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Petraphera vivescenticula, new species. *Diagnosis*: Trichome straight or slightly curved in shape, constricted at cross walls, cells cylindrical to barrel-shaped, 13 to 16 μm in diameter, 0.5 to 1 time longer than wide, end cells 12 to 15 μm long, conical, tapering into a sharp point. Akinetes intercalary, barrel-shaped, 9 to 12 μm long and 5 to 8 μm in diameter, with a smooth wall about 1 μm thick. Vegetative cells lighter and akinetes darker in color; both with smooth, nongranular texture. In Precambrian dolomitic limestone stromatolite in the eastern Transvaal, South Africa. *Etymology*: With reference to early life forms in Precambrian rocks. At the completion of this investigation the slide containing the type specimen will be deposited in the algal herbarium collection of the Academy of Natural Sciences of Philadelphia. The code of this slide is TR1A; the type specimen is marked with a diamond scribe on the cover slip.
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Chlorinated Hydrocarbons in the Sargasso Sea Atmosphere and Surface Water

Abstract. *Polychlorinated biphenyls (PCB), DDT, and chlordane concentrations were measured in air samples from a tower on the south shore of Bermuda and in Sargasso Sea surface water approximately 80 to 320 kilometers south of Bermuda. The atmospheric chlorinated hydrocarbons appeared to be gaseous, and the DDT concentration was two orders of magnitude higher than previously reported particulate values. The PCB and DDT were enriched in the surface microlayer (150 micrometers) relative to their concentrations in water at a depth of 30 centimeters. Atmospheric residence times for PCB and DDT of 40 to 50 days, calculated from the concentrations in the air and water, are 20 times shorter than values previously estimated for DDT from rainfall and DDT production data.*

The presence of polychlorinated biphenyls (PCB) and DDT (*1*) and its metabolites in fish and seabirds is a well-documented fact, and the contamination of marine zooplankton (*2*) and seawater itself (*3*) by PCB has recently been reported. Suggestions have been made that a major transport route of these pollutants to the oceans is via the atmosphere. This hypothesis has been supported by the identification of PCB and organochlorine insecticides in rainwater (*4*, *5*) and the detection of DDT in dust carried by the northeast trade winds (*6*). Recently we developed a method which allows hundreds of cubic meters of air per day to be sampled for chlorinated hydrocarbons (*7*). During the period from February through June 1973 we measured PCB, DDT, and chlordane (*1*) concentrations in the marine atmosphere and surface water in the Bermuda–Sargasso Sea area of the North Atlantic as part of a program at the University of Rhode Island to investigate the atmospheric transport and deposition of organic and heavy metal pollutants on the ocean surface.

Air was pulled at 0.4 to 0.8 m^3/min through a glass-fiber filter (20 by 25 cm) (Gelman A) and then through a 15-cm plug of polyurethane foam (10 cm in diameter). The efficiency of the collection system for PCB vapors was better than 90 percent (*7*). Air samples were collected during February through April 1973 from a tower 20 m high located at High Point, Bermuda (*8*). Samples 1 through 4 (Table 1) were collected regardless of wind direction, whereas samples 5 through 8 were taken only while the wind blew from the open-ocean sector (90°E through 240°SW). Marine air was also sampled from a tower 8 m high on the bow of the R.V. *Trident* during a cruise from Bermuda to Narragansett, Rhode Island, in June 1973. Local collections of atmospheric organochlorine compounds were made on the University of Rhode Island campus and in downtown Providence, Rhode Island, without regard to wind direction.

Seawater from the Sargasso Sea was collected in 3.8-liter glass jugs from a rubber raft operated several hundred yards away from the R.V. *Trident* or its wake. We sampled the surface microlayer (150 μm) by means of the screen technique of Garrett (*9*), using stainless steel screens 40 by 40 cm (16 mesh) (*10*). We collected subsurface water by holding the jug approximately 30 cm below the surface. The samples were preserved with dichloromethane and were analyzed within 1 month of collection.

The chlorinated hydrocarbons were recovered from the glass-fiber filter and polyurethane foam by reflux or Soxhlet extraction with petroleum ether. We extracted the unfiltered seawater with dichloromethane and removed the chlorinated solvent before analysis by adding hexane and evaporating to a small volume. The extracts were separated into PCB and pesticide fractions by silicic acid column chromatography and analyzed by electron-capture gas chromatography (Tracor Microtek 220, ^{63}Ni detectors) on OV-17/QF-1 and SE-30/QF-1 columns. The identities of DDT and chlordane were confirmed by dehydrochlorination reactions. The analytical recovery for seawater spiked with Aroclor 1254 was 80 percent. Details and analytical results for the atmospheric and seawater samples are given in Tables 1 and 2.

Only a small amount of the chlorinated hydrocarbons was found on the glass-fiber filter (Table 1), which is capable of removing 98 percent of the particles having radii greater than 0.015 μm (*11*). Most of the PCB, DDT, and chlordane was trapped on the polyurethane foam. This finding suggests that PCB and chlorinated insecticides reside in the atmosphere mainly as vapors

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Table 1. Concentrations of chlorinated hydrocarbons in marine and continental air (the total retained by the glass-fiber filter and trapped on the polyurethane foam). Filter-retained values for the Bermuda samples were less than 2 percent and less than 5 percent of the total for PCB and DDT, respectively; —, not determined; U.R.I., University of Rhode Island.

Sample	Collection dates (1973)	Location*	Volume of air (m^3)	PCB† (ng/m^3)	*p,p'*-DDT (ng/m^3)	*o,p'*-DDT (ng/m^3)	Chlordane‡ (ng/m^3)
1	2/12–2/13	Bermuda	1070	0.59	0.013	0.014	< 0.005
2	2/13–2/14	Bermuda	1320	0.30	0.012	0.012	< 0.005
3	2/15–2/16	Bermuda	918	0.65	—	—	—
4	2/16–2/18	Bermuda	1950	0.62	—	—	—
5	2/19–2/28	Bermuda	1740	0.55	0.011	0.008	—
6	2/29–3/9	Bermuda	732	0.52	0.031	0.015	0.008
7	4/8–4/11	Bermuda	1300	0.61	0.030	0.027	0.011
8	4/11–4/17	Bermuda	860	0.21	0.022	0.010	0.012
9	6/4–6/5	33°20'N, 65°14'W	300	1.6	0.016	0.009	0.090
10	6/5–6/6	34°39'N, 66°15'W	267	0.79	0.015	0.016	0.066
11	6/7–6/8	37°39'N, 68°12'W	402	—	0.009	0.013	0.039
12	6/8	38°48'N, 69°14'W	222	0.72	0.010	0.015	0.055
13	6/9	40°32'N, 70°20'W	196	0.83	0.055	0.037	0.17
14	1/18–1/19	U.R.I.	392	4.0	—	—	—
15	1/21–1/22	U.R.I.	1071	2.1	—	—	—
16	2/4–2/5	U.R.I.	744	5.8	—	—	—
17	5/8	Providence, R.I.	76	9.4	0.090	0.025	0.25

* Samples 9 through 13 were collected from the R.V. *Trident* while the ship was en route. The location marks the midpoint of the collection track. † Calculated as Aroclor 1242 or Aroclor 1248. ‡ Both *cis-* and *trans*-chlordane.

rather than adsorbed onto particulate matter. It is also possible that these organochlorine compounds volatilize from the trapped particles, pass through the glass-fiber filter, and are collected by the polyurethane foam. In either case, it is likely that earlier types of collectors of chlorinated insecticides have missed the bulk of these substances in the air. This would explain why our DDT values are two orders of magnitude greater than those of other workers who collected particulate chlorinated hydrocarbons by hanging nylon screens in the wind (*6*).

Chlordane is often used for structural pest control and, to a lesser extent, as a soil insecticide for agricultural purposes (*12*). Other references to chlorinated hydrocarbons in marine air (*6*) do not mention chlordane, but it has been identified in Hawaiian rainwater and in dust translocated from Texas to Ohio by a dust storm (*5*, *13*).

The PCB in our atmospheric samples matched Aroclor 1242 or Aroclor 1248. These PCB mixtures consist largely of tri-, tetra-, and pentachlorobiphenyls, and together account for approximately 70 percent of the U.S. domestic PCB sales prior to 1970 (*14*). Practically all the workers who have reported PCB in marine biota and seawater have indicated that the gas chromatographic pattern matched that of Aroclor 1254. Gas chromatograms of the PCB from Sargasso water showed some of the peaks with short retention times characteristic of Aroclor 1242 and Aroclor 1248 but more closely resembled chromatograms of Aroclor 1254 or Aroclor 1260, which contain mainly penta-, hexa-, and heptachlorobiphenyls. It thus appears that the more highly chlorinated biphenyls are selectively transported to the ocean or that there is a more rapid degradation of the lighter PCB in seawater.

The concentrations of chlorinated hydrocarbons were higher in the surface microlayer than in subsurface waters. This enrichment may be due to atmospheric deposition on the ocean surface or to association with surface-active organic matter which has been concentrated at the sea surface by bubbles and convection currents (*9*, *10*).

An estimate of the residence time of PCB in the atmosphere over the Sargasso Sea can be calculated from the mean concentrations in the air [5×10^{-10} g/m^3 (Table 1, samples 1 through 8)] and subsurface water (1.1×10^{-6} g/m^3) (*15*), if we make the following assumptions: (i) PCB is uniformly distributed (except for the surface microlayer) in the top 100 m (*3*) and has a residence time in the mixed layer of 4 years (*16*); (ii) the atmospheric concentration of PCB (in nanograms per standard cubic meter) is constant up to the tropopause (11.2 km) and is zero above that altitude; and (iii) the major source of PCB input into the ocean is via the atmosphere. If we use the mean atmospheric and water concentrations of PCB, the quantities of PCB in a column of air 1 m^2 up to the tropopause (6.3 km, the equivalent height of an 11.2-km air

Table 2. Chlorinated hydrocarbons in Sargasso surface microlayer (SM) and subsurface water (SS); —, not determined; PCB calculated as Aroclor 1260.

Collection date (1973)	Location	Sample	PCB* (ng/liter)	*p,p'*-DDT* (ng/liter)	*o,p'*-DDT* (ng/liter)
4/9	29°56'N, 64°40'W	SM	11.2	0.4	0.09
		SS	3.6	0.5	< 0.05
4/10	30°45'N, 66°50'W	SM	4.9	0.3	< 0.05
		SS	< 0.9	< 0.15	< 0.05
4/10	30°34'N, 66°59'W	SM	8.3	0.3	< 0.05
		SS	1.0	< 0.15	< 0.05
4/11	28°53'N, 65°07'W	SM	42.6†, 19.3	2.1†, 0.6	0.3†, 0.06
		SS	< 0.9†, < 0.9	< 0.15†, < 0.15	< 0.05†, < 0.05
4/12	29°56'N, 63°00'W	SM	3.8	0.2	0.08
		SS	< 0.9	< 0.15	< 0.05
4/13	30°00'N, 64°30'W	SM	5.6	0.7	—
		SS	1.6	< 0.15	< 0.05
4/16	31°34'N, 63°49'W	SM	5.0	0.2	0.08
		SS	1.8	< 0.15	< 0.05
4/17	31°38'N, 63°57'W	SM	8.4	0.3	0.06
		SS	< 0.9	< 0.15	< 0.05

* Blank values for PCB, *p,p'*-DDT, and *o,p'*-DDT were 0.9, 0.15, and 0.05 ng/liter, respectively, and have been subtracted in calculating the above results. The concentration of *cis-* + *trans*-chlordane was less than 1 ng/liter for all samples. † Sample taken in a *Sargassum* windrow.

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column expressed in standard cubic meters) and in a water column 1 m^2 by 100 m are 3.15×10^{-6} g and 1.1×10^{-4} g, respectively. We define residence time as

$$\tau = N/(dN/dt)$$

where N is the quantity of a constituent present in a reservoir and dN/dt is its rate of addition to or removal from the reservoir. If $\tau_{PCB,water} = 4$ years, $d(PCB)/dt = 1.1 \times 10^{-4}$ g per 4 years $= 2.8 \times 10^{-5}$ g/year, the rate of PCB transfer out of or into the mixed layer (assuming steady state). If the input is atmospheric, the apparent residence time of PCB in the Sargasso Sea atmosphere is $(3.15 \times 10^{-6}\ g)/(2.8 \times 10^{-5}\ g/year) = 0.11$ year, or 40 days. A similar calculation, based on an estimated DDT concentration in the ocean mixed layer of 6×10^{-8} g/m^3 (*15*), gives an atmospheric DDT residence time of 51 days. These are much shorter times than a proposed atmospheric residence time for DDT of several years (*17*). Concentrations of PCB in Sargasso Sea water 10 to 20 times higher than our values have recently been reported (*3*). If these results are correct, and if our atmospheric PCB concentrations are representative of the entire Sargasso Sea, the residence time for PCB in the atmosphere could be an order of magnitude shorter than 40 days. Thus it seems to us that either (i) the residence time of PCB in the atmosphere is much shorter than previously estimated for DDT or (ii) the short apparent residence time is due to significant PCB inputs into Sargasso Sea water apart from atmospheric deposition.

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References and Notes

1. Abbreviations: DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; chlordane, the *cis*- and *trans*-isomers of 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene.
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15. Maximum and minimum values for subsurface PCB concentrations of 1.4 and 0.89 ng/liter, respectively, are obtained from the data in Table 2 by averaging the results from all stations, assuming (i) 0.9 ng/liter and (ii) 0.0 ng/liter for samples containing < 0.9 ng/liter of PCB. We have taken the intermediate subsurface PCB concentration of 1.1 ng/liter for our residence time calculation. If we calculate the average DDT concentration in the surface microlayer (0.64 ng/liter) and assume the same DDT/PCB ratio in the subsurface water as in the microlayer (0.053), the DDT concentration in subsurface water is estimated at 0.06 ng/liter, or 6×10^{-8} g/m^3.
16. W. S. Broecker [in *The Sea*, M. N. Hill, Ed. (Interscience, New York, 1963), vol. 2, pp. 88–108] estimated the residence time of dissolved solids in North Atlantic 100-m water as approximately 8 to 18 years. The residence time of chlorinated hydrocarbons in the mixed layer will probably be equal to or less than this value. We have assumed a residence time for DDT and PCB in the mixed layer of 4 years, the value used by Woodwell *et al.* in their global model of DDT circulation (*17*).
17. Using DDT production figures and assuming rainfall as the dominant method of removal from the atmosphere, G. M. Woodwell, P. P. Craig, and H. A. Johnson [*Science* **174**, 1101 (1971)] estimated the atmospheric residence time of DDT as 3.3 years.
18. We thank the U.S. Naval Underwater Sound Laboratory, Tudor Hill, Bermuda, for providing a site for the construction of the air sampling tower. This work was supported by the Office of the International Decade of Ocean Exploration, National Science Foundation, under NSF grant GX-33777, Contribution No. 1500 of the Rhode Island Experiment Station.

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Protodolomite Synthesis at 100°C and Atmospheric Pressure

Abstract. *Ordered protodolomite, $CaMg(CO_3)_2$, has been synthesized at 100°C by reaction of metastable precipitated carbonates with aqueous magnesium-bearing solutions. Initial reaction products have expanded crystallographic cells, attributed to the presence of structural water. Longer reaction time produces a protodolomite approaching ideal composition and exhibiting order reflections in x-ray powder patterns.*

The long-standing problem of the origin of sedimentary dolomite has thus far successfully defied experimental studies. Attempts to synthesize dolomite under conditions approximating those encountered in natural sedimentary environments have consistently failed to produce ordered dolomite. Since ordering of the calcium and magnesium ions in dolomite is a requirement for stability (*1*), any experimental studies of dolomite formation must involve materials with demonstrable cation ordering.

Although dolomite and protodolomite exhibiting order reflections are readily synthesized at elevated temperatures and pressures, I believe this to be the first report of (ordered) protodolomite (*2*) synthesized under conditions sufficiently close to those of natural environments to allow direct comparison of the materials and of the processes of formation.

All syntheses were carried out at 100°C and atmospheric pressure in Pyrex reaction vessels. Temperature was maintained by a stirred, constantly boiling water bath. Aqueous solutions of calcium and magnesium chlorides (2 molal total cation concentration) with Mg/Ca (mole ratios) of 4 or 5 were brought to temperature in the water bath, and carbonate was introduced either as solid Li_2CO_3 or as an aqueous solution of Na_2CO_3. In order to minimize changes in solution chemistry due to the subsequent reactions, the total carbonate added amounted to less than 5 percent of the total magnesium plus calcium in solution. The reaction vessels were sealed after introduction of carbonate, but were periodically opened for sampling. Samples were removed by pipetting a portion of the suspension produced by vigorous shaking. Samples were washed with distilled water, dried at room temperature, and examined optically and by x-ray powder diffraction.

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