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CHLORINATED HYDROCARBONS IN SEAWATER: ANALYTICAL METHOD AND LEVELS IN THE NORTHEASTERN PACIFIC

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ABSTRACT

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A method is described for analyzing nanogram quantities of chlorinated hydrocarbons from 1-l samples of seawater. Seawater samples are pumped through a copper column containing a mixture by weight of 5% activated carbon powder, 10% MgO and 85% refined diatomaceous earth. The chlorinated hydrocarbons in the seawater are adsorbed or trapped on the column and subsequently eluted with 30% benzene in acetone (v/v) for analysis by gas-liquid chromatography.

This procedure was used to analyze chlorinated hydrocarbon levels in samples collected off the southern California coast. We suggest that anthropogenic chlorinated hydrocarbons can be used for the investigation of large-scale ocean currents and mixing processes.

INTRODUCTION

The objective of this work was to develop a method for analyzing small-volume samples of seawater (i.e., 1 liter) for low levels of chlorinated hydrocarbons (CHC). Although the sensitivity of modern electron-capture detectors approaches 10^{-12} g of chlorinated hydrocarbon, a more practical working limit is 10^{-10} g. This allows the detection of 0.1 parts per trillion (pptr) from a 1-l sample of water. In practice, contamination from reagents and containing vessels is a more stringent restriction on sensitivity than is the detection limit of the electron-capture detector. We have found that solvent extraction (using polar and non-polar solvents) becomes less than 100% efficient when the ratio of sample volume to solvent volume exceeds about 15:1. The procedure described here was designed to minimize manipulative steps and to reduce contamination introduced through reagents by allowing a sample volume to reagent volume ratio of at least 63:1 (with 0.5 g of adsorbent, 15.5 ml of solvent and a 1-l sample).

It is reasonable to expect some portion of the chlorinated hydrocarbons

present in seawater to be adsorbed on colloidal particles (Pfister et al., 1969). Fox et al. (1952) have demonstrated the retention of colloidal micelles by adsorptive filters composed of MgO and refined diatomaceous earth. Presumably, CHC associated with colloids will be trapped by a column containing a bed of polar adsorbents. The presence of a non-polar adsorbent (i.e., activated carbon) in the filter bed will scavenge CHC from the dissolved state in water (Burchfield and Johnson, 1965). Chlorinated hydrocarbons trapped in the interior of a micelle of surface active material suspended in seawater can be recovered in a mixed bed of polar and non-polar adsorbents if the micelle is disrupted by viscous shear forces, so that the CHC can adsorb onto the non-polar surfaces or if the micelle is adsorbed without disruption in the filter bed.

A column packed with fine-grained adsorbents has many advantages. Among these are:

(1) chlorinated hydrocarbons desorbing from the surface of a colloid must be transported to the non-polar adsorbent surface by molecular and turbulent diffusion. Small distances between particles in the adsorbent bed mean smaller distances and times over which these diffusive processes must operate.

(2) Viscous shear forces are greater in a column containing an adsorbent with small particle diameter.

(3) Since finer-grained adsorbents have a higher specific surface, smaller columns can be used which reduces the amount of solvent necessary for elution of the adsorbed material.

(4) Tailing during elution is also minimized because finer-grained particles of carbon have less extensive pores within each adsorbent particle.

These considerations guided our choice of a small column with a mixed bed or polar and non-polar adsorbents having high specific surface area and small particle diameter.

In the work reported here we have tested the efficiency and reproducibility of a column-scavenging method for analyzing chlorinated hydrocarbons in 1-l samples of seawater and we report levels found in samples taken off the southern California coast.

METHODS AND MATERIALS

Seawater samples are pumped through a column containing a mixture by weight of 5% activated carbon powder (Matheson, Coleman and Bell), 10% MgO powder (Mallinckrodt), and 85% refined diatomaceous earth (Celite$^{t.m.}$, Johns-Mansville). The chlorinated hydrocarbons in the seawater are adsorbed or trapped on the column and subsequently eluted with a 30% benzene in acetone (v/v — all solvents Mallinckrodt "nanograde" redistilled in glass). Batches of the adsorbent are cleaned in a 29 x 2.2 cm I.D. glass column by eluting with a combination of strongly polar and non-polar solvents. We have found that elution with a combination of water—acetone, acetone—benzene, and finally with benzene is most effective in removing interfering CHC from

the adsorbent. The clean adsorbent is dried in a rotary evaporator and stored in a sealed container.

The scavenging columns are made of copper tubing (100 x 5 mm I.D.) with a short length of smaller copper tubing (2 mm I.D., 3.5 mm O.D.) soldered to one end to serve as a tip. The tip is plugged with glass wool before adding the adsorbent. Organic solvents are pumped through the column with compressed air by attaching a glass pipette containing the solvent to the column with a short piece of PTFE tubing (5 mm I.D., 1 mm wall thickness). The mouthpiece of the pipette is connected to the compressed air source with a piece of pliable tubing. The water sample is pumped through the column by a high-pressure chemical feed pump (Precision Control Products Corporation, Model #16501-11). The piston and valves are made of stainless steel and PTFE. Swagelock fittings are used to connect the pump, tubing and column.

Procedure

The column is packed with 0.5 g of clean, dry adsorbent by gentle tapping. The packed column is rinsed by passing through the column 10 ml of benzene, followed by 20 ml of 30% benzene in acetone. The last 5 ml of the 30% benzene in acetone is collected to serve as a reagent blank. The blank is concentrated under vacuum at room temperature and an appropriate amount is analyzed by gas-liquid chromatography (GLC). If necessary, the column is rinsed again until a suitable blank is obtained. Before each use, the column is rinsed with 5 ml of acetone and dried with compressed air (check the air for CHC contamination). It is not essential to dry the column completely. A 1-l sample of seawater is pumped through the column at the rate of 10 ml/min. Excess water is forced off the column with compressed air before the chlorinated hydrocarbons are eluted with 10—15 ml of 30% benzene in acetone. The solvent is separated from the water fraction of the eluate and saved. The remaining eluate water (<0.5 ml) is extracted with 0.5 ml n-hexane which is pooled with the solvent fraction. The solvent—CHC residue fraction is concentrated under vacuum at room temperature and cleaned-up on alumina (McClure, 1972) prior to analysis by GLC. Typically, after alumina clean-up, the CHC residue from a 1-l sample of seawater containing between $1—10 \cdot 10^{-9}$ CHC/l is evaporated just to dryness, reconstituted in 100 μl of iso-octane from which 20 μl is analyzed by GLC. Generally, pesticide residues are also separated from polychlorinated biphenyls (PCB) on silica-gel prior to analysis (McClure, 1972).

Chlorinated hydrocarbons were analyzed on a Hewlett-Packard Model 5700 gas-liquid chromatograph with a ^{63}Ni electron-capture detector. The glass column (2 mm x 6 ft) was packed with 1.5% SP2250, 1.95% SP2401 on 100/120 Supelcon AW-DMCS. Injection port, oven, and detector temperatures were 250° C, 200° C, and 300° C, respectively. The chlorinated hydrocarbons detected in seawater samples were identified by comparison with

known standards, the retention times using gas-liquid chromatography and R_f values from liquid—solid column chromatography on silica-gel (McClure, 1972). Pesticide standards were supplied by the Environmental Protection Agency, Perrine Primate Laboratory, Florida, U.S.A. PCB standards were supplied by the Monsanto Company, St. Louis, Missouri, U.S.A. The predominant PCB found in the seawater samples was Aroclor 1254 (trade mark of the Monsanto Company; the last two digits specify weight percent chlorine). Unless indicated otherwise, "PCB" will refer to the 54% chlorine mixture in the following text.

Introduction and analysis of ^{14}C-DDT in seawater

^{14}C-DDT was added to seawater so that we could test the efficiency of the adsorbent in removing CHC from seawater and the recovery of CHC from the column during elution. ^{14}C-DDT was introduced into seawater either in the vapor state and/or associated with airborne particles smaller than 0.45 μm. $5 \cdot 10^{-5}$ g ^{14}C-DDT dissolved in 200 μl of n-hexane was pipetted onto a glass wool plug stuffed into a short section of glass tubing (4 mm I.D). After allowing the n-hexane to evaporate, the upstream end of the tubing was connected to a membrane filter (pore size, 0.45 μm). Downstream, the tubing was connected to another membrane filter (pore size, 0.45 μm) and then to the inlet port (glass tubing, 6 mm O.D.) of a 20-l glass carboy filled with membrane-filtered seawater (pore size, 0.45 μm). The carboy was sealed with a cork stopper. The inlet tube extended to the bottom of the carboy and was fitted at the end with an airstone. The glass exit tubing originated from above the water level in the carboy. Between the carboy exit port and a vacuum source was connected an 8-mm diameter by 50-mm long air-trap tube filled with glass wool impregnated with mineral oil in series ahead of an impinger (to catch excess oil blown off the glass wool). By applying a vacuum to this system, laboratory air was drawn through the filter, over the solid ^{14}C-DDT and bubbled through the seawater. Presumably, the majority of the ^{14}C-DDT leaving the glass wool was in the vapor state. However, the possibility exists that some of the ^{14}C-DDT became associated with sub 0.45 μm airborne particles or that solid particles of ^{14}C-DDT (<0.45 μm) passed through the system. As the ^{14}C-DDT passed through the seawater some of it remained, either in the dissolved state (Bowman et al., 1960) or associated with particles. Any ^{14}C-DDT that did not remain in the seawater was collected by the air trap as it left the system. The seawater was monitored as the ^{14}C-DDT was introduced until the desired concentration was achieved.

Seawater samples containing ^{14}C-DDT were analyzed using the procedure described in this report except that the ^{14}C-DDT residues were measured with a Beckman LS-100C Liquid Scintillation Counter. The results were verified by solvent extraction of replicate seawater samples using mixed polar and non-polar solvents. A 1-l sample of seawater was extracted twice with a

mixture of 40 ml of hexane and 20 ml of acetone. The pooled solvent extracts were concentrated on a rotary evaporator, dried with Na_2SO_4, evaporated just to dryness under vacuum at room temperature and transferred into scintillation fluid with 2 x 100 µl aliquots of iso-octane. The CHC contamination inevitably introduced from such a large volume of solvent did not interfere with measurements based upon ^{14}C activity.

RESULTS AND DISCUSSION

To test the efficiency of the scavenging column it was necessary to prepare quantities of seawater containing known amounts of radiocarbon-labeled chlorinated hydrocarbons which were dispersed in the water in states of aggregation approximating those in ambient nearshore oceanic conditions. Although it is likely that slightly soluble (~1 part in 10^9) organics associate with natural surface-active materials in the sea, it was not thought proper to introduce additional surface-active solvents (such as methanol or acetone) as is the usual practice for dispersing slightly soluble pollutants. The method described above for introduction of ^{14}C-DDT as an aerosol or vapor was therefore employed and resulted in solutions (or dispersions) which remained stable for periods of at least eighteen days in sealed carboys.

Procedure evaluation

Ten 1.0-l replicate samples of seawater containing ^{14}C-DDT were analyzed to evaluate the procedure presented here. We tested the efficiency of the adsorbent in removing DDT from the seawater, the recovery of the DDT from the adsorbent by elution, and the reproducibility of the procedure. The analyzed samples were subsequently extracted with mixed polar and non-polar solvents to recover any of the ^{14}C-DDT not adsorbed onto the column. At a flow rate of 10 ml/min, 99.3% of the ^{14}C-DDT was removed from the seawater by the column. Ten ml of 30% benzene in acetone eluted 97.7% of the ^{14}C-DDT from the column. A total of 15 ml was required for 100% recovery. The average ^{14}C-DDT concentration was $13.4 \cdot 10^{-9}$ g l^{-1} (13.4 pptr) with a standard error of ±0.3 pptr. Additional samples were solvent-extracted to confirm these results.

PCB recovery from the adsorbent bed

Recovery of PCB from the adsorbent bed was tested by wetting the column with 10 ml of seawater, spiking the column with 20 µl of iso-octane containing $2 \cdot 10^{-8}$ g of Aroclor 1254 (Monsanto), followed by another 10 ml of seawater before elution with 30% benzene in acetone. In five repetitions of this test, recovery was always complete. This test also demonstrates that the column is not overloaded by 20 µl of a non-polar material. Total dissolved organic matter

in seawater is frequently about 10 mg l^{-1} (Fox et al., 1952). In one liter, the volume of organic matter having a density of 0.5, present at 10 mg l^{-1} would be 20 μl. Since some fraction of the total organic matter in seawater is polar and is therefore not in direct competition with non-polar CHC for adsorption sites on the column, the column-loading achieved in this test is equivalent to the passage through the column of a 1-l sample of seawater containing somewhat more than 10 mg l^{-1} of dissolved organic matter.

Replicate samples of La Jolla seawater

Seven 1.0-l replicate samples from the seawater system at the Southwest Fisheries Center, La Jolla, California, were analyzed for chlorinated hydrocarbons. The average concentration of Aroclor 1254 was $2.9 \cdot 10^{-9}$ g l^{-1}. The range was $2.5—3.3 \cdot 10^{-9}$ g l^{-1}. Standard error was $\pm 0.3 \cdot 10^{-9}$ g l^{-1}. DDT and DDE levels for these replicate samples were less than $0.1 \cdot 10^{-9}$ g l^{-1}.

Seawater samples from the Gulf of Santa Catalina

Table I lists values and Fig.1 shows locations of CHC measurements made April 8—12, 1974, in the Gulf of Santa Catalina, south of Los Angeles. Analyses were performed aboard the R/V "David Starr Jordan", within 4 h of sampling. Samples were taken with 2-l sampling bottles machined from hard, unplasticized Lexan with ball-valve seats of PTFE. No plasticized elastomers or lubricants were employed. The bottles were checked for contamination by rinsing them with equal parts n-hexane and acetone, concentrating the rinse and analyzing the concentrate. Pre-extracted seawater was also stored overnight in a Lexan bottle and reanalyzed in order to assess contamination from the entire sample-taking and analysis procedure. Blanks ranged from below the detection limit to 1 pptr for PCB and to 0.1 pptr for DDT. (We discovered that the blanks were negligible when the efflux from the first extraction was collected in a covered vessel. Aerosol deposition of PCB in southern California is commonly in the range $10^{-6}—10^{-7}$ g m^{-2} day^{-1} (McClure and La Grange, MS) and this flux was shown to contribute $\sim 10^{-9}$ g to the uncovered 1-l efflux-collecting vessel during the 100 min required to do the initial extraction. This contamination influenced only the blanks since the samples were always kept covered.)

Bucket samples were taken while under way from the weather bow of the ship and the surface Lexan bottle samples were taken at 1 m depth after first lowering to 50 m to rinse the bottle.

The most prominent CHC detected in the seawater samples most closely matched the Aroclor 1254 standard (Fig.2). Various other GHCs were present in cluding additional PCB homologues, pp'-DDE and pp'-DDT.

The CHC concentrations detected by us in the Gulf of Santa Catalina are comparable to the levels measured by Pavlou et al. (1974) off the southern California coast using polyurethane foam to scavenge CHCs from the seawater.

TABLE I

Chlorinated hydrocarbon concentrations in seawater at various depths off southern California in pptr (10^{-9} g l^{-1})

Station position	Sampling method	Depth (m)	PCB (1254 Aroclor)	p,p′-DDE	p,p′-DDT	Date
San Diego Bay	bucket	surface	9.5	0.4	0.2	4/8/74
1 C 33°18.8′N 118°36.6′W	bucket	surface	3.0	<0.1	0.3	4/8/74
L I 33°10.5′N	Lexan	surface	7.5	<0.1	0.4	4/9/74
118°27.5′W	Lexan	500	7.2	1.1	0.1	4/9/74
L II 33°24.9′N	Lexan	surface	9.6	1.0	0.1	4/9/74
118°49.6′W	Lexan	500	7.7	0.9	0.7	4/9/74
”	Lexan	1,000	10.3	0.3	0.5	4/9/74
San Pedro Harbor	bucket	surface	35.6	4.6	1.9	4/9/74
San Onofre	bucket	surface	14.0	0.8	0.3	4/9/74
L III 33°12.5′N	Lexan	surface	9.4	0.2	<0.1	4/9/74
117°44.0′W	Lexan	500	6.1	0.5	0.2	4/9/74
”	Lexan	800	4.2	1.2	0.6	4/9/74
L IV 32°31.0′N	Lexan	500	2.9	0.3	N/D	4/11/74
118°03.0′W	Lexan	1,500	2.3	0.3	N/D	4/11/74

In that study, inshore surface samples contained an average of $5.4 \cdot 10^{-9}$ g l^{-1} ΣPCB and $0.9 \cdot 10^{-9}$ g l^{-1} ΣDDT. Offshore samples contained an average of $3.6 \cdot 10^{-9}$ g l^{-1} ΣPCB and $0.5 \cdot 10^{-9}$ g l^{-1} ΣDDT. Slightly lower concentrations of CHCs were detected by Bidleman and Olney (1974) in the Sargasso Sea using a dichloromethane extraction method (average level in subsurface water, $1.1 \cdot 10^{-9}$ g l^{-1} PCB). Harvey et al. (1973) detected higher levels in the North Atlantic (average, $35 \cdot 10^{-9}$ g l^{-1} PCB) using Amberlite XAD-2 resin to extract CHCs from the seawater.

Profiles of salinity and temperature were taken at each station where Lexan-bottle casts were made and the depth of the mixed layer (pycnocline or main thermocline) was found to be less than 200 m in every case. The fact that the

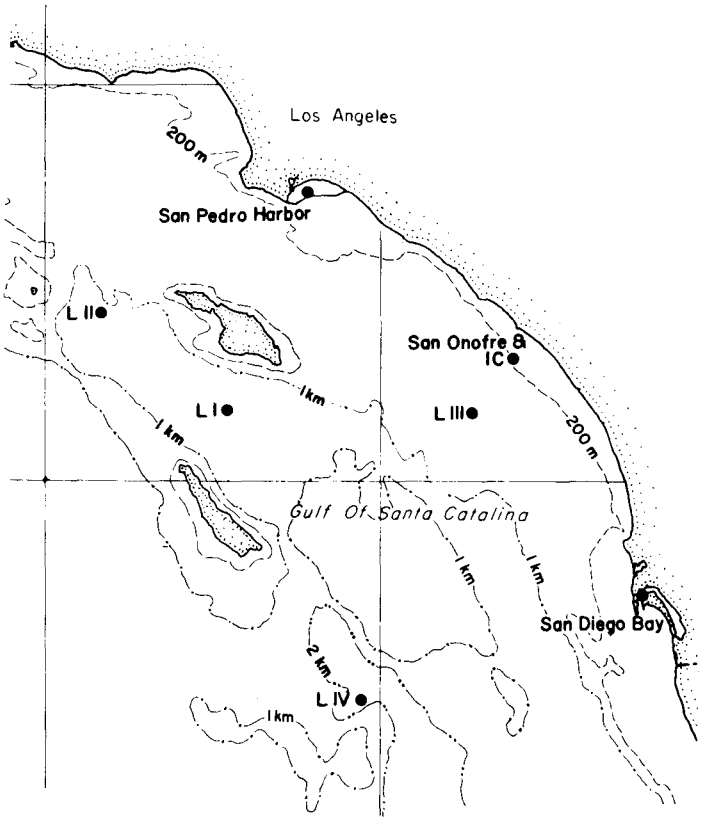

Fig.1. Sampling stations and bathymetry off southern California.

CHCs are not confined to the mixed layer and at some stations were as abundant below as in the mixed layer indicates that sedimentary processes are at least as important as advection in the dispersal of lipophylic materials in the ocean. Harvey et al. (1973) reported a decrease in PCB concentration with depth in the North Atlantic, but those stations were taken at a greater distance off shore. It is likely that the dispersal of CHC downward through the water column is associated with sedimentary processes which decrease with distance from the shore.

CONCLUSION

The procedure described in this paper is a convenient and reliable method for the determination of nanogram quantities of CHC from 1-l samples of seawater. Procedure blanks are easy to run and the location of sources of contamination is simplified since the number of solvents, reagents, articles of glassware and manipulative steps in the procedure have been held to a minimum.

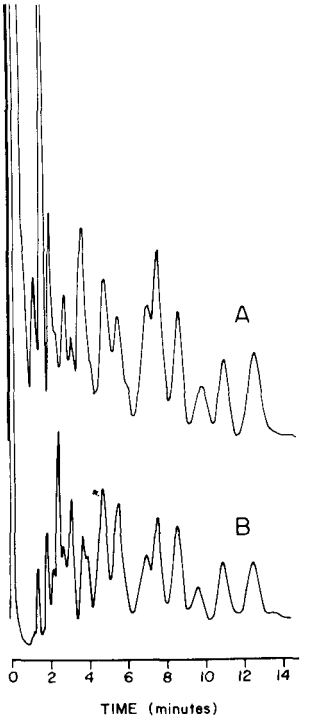

Fig.2. Gas chromatogram of CHCs from a surface sample taken in the northeastern Pacific (A) and an Aroclor 1242—1254 standard (B).

The highly chlorinated polychlorinated biphenyls are among the most refractory of synthetic organic chemicals to both chemical and biological degradation. Samples of water from the eastern Pacific all yield gas chromatograms (after preliminary liquid chromatographic separation of pesticides — McClure, 1972) which are nearly identical to the Aroclor 1254 mixture with regard to ratios of isomers present. This is strong evidence for the anthropogenic nature of PCBs in the ocean. To be consistent with these measurements, any degradation must take place in such a way that all isomers present in the Aroclor 1254 mixture be degraded at very nearly the same rate or the degradation rate must be slow compared to the characteristic times for dispersal or sedimentation from the water.

The strengths and distribution of sources of PCB to the ocean are amenable to measurement and the resulting distribution of pollutants in the sea will provide useful information about the horizontal and vertical transport of the whole class of low-vapor-pressure, non-polar nutrients as well as pollutants.

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