Monsanto INDUSTRIAL CHEMICALS CO.

FROM (NAME & LOCATION): E. S. Tucker - T2F

DATE: November 20, 1973

SUBJECT: PCBs

REFERENCE:

TO: W. B. Papageorge
B2NA

cc H. S. Bergen - B2SL
R. E. Keller - T1B
R. H. Munch - T1B
W. R. Richard - T3A

While attending a NAS workshop on marine pollutants held at the Marine Biological Laboratories, Woods Hole, Mass., I talked at length with Bob Risebrough (Canadian Wildlife Service/University of California) and George Harvey (Woods Hole Oceanographic Institute) regarding PCBs. The following is a summary of our conversations.

Bob Risebrough reported (1) that the levels of PCBs in sewage outfalls (unspecified locations - probably California) have begun to drop significantly; (2) that they had qualitatively observed low levels of chlorinated furans in some Aroclors via GC/mass and that they were in the process of attempting to quantitate their findings. He would not even guess the level, indicating that, if they have not mistaken chlorinated methyl biphenyls (same m/e) for the furans, the levels are probably sub-ppm. I reiterated that we had not detected furans in any of our Aroclor products to date; and (3) he expressed special interest in the possible presence of furans in used PCB heat transfer fluids. I reminded him that PCBs were no longer used as heat transfer fluids, having been replaced with non-halogen containing fluids and that the used PCB fluids were recovered and incinerated.

George Harvey reported that the PCB levels found in marine samples which he obtained during their most recent cruise had decreased by a factor of 10. He was puzzled by this rapid drop and did not have an explanation for it. My own feeling is that he is being much more careful about how he collects and analyzes marine samples for PCBs and that the ships they use to collect the samples are now relatively PCB free.

It will be interesting to see how he eventually rationalizes this dramatic decline in ambient PCB levels. George also gave me a pre-publication copy of a paper to be published in Atmospheric Environment (copy attached).

IN - 10 REV. 1/72

Generally speaking, I would say that Harvey's and Risebrough's attitude toward Monsanto and the environmental impact of PCBs have undergone a remarkable improvement.

Scott

E. S. Tucker

js

ATMOSPHERIC TRANSPORT OF POLYCHLOROBIPHENYLS TO THE NORTH ATLANTIC

by

George R. Harvey
William G. Steinhauer

Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

Woods Hole Oceanographic Institution Contribution Number 3173.

Submitted: August, 1973
Revised: October, 1973
Atmospheric Environment

MONS 206149

INTRODUCTION

Polychlorobiphenyl (PCB) concentrations have been measured in the water and organisms of the oper Atlantic Ocean (Harvey et al., 1973). It has generally been assumed that PCBs would be delivered to the open ocean mainly by the wind (Nisbet and Sarofim, 1972) similar to DDT (Seba and Prospero, 1971) with fluvial and sewage inputs contributing smaller quantities (Corcoran and Lee, 1970; Holden, 1970). However, no atmospheric PCB measurements have been reported. Risebrough (1972) was unable to detect PCBs on equatorial Atlantic dust collected on Barbados (Risebrough et al., 1968). Therefore, it seemed likely that PCBs were transported mainly in the vapor or aerosol phase and we set out to design a sampling system capable of trapping both particulate and vapor phase chlorinated hydrocarbons. Atmospheric PCB measurements were important to our studies because we had previously observed no inshore - open ocean gradient of PCBs in the surface waters of the North Atlantic (Harvey et al., 1973). Thus, we wished to determine if the atmospheric concentrations of PCB reflected this observation.

In this paper we present a new atmospheric sampling technique, and the results of our PCB measurements at four stations over the western North Atlantic. The sampling was performed during the first half of 1973.

MONS 206150

PROCEDURES

The sampling system consisted of a Hurricane Air Pump (Bendix Corp.) fitted with a 102 mm filter holder on the intake port. The exhaust pipe was fitted with several meters of extension so as not to interfere with the intake. A 0.3 μ glass fiber filter, which had been baked at 500° for 12 hours, was used on the intake. The filter holder chamber, behind the filter was filled with 1/4" ceramic saddles (distillation column packing, Fisher Scientific) which were coated with 0.25% OV-17 silicone oil. The pump was run on low speed and generally achieved a flow rate of 22-24 cu. ft./min.

The saddles had to be cleaned initially by distilling several liters of water through a column packed with about 500 g. of the commercial product. The OV-17 was purified by applying 1.25 g to the top of a 1.5 x 15 cm column of silica. Interfering impurities were eluted with 80 ml of hexane. The OV-17 was eluted with 150 ml of benzene. The benzene solution was diluted with 100 ml of hexane and 500 g of steam cleaned saddles were added. The solvent was evaporated to dryness on a rotary evaporatory at 50° with a water aspiratory. The coated saddles could be stored in glass jars or used immediately. About 125 g are required to fill the filter holder chamber.

Recovery of the chlorinated hydrocarbons from the coated saddles was accomplished by shaking with two 100 ml portions of hexane in a separatory funnel. The hexane solution was dried with sodium sulfate and concentrated to 10 ml by distillation. The extract was applied to the top 1.5 x 15 cm column of silica and the chlorinated hydrocarbons were eluted with 80 ml of hexane. The hexane eluate was concentrated to 1 ml in a Kuderna-Danish concentrator. If necessary, the hexane was further concentrated with a stream of Florisil-purged nitrogen. No further cleanup was necessary before gas chromatography.

The concentrated extract was analyzed on a gas chromatograph equipped with a ^{63}Ni electron capture detector. The column was a 2m x 2mm (i.d.) glass coil packed with a 1:1 mixture of 8% QF-1 and 2% OV-17 on 100-120 mesh Anakrom. The oven temperature was 190°. The chromatogram was quantified by comparing the heights of seven peaks in the sample with the same matching peaks in a standard of commercial Aroclor 1254 (Monsanto) as shown in Figure 1. The blank (A) was produced by leaving the entire apparatus at the sampling site for twenty-four hours without running the pump. The saddles were then extracted and chromatographed as described above. The sample chromatogram (B) is from the Grand Banks. The presence of the PCBs was confirmed by perchlorination to decachlorobiphenyl according to the procedure of Armour (1973). The decachlorobiphenyl synthesized from the Bermuda samples was further confirmed by mass spectrometry.

Extraction of the glass fiber filters with hexane followed by concentration and chromatography revealed PCB concentrations which ranged

from undetectable in the Grand Banks samples to 0.04 ng/m^3 in the Vineyard Sound samples.

The efficiency of trapping was tested by applying known quantities of 3,4,2'-trichlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl (Analabs, Inc.) or Aroclor 1254 (Monsanto Co.) on the glass fiber filter. The average recovery after twenty hours of pumping was 70% for the pure isomers or the mixture.

The sampling stations are shown in Figure 2. Vineyard Sound (Massachusetts) samples were collected from the roof of the pilot cabin of the W.H.O.I. vessel R/V ASTERIAS. The Georges Bank collections were made from the 01 deck of the R/V ALBATROSS IV (National Marine Fisheries Service). The Bermuda samples were taken from a 20 m tower on the southwest shore of the island. Finally, the collections on the Grand Banks were performed from the exploratory drilling rig Sedneth 1 of Amoco Canada Ltd. at Station Razorbill. Procedural blanks from each station averaged .03 ng/m^3 for 500 m^3.

RESULTS

The analytical results for the four stations were set out in Table 1. In addition, the DDT family (t-DDT) was detected in the Bermuda samples. The concentration of DDT in the four samples decreased from 5.3×10^{-11} g/m^3 on February 12th, to 1.7×10^{-11} g/m^3 on February 15th (1973). The most likely source was the southeastern U. S. cotton fields directly

to the west. At the other sampling sites the t-DDT concentration was less than 1×10^{-12} g/m^3. The PCB/t-DDT ratio was also found to be greater than 30 in the surface water (Harvey et al., 1973). The PCB concentrations were highest in Vineyard Sound which lies only 150-250 km from the nearest windward industrial sources, i.e. the Boston-Hartford-New York-New Jersey complex. The concentrations of PCB over the Grand Bnaks which are over 2,000 km from the industrial complex of the northeast United States were 100 times less than in Vineyard Sound. In fact, when the average concentrations at each station are plotted against the average distance of the site from major industrial centers (Bermuda is equidistant from both northeast and southeast U. S. industrial complexes) the seaward decrease is actually exponential (Figure 3). Similar observations have been made for wind transport of industrial particulates over the ocean (Folger, 1970) and bomb fallout over the United States after nuclear tests (Eisenbud and Harley, 1953).

DISCUSSION

In our opinion the collection method used can only approximate the relative concentrations of chlorinated hydrocarbons in the particulate and vapor-aerosol phase. Hydrocarbons in the vapor or aerosol phase will easily pass through the glass fiber filter and be trapped in the silicone oil at an efficiency similar to the spiking experiments. Hydrocarbons adsorbed on solid particles which are trapped by the filter still have equilibrium vapor pressures with the surrounding air. At the high flow

rates used these adsorbed hydrocarbons could be entrained in the flow and swept into the vapor trap. The process is similar to that utilized in gas-liquid chromatography. However, if we can assume that particulates are being collected throughout the sampling period, the observation that only 1% or less of the total chlorinated hydrocarbon concentration in the sampled air is found on the filter argues strongly against significant particulate transport.

It seems likely that during the atmospheric lifetime of chlorinated hydrocarbons the vapor, aerosol and particulate states will equilibrate and exchange many times depending on temporal meterological parameters. Thus, the state in which they happen to be captured at a particular geographical location is relatively unimportant to considerations of total atmospheric transport. Thus, the concentrations reported in Table 1 should be regarded as total PCB per m^3.

The strong dilution and fallout gradient observed over the western North Atlantic is not reflected in the surface water concentrations. However, since the highest concentrations of suspended matter are in coastal waters (Manheim et al., 1970) adsorptive scavenging by organisms and sedimentation must deplete these waters of dissolved PCBs at rates comparable to the delivery. In contrast, only a small fraction of the discharged PCBs reach the open ocean, but that which does must remain dissolved in the surface waters for a long time because of the low concentration of suspended matter and the slower sedimentation rate. The result of these processes is that the

concentration of dissolved PCBs from near shore water and the open sea is about the same (Harvey et al., 1973). Sediments should reveal a gradient of PCBs from inshore to the abyssal plains. Analyses of bottom feeders support this prediction (Harvey et al., 1973b).

Since the relative unimportance of river transport of chlorinated hydrocarbons has been noted (Seba and Prospero, 1971; Hartung and Klinger, 197D; Corcoran and Lee, 197D; Seba and Corcoran, 1969) wind transport is the major source of chlorinated hydrocarbons in the oceans.

ACKNOWLEDGEMENTS

We thank Drs. R. Duce and T. Bidleman, University of Rhode Island for permission and assistance in using their Bermuda tower. Dr. M. Grosslein made space available aboard R/V ALBATROSS IV, National Marine Fisheries Service. We are especially grateful to Mr. G. Medieros for collecting the samples on ALBATROSS IV. Finally, we are indebted to Mr. Neil Greer (Amoco Canada Ltd.) for making accomodations available on the Sedneth 1. This work was supported by the International Decade of Ocean Exploration, National Science Foundation, Grant GX-35212.

MONS 206156

REFERENCES

Armour, J. A. (1973). Quantitative perchlorination of polychlorinated biphenyls as a method for confirmatory residue measurement and identification. J. Assoc. Off. Agric. Chem., in press.

Corcoran, E. F., and Lee, C. C. (1970). The distribution of chlorinated hydrocarbon pesticides in the Mississippi River Delta and adjacent Gulf of Mexico. Paper presented before American Chemical Society, December 4, New Orleans, Louisiana.

Eisenbud, M., and Harley, J. H. (1953). Radioactive dust from nuclear detonations. Science 117, 141-147.

Folger, D. W. (1970). Wind transport of land derived mineral, biogenic and industrial matter over the North Atlantic. Deep Sea Res., 17, 337-352.

Hartung, R., and Klinger, G. W. (1970). Concentration of DDT by sedimented polluting oils. Environ. Sci. Technol. 4, 407-410.

Harvey, G. R., Steinhauer, W. G., and Teal, J. M. (1973). Polychlorobiphenyls in North Atlantic Ocean water. Science 180, 643-644.

Harvey, G. R., Miklas, H. P., Bowen, V. T. and Steinhauer, W. G. (1973b). Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms. J. Mar. Res. (in press).

Holden, A. V. (1970). Source of polychlorinated biphenyl contamination in the marine environment. Nature 228, 783-784.

Manheim, F. T., Meade, R. H., and Bond, G. C. (1970). Suspended matter in surface waters of the Atlantic continental margin from Cape Cod to the Florida Keys. Science 167, 371-376.

Risebrough, R. W., Huggett, R. J., Griffin, J. J., and Goldberg, E. D. (1968). Pesticides: Trans-Atlantic movements in the northeast trades. Science 159, 1233-1235.

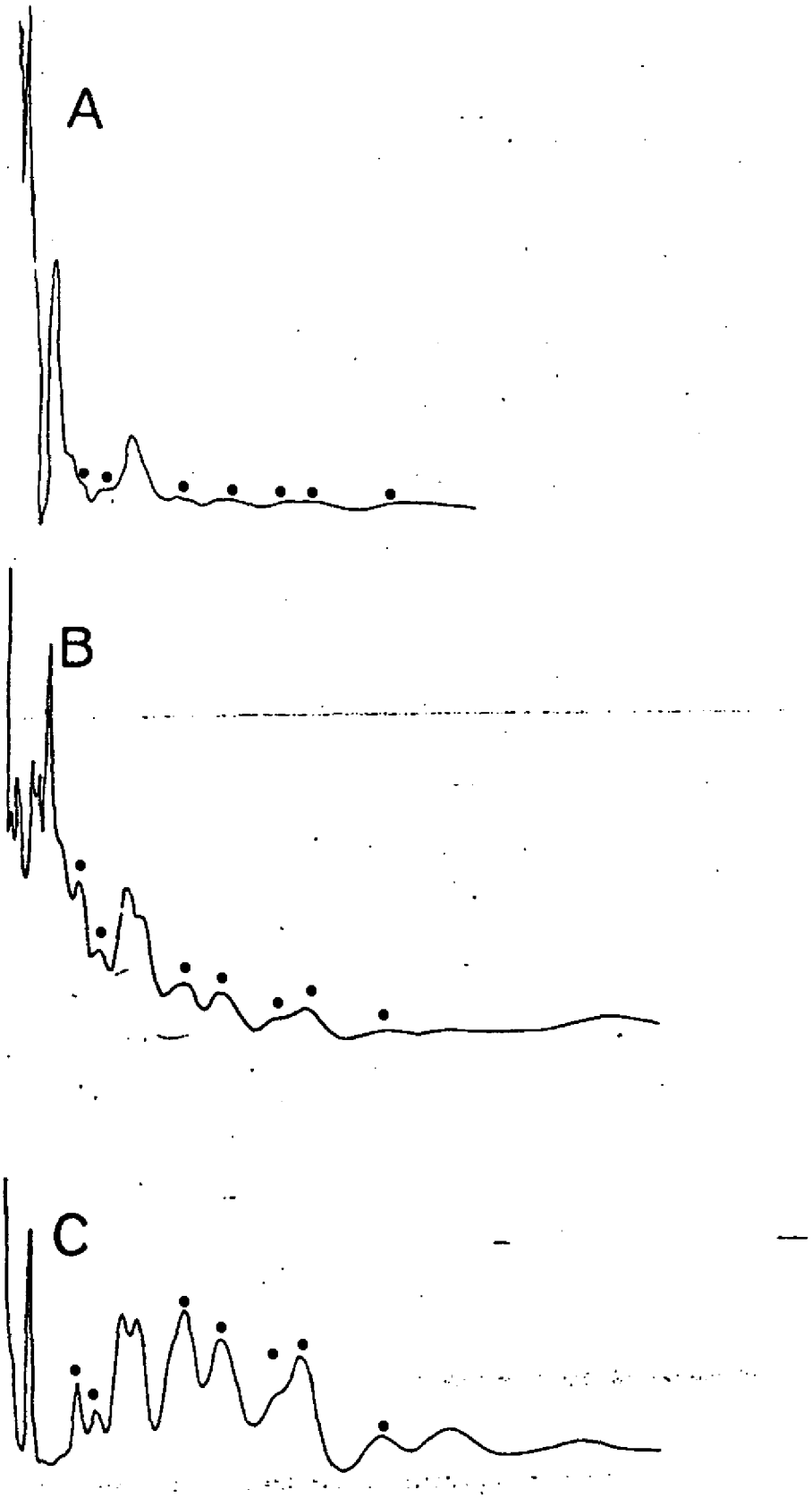
Risebrough, R. W. (1972). Personal communication.

Seba, D. B., and Corcoran, E. F. (1969). Surface slicks as concentrators of pesticides in the marine environment. Pest. Monit. J. 3, 190-193.

Seba, D. B., and Prospero, J. M. (1971). Pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. Atmos. Environ. 5, 1043-1050.

Figure 1. Typical PCB chromatogram of a Grand Banks air sample (B). The standard Aroclor 1254 is shown in C and the blank is shown in A. The seven dotted peaks were used for the quantification.

MONS 206159



MONS 206160

Figure 2. Sampling sites over the western North Atlantic.

MONS 206161

Figure 3. Relationship of atmospheric PCB and distance from industrial sources.

MONS 206162

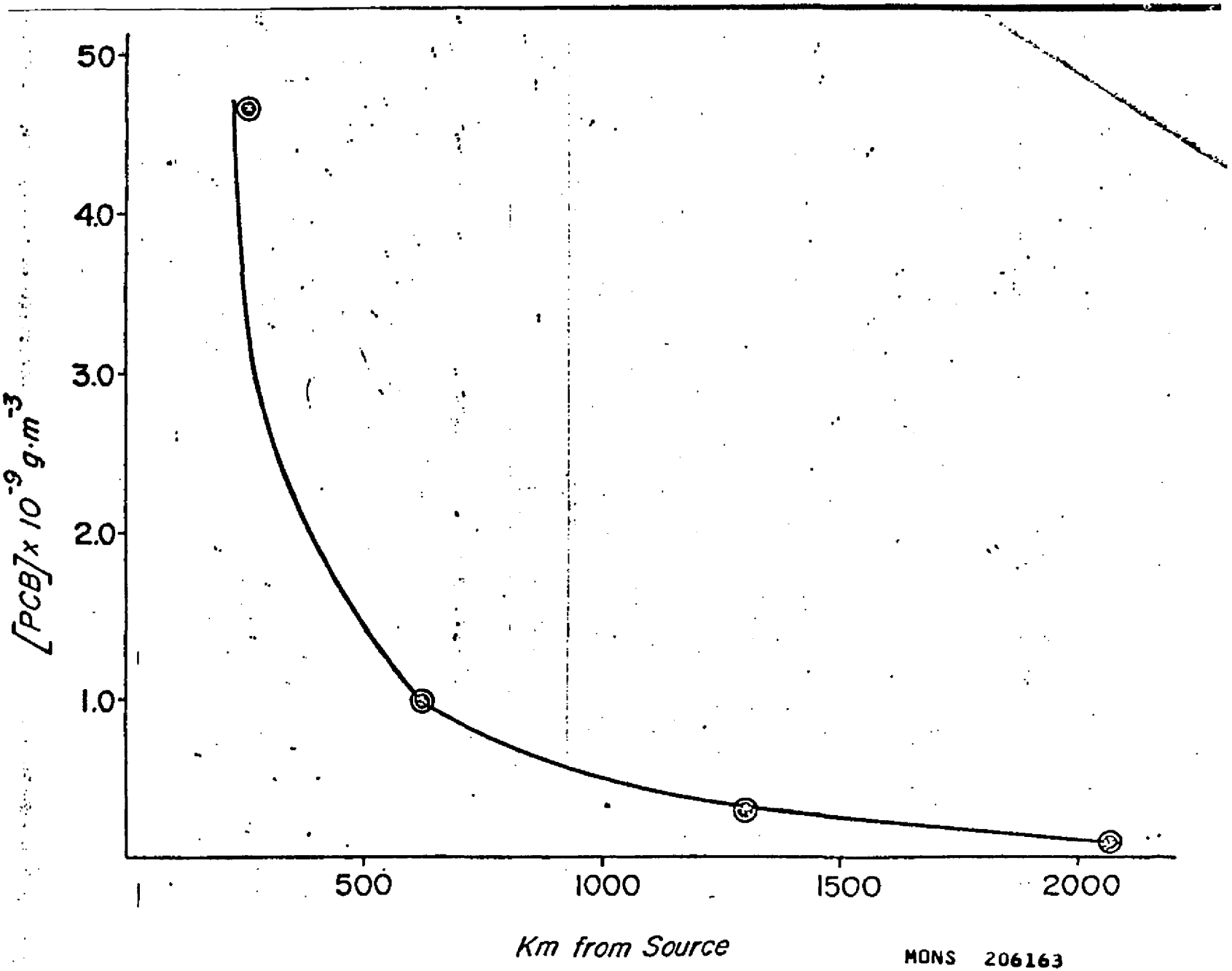

50
4.0
3.0
2.0
1.0
[PCB] x 10^-9 g·m^-3
500
1000
1500
2000
Km from Source
MONS 206163

TABLE 1

Station	Date (1973)	Sample Volume m^3	Wind Direction	PCB ng m^{-3} (calc. as Aroclor 1254)
Bermuda	2-12	560	WNW	0.5
($32^{o}20'N;64^{o}4D'W$)	2-13	480	W	0.4
" "	2-14	820	Var.	0.16
" "	2-15	500	S	0.15
Georges Bank	4-10	105	NW	1.4
($41^{o}40'N;67^{o}30'W$)	4-13	675	NW	0.82
" "	4-15	660	NE	0.58
" "	4-17	655	NW	0.61
" "	4-19	640	SW	0.80
" "	4-21	650	SW	1.60
Vineyard Sound	4-13	105	SW	3.9
($41^{o}20'N;70^{o}50'W$)	4-30	224	SW	5.3
Grand Banks	6-25	780	SSW	0.05
($45^{o}16'N;52^{o}08'W$)	6-26	960	SW	0.07
" "	6-27	840	WSW	0.10
" "	6-28	940	WSW	0.16
" "	6-29	540	W	0.05

MONS 206164