munities through a prolonged period of geologic time. Diversity, expressed as the number of variable niches, should be limited by the monotony of environmental conditions in offshore waters, but also by the wider fluctuations of physical parameters in nearshore environments. There is marked increase in generic diversity from nearshore to offshore communities, but an accompanying decrease in community stability. Presumably an Early Paleozoic selection for species efficiency established the linguloid, bellerophontid, and nuculoid fauna in the rigorous nearshore physical regime, and favorable selection continued throughout the Paleozoic to perpetuate a stable nearshore community structure, with the replacement of only some taxa. Simple or uncomplicated community structure (abundant individuals but few species) does not necessarily mean that the community is at an early stage of evolution (*5*), but may show that it is quite stable and possibly very old. The linguloid-molluscan association at the end of the Paleozoic demonstrates an old but stable community structure. I suggest that further evolutionary studies of benthic marine communities of invertebrates will show more-rapid faunal changes (that is, less community stability) in the physically monotonous outer sublittoral communities.

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21 December 1967

Pesticides: Transatlantic Movements in the Northeast Trades

Abstract. *Concentrations of chlorinated hydrocarbons in airborne dust carried by the trade winds from the European-African land areas to Barbados range from less than 1 to 164 parts per billion. The lower limit of the average content of 1 cubic meter of air is* 7.8×10^{-14} *gram. The contributions of river-borne and atmospherically transported pesticides to parts of the marine environment are calculated approximately and compared. The amounts of pesticides contributed to the tropical Atlantic by the trade winds appear to be comparable to those carried to the sea by major river systems.*

The transport and distribution of pesticides through the world ecosystem have been attributed to a combination of atmospheric and hydrospheric (oceanic and fluvial) currents (*1*), yet their relative contributions remain unclear. The high concentrations of residues of pesticides found in shearwaters *Puffinus tenuirostris* and *P. griseus* from the Pacific Ocean and skuas *Catharacta skua* from Antarctica suggest that coastal areas are not the sites of ingestion (*1*).

Various lines of evidence indicate air transport: (i) the codistillation of chlorinated hydrocarbons with water (*2*), and (ii) their detection in air and rainwater (*3*) and in atmospheric dust originating in Texas and subsequently deposited in Ohio (*4*). These observations, however, are not sufficient to support the hypothesis that much of the pesticides present in marine organisms was atmospherically transported to the oceans from the continents.

Complementing such work is the observation that the mineral talc that is used as a carrier and diluent for pesticides occurs in the solid-mineral phases of rains, glaciers, and rivers and in dusts recovered from the atmosphere in concentrations much higher than expected from natural occurrences (*5*); its existence in airborne particulate matter over the sea (*6*) suggests a link with the global dispersion of pesticides.

Although talc is perhaps diagnostic of the presence of insecticides, its use as a quantitative tracer is not fully warranted; it is gradually being displaced in pesticides by water or light petroleum bases. Furthermore, some insecticides are dispersed in Fuller's earth, a mixture of minerals not readily analyzed by x-ray diffraction.

Large-scale tropospheric transport from continents to oceans can best be approached by investigation of the three main zones of movement of air masses: the equatorial easterlies, the temperate westerlies, and the polar easterlies. Gram quantities of airborne particulate matter carried by the equatorial easterlies, the trade winds, over 6000 km from Europe and Africa across the Atlantic to Barbados were collected (*7*). Pronounced seasonal variations in the magnetic and biological fractions correlated with wind patterns off the African coast. Mineralogical and biological observations pointed to a continental origin of the solids, with Europe and Africa as the most likely sources. Each sample comprised a large fraction of the particulate material in several million cubic meters of air. An input rate of solid phases to the tropical Atlantic sediments of 0.6×10^{-4} cm/year was suggested (*6*). Knowledge of the pesticide levels in such materials would permit similar calculations of their inputs, for which purpose the Barbados samples have been analyzed.

The collecting screens (*6*), facing the wind, were made of 0.5-mm-diameter monofilament nylon woven to give about 50 percent voids; they were coated with a 50-percent water solution of glycerin for our work; collection efficiency was about 50 percent for particles larger than 1 μ. Rigorous standards of cleanliness minimized contamination by local dusts, which has always proved to be trivial. For blank runs for the pesticide analyses, acetone-washed dust was applied to screens, with subsequent treatment as for the real samples. Less than 100 pg of any of the DDT compounds (*8*) or other pesticides per gram of sample was found.

The dust samples were Soxhlet-extracted for 6 hours with a 2:1 mixture of hexane and acetone. Blank runs, using the same solvent volumes, extraction times, and glassware, were made before and several times during the course of the analyses; less than 250

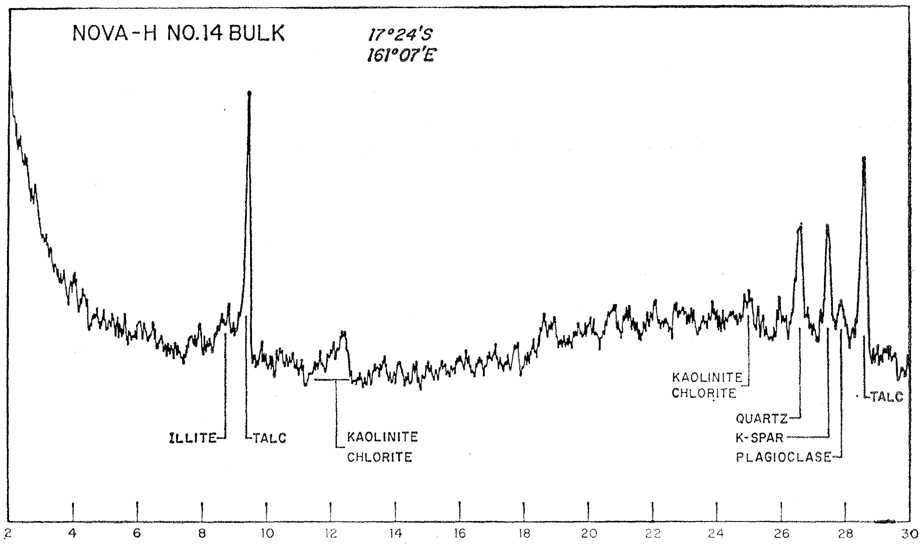

Fig. 1. X-ray diffractogram (Cu$K\alpha$ radiation) of atmospheric dust collected over the Coral Sea, with talc predominating.

pg of any pesticide per gram of sample was present in the controls.

The extracts were concentrated and analyzed with a Micro Tek-220 gas chromatograph equipped with Ni-63 and H-3 electron-capture detectors. Two columns, a 5-percent QF-1 and a 10-percent DC-200, both on hexamethyl disilazane–treated Chromosorb W, 80- to 100-mesh, were used simultaneously. Differences in retention time between the polar and nonpolar columns, combined with occasional spiking of extracts with standards, initially confirmed the identities of several of the peaks observed. Peaks of unknown compounds fluctuating in intensity over the year were present in all Barbados extracts and occasionally interfered with determination of *p,p′*-DDE and *o,p′*-DDT.

Extracts of samples between January and September were pooled and placed on a thin-layer plate covered with silica gel G that had been washed until chromatographically clean. A small fraction of the sample extract, mixed with standards, was applied to another area of the plate. After development with 10 percent ethyl ether in hexane, the plate was divided into two sets of 13 1-cm strips which were scraped off and washed with petroleum ether. A concentrate of the petroleum ether was then injected into both columns of the gas chromatograph.

Dieldrin, *p,p′*-DDT, and *p,p′*-DDD were quantitatively recovered from the corresponding areas of the plate occupied by the standards. In several extracts the interfering peaks made measurements of *p,p′*-DDE and of *o,p′*-DDT impossible; the thin-layer recoveries of these compounds were 150 percent. A trace amount of a compound having the retention times of *o,p′*-DDE was also recovered, but a small peak provisionally attributed to heptachlor epoxide in one extract was not confirmed by thin-layer techniques. None of the unidentified peaks had retention times equivalent to those of the polychlorinated biphenyls (PCB), industrial pollutants widely dispersed in marine ecosystems (*9*). No attempt was made to isolate chemically pure pesticides from the thin-layer extracts in order to obtain infrared spectra; instead, several of the thin-layer extracts were treated with alcoholic KOH under conditions such that *p,p′*-DDT, *o,p′*-DDT, and *p,p′*-DDD are converted to their dehydrochlorinated derivatives, which have characteristic retention times on QF-1 and DC-200 columns.

The thin-layer extracts containing most of the *p,p′*-DDT, *p,p′*-DDD, *o,p′*-DDT, and dieldrin peaks were evaporated almost to dryness in a graduated test tube to which 1 ml of 10 percent KOH in ethyl alcohol was added. After heating for 5 minutes in a steam bath, water and hexane were added and the solution was swirled. Analysis of the hexane layer showed that the *p,p′*-DDT, *p,p′*-DDD, and *o,p′*-DDT peaks had

Table 1. Pesticides in airborne particles over Barbados. Concentrations in air are based on 50-percent efficiency of the collecting net; ND, not detected.

Date (1965–66)	Air volume (× 10^3 m^3)	Material dry wt (g)		Pesticide concentrations						
				In samples (ppb)						Total in air (g × $10^{-15}/m^3$)
		Total	Analyzed	*p,p′*-DDT	*p,p′*-DDE	*o,p′*-DDT	DDD	Dieldrin	Total	
4–6 Oct.	2.3		0.82	52	12	13	7	3.4	87	150-380*
26–28 Oct.	3.3	17.8	7.70	<1.2	ND	ND	ND	ND	<1.2	<13†
7–21 Nov.	16.3	8.9	2.67	71	19	ND	ND	ND	90	99
1–15 Dec.	16.1	5.2	2.62	10	ND	ND	ND	ND	10	6.5
23–25 Dec.	2.3	1.7	1.33	88	49	13	8	6	164	242
26–28 Jan.	2.3	1.0	0.97	30	ND	ND	10.7	8.1	49	42
15–17 Feb.	3.2	3.3	3.32	18	13	6	ND	ND	37	77
17–19 Feb.	2.9	1.4	1.42	67	ND	17	ND	4.8	96	93‡
25–27 Mar.	2.4	1.3	1.04	14	2.1	ND	6.3	2.1	25	27
12–14 Apr.	2.8	4.7	3.10	11	ND	ND	ND	ND	11	37
14–16 May	1.5	9.0	5.43	2.7	ND	ND	ND	1.3	4.0	48
11–13 June	2.1	2.6	2.69	7.6	ND	ND	ND	3.1	10.7	28
21–23 July	1.5	6.8	2.29	5.4	3.4	0.9	1.1	1.3	12.1	110
10–12 Aug.	1.9	8.6	4.59	4.3	3.1	.4	1.4	1.2	10.4	90
13–15 Sept.	1.7	7.8	4.15	8.3	1.5	1.1	1.0	1.5	13.4	120

* Total dry weight not measured. † Zero dust collected on 12 previous days. ‡ Peak, with retention time of heptachlor epoxide also present, 7.2 ppb.

disappeared, but peaks having the retention times of *p,p′*-DDE, *p,p′*-DDMU, and *o,p′*-DDE had appeared in the respective extracts. The recoveries of these dehydrochlorinated derivatives were equivalent to those obtained in the saponification of chromatographically pure standards. No other breakdown products producing peaks in the electron-capture detector were identified. The dieldrin peak was not affected by the alkaline-alcohol treatment but could not be found after concentrated sulfuric acid was added to the evaporated extract.

All extracts were analyzed with both DC-200 and QF-1 columns, and each value presented (Table 1) is the average from two or more injections of a sample. The total concentrations of the chlorinated hydrocarbons in the dust were higher during the winter months, but the total pesticide content of the air displayed no evident seasonal changes during 1 year. A relatively high content of magnetic dust had been reported (*6*) for September, October, and April when the wind circulations suggest that the dust originates in Morocco; on the other hand, the content was less between October and March, when the dust probably comes from tropical Africa south of the Sahara. Most of the biological material was present in the winter samples; fungal hyphae abounded, and bacteria, fragments of vascular plants, and marine and freshwater diatoms were observed. Among the last were *Melosira granulata,* which is worldwide in distribution, and *Denticula elegans*, which is found in the running waters of cold mountainous regions. There was no correlation between the pesticide content of the air and either the magnetic content or the number of fungal hyphae reported (*6*).

The pesticide concentration in air averages 7.8×10^{-14} g/m^3, or 41 ppb (parts per billion) by weight in the dust. Utilizing the sedimentation calculations on this dust (*6*), we can calculate the introduction of pesticides to the equatorial Atlantic by atmospheric transport in the following way. We assume that the area involved in dissemination by the trade winds lies between the equator and 30°N latitude, covering 1.94×10^{17} cm^2. The reported (*6*) rate of sedimentation for this area is 0.06 cm/1000 years, equivalent to an annual input of dust solids of 9.70×10^{12} g (density of dust, 2.5 g/cm^3; water content of the sediments, 50 percent). The value of 41 ppb of insecticides in the dust yields 600 kg/year.

The input of pesticides into San Francisco Bay, measured by the average total concentration in the San Joaquin River at Antioch (*10*) (0.1 μg/liter) and the mean outflow of 18.9×10^{12} liter/year, amounts to 1900 kg/year. A similar calculation for the Mississippi yields an input into the Gulf of Mexico of 10^4 kg/year (*11*).

These rates of input indicate the relative significance of wind and river transport to the marine environment. The atmospheric rate is clearly an underestimate inasmuch as the method of collection of the dusts fractionates against materials carried on particles of less than several microns or as vapors. We must conclude that the atmosphere can transport significant quantities of pesticides to the open-ocean ecosystem; where ocean currents and river drainages cannot explain the presence of residues, wind systems may provide conveyance from continents.

Similarly we have examined samples of airborne particulate matter from the central Pacific collected on glycerin-coated nylon nets mounted on the mast of R.V. *Argo* (*12*) at 12 stations between 17°N and 18°S near 180° longitude during the summer of 1967. No sample carried a detectable pesticide residue, but the weight of each sample did not exceed 1 or 2 mg, and less than 1 part per million or 1 ng of a pesticide would have been undetectable. However, the presence of talc, the most important diffracting mineral, suggested the presence of pesticides (Fig. 1).

Dust collected from an ocean pier at La Jolla, California, between June and October 1967 yielded total pesticide contents in air ranging from 6 to 270×10^{-12} g/m^3 and averaging 7.0 $\times 10^{-11}$ g/m^3; the prevailing winds are landward, with an unknown admixture of air from neighboring agricultural areas. This average value is 1000 times greater than its Barbadian counterpart. Such is the difference in pesticide load between marine air adjacent to agricultural areas in which pesticides are used intensively and marine air remote from sites of application.

Extracts of the La Jolla dust samples were pooled, concentrated to a volume of about 1 ml, and refluxed for 10 minutes in 100 ml of 5 percent KOH in ethyl alcohol before 100 ml of hexane and 300 ml of concentrated aqueous solution of NaCl were added. The hexane layer, after concentration to a small volume, was then analyzed for PCB. Such treatment of extracts of marine fish from coastal waters in California reveals the characteristic profile, on gas chromatograms, of the PCB peaks (*9*); PCB are present in higher concentrations in marine birds, and the profile of the various peaks is usually evident in unsaponified extracts. No PCB, however, was detectable in the La Jolla dust samples; if PCB was present, its maximum concentration in the airborne particulates was 5 ppb—10,000 times lower than that of total pesticides. The PCB are toxic compounds widely used in industry in the manufacture of plastics, paints, and many other products, and are components of industrial air. Unlike the chlorinated-hydrocarbon pesticides, which they resemble somewhat in chemical structure, they apparently persist to a greater extent in the vapor phase. The concentration ratios of total PCB to total DDT in many seabirds, including two species of Pacific shearwaters that nest in Alaska, and in petrels and resident peregrine falcons from remote areas of Baja California are of the same order of magnitude (*9*); this fact suggests that PCB and pesticides are similarly dispersed. With other pollutants, including products of atomic explosions (*13*), they are probably universally present in air; thus their distribution in marine and terrestrial ecosystems remote from sites of application can be expected to depend on the prevailing patterns of wind circulation and the rates of fallout.

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7 February 1968

Microstructure of Sediments: Investigation with Ultrathin Sections

Abstract. *Examination of ultrathin sections of "undisturbed" marine sediments from the Gulf of Mexico indicates that they are characterized by a loose, open, random arrangement of particles. The microstructures do not appear to conform entirely to either cardhouse or honeycomb structures.*

The microstructure ("fabric") of marine sediments has received little attention from geological oceanographers. Two popular theories prevail as to the nature of the particle arrangement in the sediments. Terzaghi (*1*) suggested a "honeycomb" structure, with adhesive forces causing the particles of clay mineral to stick together on contact; each cell of the structure consists of many adhering particles (Fig. 1A). Later was suggested (*2*, *3*) a somewhat different structure in which the clay-mineral aggregates, having a platy morphology, were arranged generally in an edge-to-face fashion forming a "cardhouse" structure (Fig. 1B). Tan (*4*) presented a three-dimensional idealization of cardhouse structure (Fig. 1C).

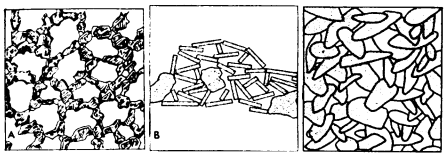

Fig. 1. (A) Honeycomb structure [after Terzaghi (*1*)]. (B) Cardhouse structure [after Lambe (*3*)]. (C) Cardhouse structure [after Tan (*4*)].

While some orientation studies, using polarized light and x-ray diffraction techniques (*5*), can reveal gross trends toward preferred or random orientation of particles, they do not reveal details of the microstructure. Most information has come from the electron microscope. Rosenquist (*6*) used the electron microscope and the replication technique to obtain stereomicrographs showing the microstructure of undisturbed marine clays; he concluded that the microstructure of such clays "corresponds to the cardhouse structure suggested by Goldschmidt and later by Lambe, and in fact exactly corresponds to the imaginative drawing of Tan." Use of the same technique for studying illitic Pleistocene clays led to a similar conclusion (*7*).

Whereas the electron microscope offers the best means available for study of sediment microstructure in detail, the replication technique does not provide easily interpretable results. My purpose is to illustrate the microstructure in samples of sediment from the Gulf of Mexico as revealed by ultrathin sections of the sediment, and to point out that this technique provides more easily interpretable results.

The samples (Table 1) came from cores taken by R.V. *Alaminos* (*8*). Only cores were selected that had been properly sealed and stored to preserve as well as possible the natural state of the sediment. From each core a cubic sample of 2 to 5 cm was carefully cut with a thin-bladed knife or spatula. A larger portion was cut initially in order to retain an undisturbed portion in the center of the sample; likewise, the sample itself was taken from the center of each core. From each sample, smaller samples (1 to 2 cm by 2 to 3 mm^2) were cut with a taut, very thin wire; the outer, disturbed portion of each large sample was first trimmed with the wire to expose the inner, undisturbed portion. The small samples were freeze-dried; this technique is recommended (*6*, *9*) because it entails less particle disturbance due to effects of surface tension than do standard oven- or air-drying techniques.

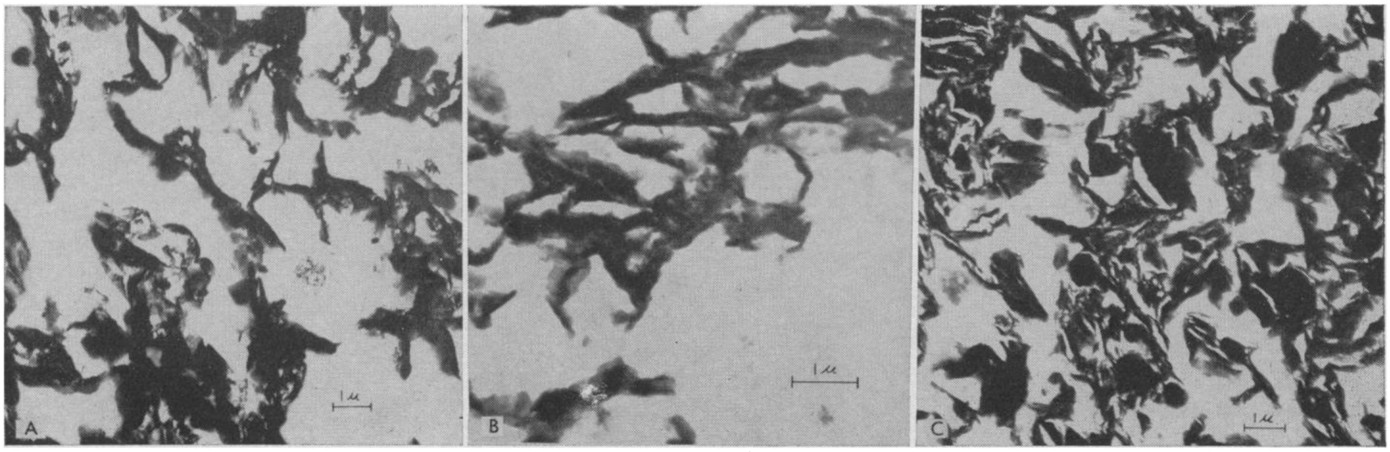

Fig. 2. Ultrathin sections showing the microstructures of undisturbed sediments from an abyssal plane (A), a continental slope (B), and a continental shelf (C).