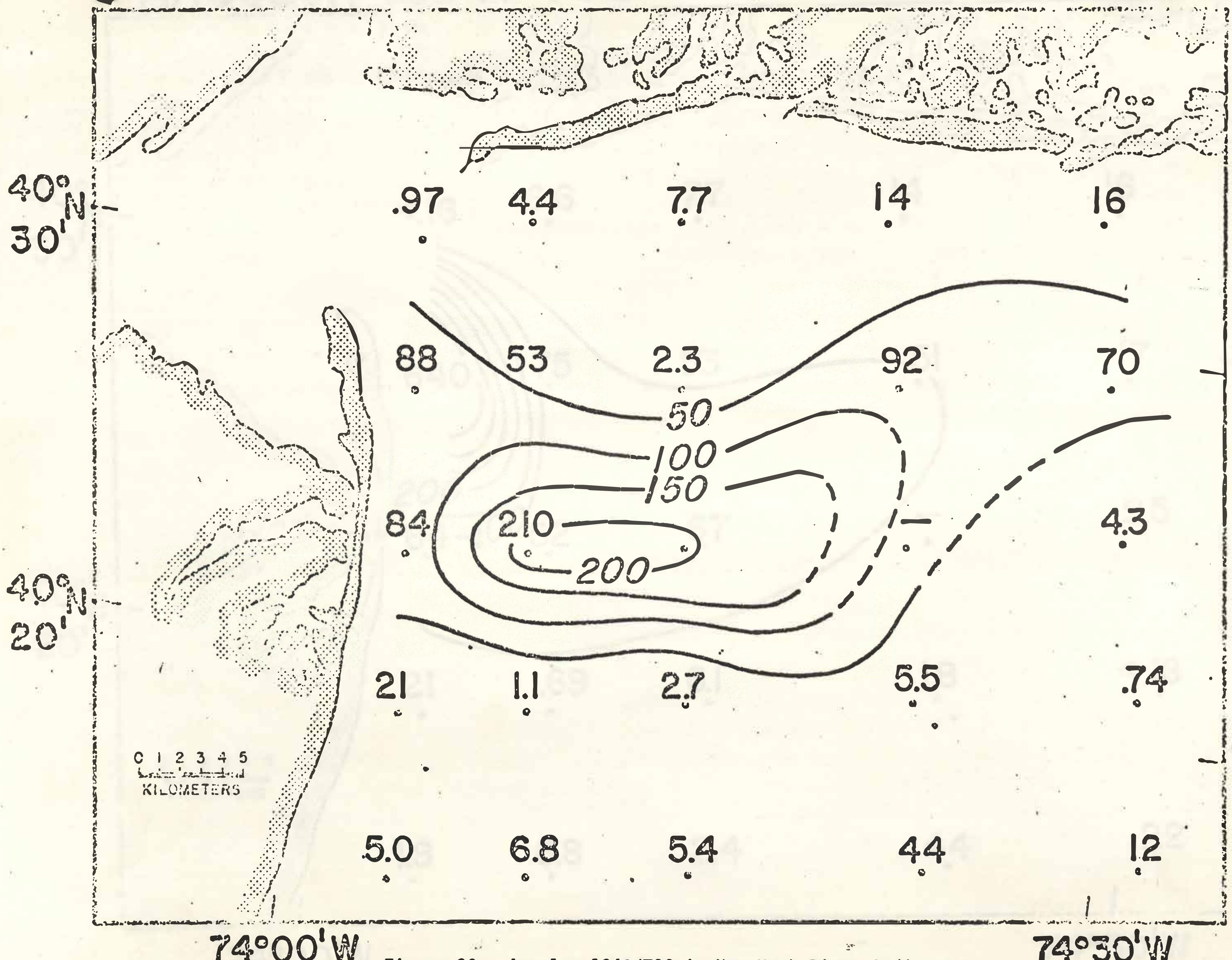

Figure 20. Aroclor 1248/TOC in New York Bight Sediments.

AROCLOR 1254/TOC

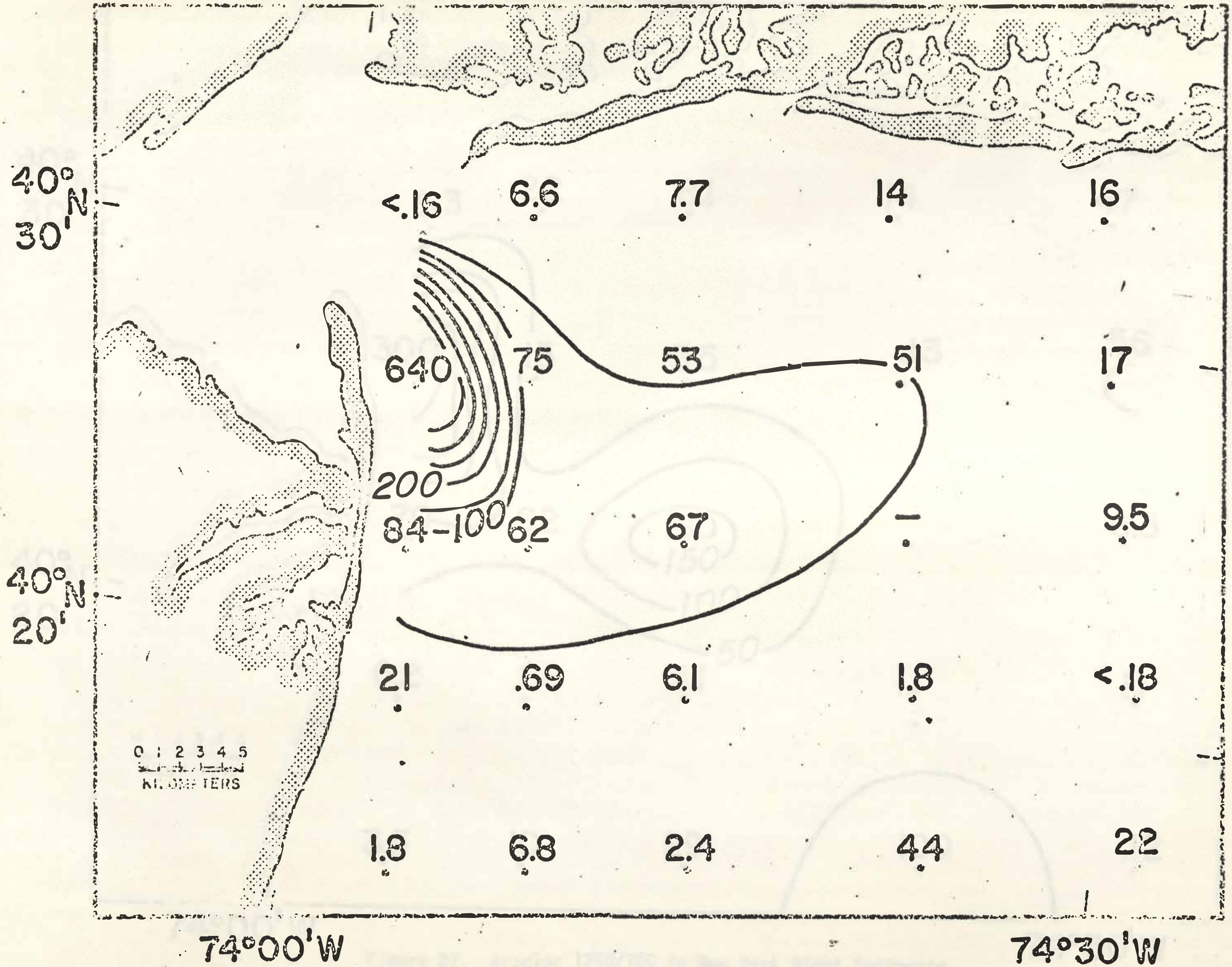

Figure 21. Aroclor 1254/TOC in New York Bight Sediments.

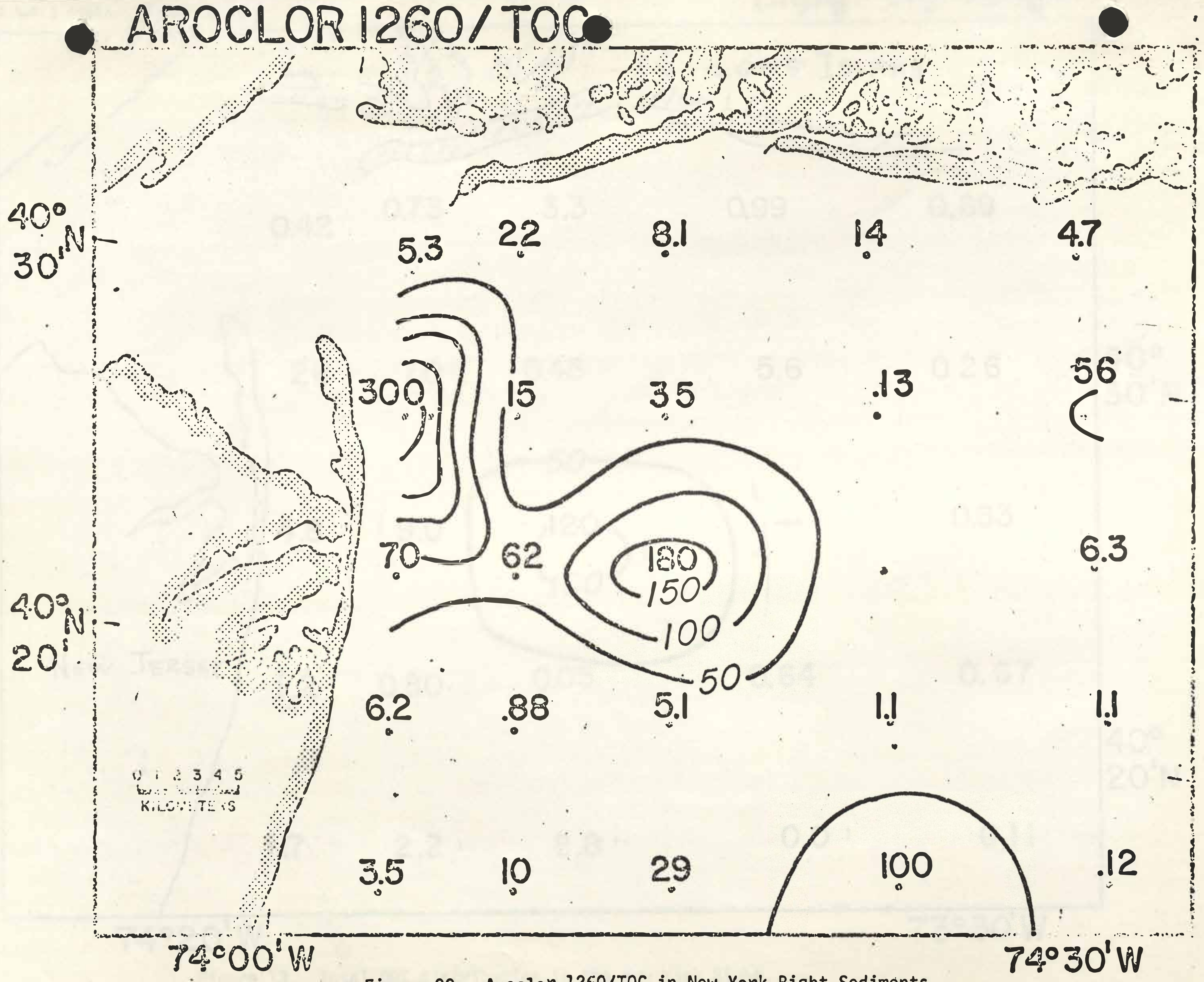

Figure 22. Aroclor 1260/TOC in New York Bight Sediments.

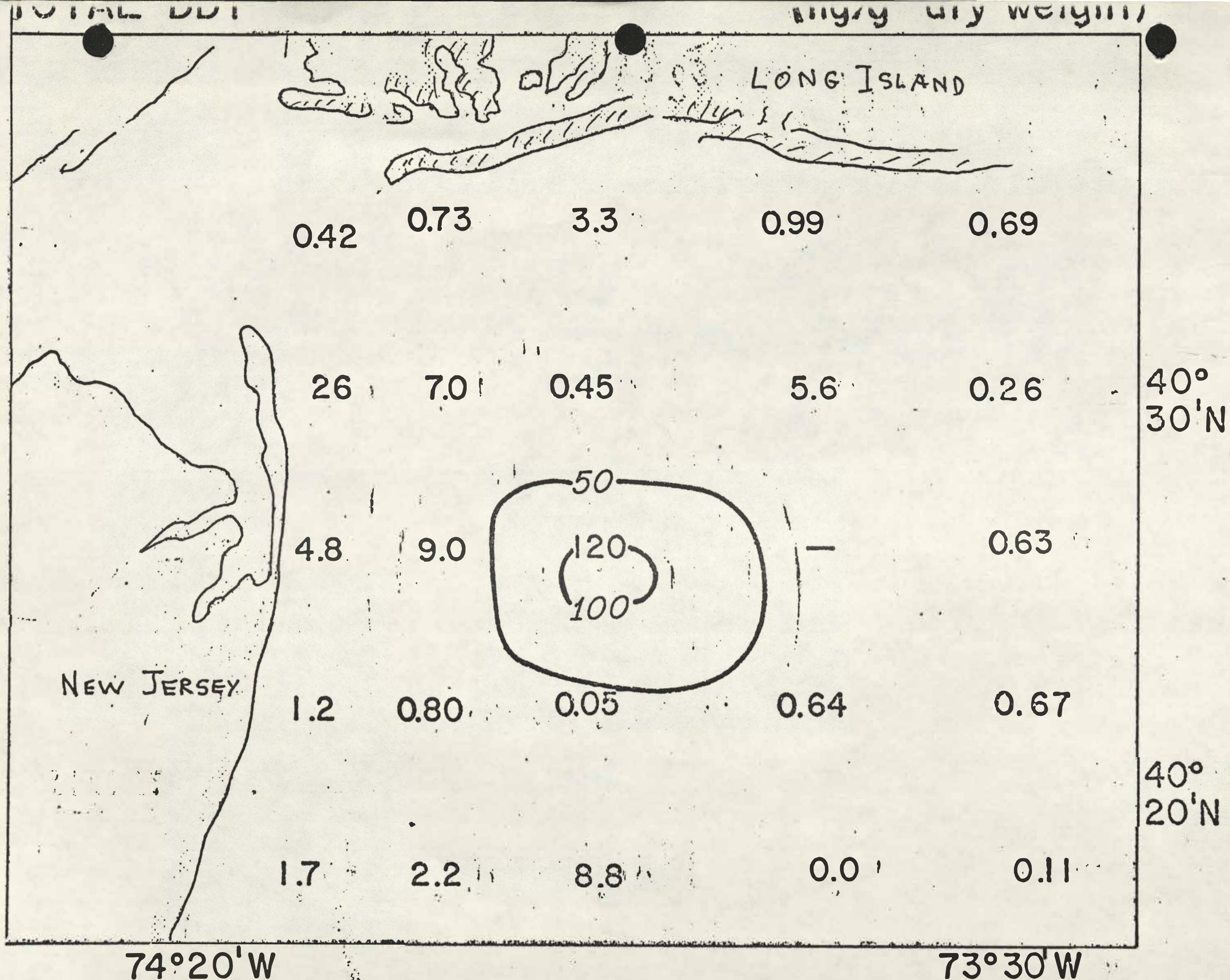

Figure 13. Total DDT distribution in the New York Bight.