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Decline of PCB concentrations in North Atlantic surface water

POLYCHLOROBIPHENYL (PCB) concentrations in North Atlantic surface waters have declined fortyfold since 1972, following the cessation of certain industrial uses of those compounds. Industrial sales of PCB for use in products which would allow leakage to the environment, for example in plastics, inks and paints were stopped in the United States and Sweden during 1970-71¹; and in 1972-73 other European countries and Japan initiated a similar action². In 1971 and 1972 average surface concentrations of PCB in the open North Atlantic Ocean were about 30 ng l⁻¹ (ref. 3 and C. E. Olney and J. J. Quinn, unpublished). By April of 1973 the concentration in the Sargasso Sea had been reduced to 1 ng l⁻¹ (ref. 4); five months later we found that the decline had levelled at 0.8 ng l⁻¹, a concentration which was still present in February 1974 in the north-west Atlantic. The accumulated data are presented in Table 1. These observations revealing a reduction in surface water concentrations of PCB compare well with our February 1974 measurements of a tenfold decrease of PCB in the atmosphere over the north-west Atlantic since 1973 (ref. 5), and a fivefold decrease

Table 1 PCB concentrations in North Atlantic surface waters* 1971-74

Date	Mean PCB† (ng l ⁻¹)	Sampling region	No. of samples	Analytical‡ method	Ref.
8/71	25	Iceland to Nova Scotia	8	A	§
7/72	41	Newfoundland to Portugal	8	B	3
8/72	36	Portugal to Norwegian Sea	11	C	3
9/72	30	Woods Hole to Bermuda	27	C	3
4/73	1	Sargasso Sea	8	A	4
9/73	2	Azores to 09°N, 40°W to Barbados	10	C	3
9/73	0.8	Sargasso Sea to New York Bight	9	C	3
2/74	0.8	New England Continental Shelf	6	C	3

* 0-30 m.

† Blank values for PCB in methods A, B and C were 0.9, 0.5 and 0.3 ng l⁻¹, respectively. Replicate analyses using methods B or C showed an average variation of $\pm 20\%$ at the 1 ng l⁻¹ level. Quantitation methods are presented in refs 3, 5, 6.

‡ A, Extraction of 0.5-3.8 l with chloroform or dichloromethane; B, extraction of 20 l with 5% ether in hexane; C, passing 40-60 l through Amberlite XAD-2 resin followed by elution with boiling acetonitrile.

§ C. E. Olney and J. J. Quinn, unpublished information.

since 1972 in ¹³⁷Cs content of mixed plankton collected along 09°N latitude in September of 1973 (ref. 6).

The data require that about 2×10^4 tons of PCB were lost from the upper 200 m in less than one year³. To explain this loss, four processes must be seriously considered: (1) apparent dilution of dissolved PCB by vertical and horizontal advection and diffusion; (2) association of PCB with sedimenting particles; (3) evaporative codistillation into the atmosphere and (4) biological and chemical degradation.

The information obtained from the monitoring of bomb fallout radionuclides is relevant to the present problem because like PCB, they are delivered to the ocean from the atmosphere, can exist in dissolved and particulate phases, and experienced a similar decreased input after the nuclear test ban agreements of

Table 2 PCB concentrations in North Atlantic subsurface waters*, 1973

Date of collection and analyses†	Position Latitude Longitude	Depth (m)	PCB (ng l ⁻¹)
19/9/73	09° 00' N 40° 00' W	10	4.3
		100	2.0
		200	1.4
		400	1.1
		500	1.3
		700	1.5
		1,000	1.0
		2,000	2.1
2/10/73	32° 25' N 70° 20' W	3,000	1.0
		10	0.6
		100	0.8
		300	0.9
		600	0.5
		900	1.9
		5,100	0.4

* Reproducibility at the 0.5 ng l⁻¹ level was $\pm 40\%$. The blank was produced by recycling 40 l of XAD-2 extracted seawater through the entire procedure and averaged 0.3 ng l⁻¹.

† Method C was used.

1963. For example, strontium-90 which is mainly in the dissolved state in seawater, required more than five years after the test ban treaty to decline to one-half the surface water concentrations of 1963 (ref. 7). Thus, depletion of dissolved PCB from the upper ocean by advection and diffusion seems too slow to explain the observed rate. The rate of PCB removal from the surface waters more closely resembles the behaviour of the plutonium nuclides ²³⁹-²⁴⁰Pu which are believed to be associated with particulates⁸. The vertical distribution of plutonium isotopes in the Atlantic was best explained as being associated with particles falling at rates of 70-392 m yr⁻¹. The well known affinity of PCB for solid surfaces suggests that adsorption on falling particles could be a major transfer mechanism. In fact, if 2×10^4 tons or less of PCB has been transferred to the deep ocean each year (1970 was the peak production year) for the past 10-15 yr and was dispersed throughout the entire water column, the concentrations to 3,500 m would still be less than 2 ng l⁻¹. Two 1973 profiles of PCB in the water column are presented in Table 2. The profile at 40° 00'W was typical of eight other stations in the North African and Cape Verde Basins; in contrast, the station at 70° 20'W revealing very low PCB levels at the surface, was similar to nine other stations in the North American Basin the same year.

We are, at present, unable to ascertain the relative importance of evaporative codistillation of PCB from the surface water or of biogeochemical degradation. Either process could explain the lower surface water concentrations in the North American Basin. There is, as yet, no evidence of biological metabolism of PCB in the marine environment.

We note the rapid response of the open-ocean mixed layer to the reduction of industrial discharges of PCB. Efforts to

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determine the mechanism of this electron transfer process are in progress.

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Origin proposed for non-protein amino acids in meteorites

THE amino acids that have been identified in several meteorites^{1,2} can be divided into two classes: those present in proteins and those which are not. The presence of the non-protein amino acids, D- and L-β-aminoisobutyric acid and β-alanine, is described as evidence for the indigenous origin of meteorite amino acids and against terrestrial contamination¹. It is implied that these β-amino acids arise by prebiotic condensation of ammonia, methane, hydrogen, water and other simple primordial molecules³. The β-amino acids and other amino acids can arise from simple molecules by Fischer-Tropsch synthesis in the laboratory. Hydrogen, carbon dioxide and ammonia were heated to high temperatures in the presence of natural catalysts expected to be present in the solar nebula⁴.

In other experiments, thermal synthesis of amino acids occurred in a simulated primitive atmosphere of methane, ammonia and water, followed by acid hydrolysis of the products. β-Alanine was obtained in high yield, relative to other amino acids, and the straight-chain compound, β-amino-n-butyric acid⁵. These amino acids were postulated to arise respectively from hydrolysis of β-aminopropionitrile and the nitrile intermediate arising from addition of ammonia to crotononitrile. Evidence for this route was the identification of succinic acid and N-methyl-β-alanine which are likely hydrolysis products of nitrile intermediates. Production of β-aminoisobutyric acid was not reported in these experiments⁶.

β-Aminoisobutyric acid is a rare amino acid with a curious distribution in nature. It has been isolated only from human urine⁷, iris bulbs⁸, flatworms⁹ and edible mussels⁹. Man is probably the only mammalian species to excrete D-(−)-β-aminoisobutyric acid¹⁰ though there is chromatographic evidence for its presence in rabbit urine¹¹. Metabolic experiments suggest that the pyrimidine base thymine, from nucleic acid catabolism, is the precursor of β-aminoisobutyric acid in the human¹²⁻¹⁴. Similarly, metabolic production of β-alanine in rat liver is from the pyrimidine uracil¹⁵.

By analogy with these known reaction sequences catalysed biologically, I suggest that heterocyclic compounds could also act as precursors for the β-amino acids found in meteorites. In this case, scission of the ring of heterocyclic compounds formed prebiotically would occur under the catalytic conditions of extremes of temperature and radiation thought to occur in space.

The purines, adenine and guanine, and a substance resembling uracil have been detected in the Orgueil meteorite¹⁶. Xanthine, thymine, uracil and derivatives have also been obtained experimentally by mimicking supposed prebiotic conditions⁴.

This chemical route to certain non-protein amino acids described above would presumably give racemic mixtures of both stereoisomers, for example, both D- and L-β-aminoisobutyric acid, as found in meteorites¹. It would be interesting to know if thymine, dihydrothymine, uracil and related compounds, when heated under supposed prebiotic conditions, did give traces of the β-amino acids.

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Evidence for downwind flights by host-seeking mosquitoes

THE behaviour of flying insects which make use of airborne chemicals in their search for food, oviposition sites or sexual partners can be separated into two phases, the search flight bringing them into contact with the attractant plume and the approach flight leading them to its source^{1,2}. The second phase is characterised by upwind orientation in response to the appropriate chemical stimuli³⁻⁵. Mosquitoes are known to fly upwind as they approach a warm-blooded host⁷⁻⁹. For most insects relatively little is known of the pattern of the preceding search flight which Haskell² described as 'wandering', but where the wind is light it may be upwind¹. Experiments in West Africa have shown that the majority of mosquitoes entered flight traps from the downwind side, that is they appeared to have been flying upwind, regardless of the presence or absence of a host (ref. 10 and W. F. Snow, unpublished). Here we report experiments that unexpectedly provide evidence for the opposite type of behaviour.

If the search flight is in a generally upwind direction, it should be possible to divert mosquitoes round a host by setting up a barrier on the downwind side and so provide a measure of protection from their attacks. The barrier would need to be sufficiently far away for the mosquitoes to encounter it before they detected the presence of the host, so that directed responses towards the host would not be elicited. This distance was estimated by Gillies and Wilkes¹¹ to be less than 18 m for a host the size of a man. A host stationed at this distance upwind

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