

morphological pattern as assessed by the 12 measurements taken, SK 84 is excluded with 95 percent probability from membership in any group, including *Homo sapiens*. The closest approach by the fossil to a centroid in the discriminant space occurs in the case of *Pan*, the sample to which assignment is subsequently made and in fact the only group for which membership is not excluded with 99 percent probability. (Chi-squares relating the fossil to the chimpanzee centroid are 8.36 and 10.12 with three degrees of freedom, for distal height measurements including and omitting the beak, respectively.)

This does not, of course, prove that *Paranthropus* at Swartkrans possessed a thumb (or hand) precisely like that of a modern chimpanzee. But a degree of similarity is certainly implied, with respect to measurable morphological structure and presumably in matters of function as well. The chimpanzee metacarpal and thumb are short relative to the other digits, and there is some limitation on movement at the carpometacarpal joint imposed by the surrounding "cuff" of thenar musculature (8). Thus, despite the potential for mobility at the well-developed saddle joint, the animal is seldom, if ever, observed to oppose the pulp of the thumb to the pulp surface of one or all of the remaining fingers. A true "precision grip" is not performed, although various imperfect approaches to this grip are possible (8, 9). The degree of thenar muscle development, the morphology of the articular capsule itself (whether loose or closely constructed), and the relative lengths of the pollex and other digits are unknown for *Paranthropus*, but in overall length and articular surface configuration, and in other characteristics emphasized in the discriminant analysis, the fossil metacarpal approximates the chimpanzee condition and may thus have fitted a hand with similar functional limitations.

In any case, despite its robust nature and tentative association with specimens of *Homo* on functions 1 and 2, the Swartkrans bone is far from fully modern in its morphology. Further study of such materials, including the judicious application of multivariate statistics, is necessary in order to detail the locomotor and manipulative capabilities of *Paranthropus* and early *Homo*.

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tion of the discriminant weights. Gibbon and baboon centroids were thus not obtained, although these individuals can be related to the centroids of the other "original" groups in the analysis.

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10. I thank Dr. C. K. Brain for permission to examine the Swartkrans metacarpal and Prof. W. W. Howells for the loan of indispensable measuring equipment. Project support was provided by the Research Foundation of the State University of New York.

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Enrichment of Heavy Metals and Organic Compounds in the Surface Microlayer of Narragansett Bay, Rhode Island

Abstract. Concentrations of lead, iron, nickel, copper, fatty acids, hydrocarbons, and chlorinated hydrocarbons are enriched from 1.5 to 50 times in the top 100 to 150 micrometers of Narragansett Bay water relative to the bulk water 20 centimeters below the surface. Trace metal enrichment was observed in the particulate and organic fractions but not in the inorganic fraction. If these substances are concentrated in films only a few molecular layers thick on the water surface, the actual enrichment factor in the films may be well over 10^4 , resulting in extremely high localized pollutant concentrations in the surface microlayer.

From a pollution standpoint, the air-sea interface is perhaps one of the most important but most poorly characterized regions of the marine environment. The surface microlayer of the ocean has many unique chemical and physical properties, most of which are little understood. The organic and trace metal chemistry of this microlayer has received scant attention. The few studies of this region (1) indicate the presence of a variety of surface-active substances (for example, fatty acids and fatty alcohols) at the interface. These materials often form a coherent film which becomes evident as a result of the localized damping of capillary waves. Even when this film or slick is not visible, the surface microlayer may still be enriched with surface-active compounds. The major source of these compounds in the open ocean is the reservoir of natural marine organic matter in the mixed layer. The process of slick formation is complex, but surfactants are probably concentrated in the surface microlayer by convection currents, rising bubbles, and diffusion. The most surface-active of these materials displace the less active compounds, and eventually the microlayer is enriched with lipid material and a coherent slick is formed.

Many pollutants may be concentrated and stabilized in this layer after its for-

mation or may in fact be incorporated into it directly. This is especially true for lipophilic pollutants such as chlorinated hydrocarbons (2) and petroleum hydrocarbons. Trace metals may also be concentrated in the microlayer. Organic acids, proteinaceous material, and other surface-active organic substances may provide complexing sites for many heavy metals and thus be responsible for the transportation and concentration of these metals at the water surface.

The sources of the various pollutants that can reach and eventually concentrate in the surface microlayer are numerous. They include atmospheric transport, rivers, sewage and industrial effluents, dumping, pumping, and spills. Once concentrated, pollutants are readily accessible to bacteria and other microorganisms as well as phytoplankton and zooplankton at the surface. In this way, pollutants initially in the surface microlayer can enter the food chain and eventually be concentrated in the higher trophic members of the marine community.

Since the chemical nature of the surface microlayer is poorly understood, both in terms of its natural composition as well as in terms of its pollution gradients, it would seem appropriate to characterize more fully this region of the marine environment. This report de-

Table 1. Concentrations and enrichment factors of organic compounds and metals in surface microlayer samples from Narragansett Bay, Rhode Island.

Substance	Sample 1			Sample 2		
	Concentration ($\mu\text{g}/\text{liter}$)		Enrichment* factor	Concentration ($\mu\text{g}/\text{liter}$)		Enrichment* factor
	Surface	Subsurface		Surface	Subsurface	
Fatty acids	128 \pm 26	36 \pm 7	3.6 \pm 1.0	94 \pm 19	62 \pm 12	1.5 \pm 0.4
Hydrocarbons	NA†	NA†	NA†	8.5 \pm 1.7	5.9 \pm 1.2	1.4 \pm 0.4
PCB's‡	4.2 \pm 1.0	0.15 \pm 0.04	28 \pm 10	0.45 \pm 0.11	\leq 0.05	\geq 9
Lead						
Particulate	1.4 \pm 1.1	0.24 \pm 0.17	5.8 \pm 6.1	1.5 \pm 0.2	0.28 \pm 0.10	5.4 \pm 2.0
Organic	1.0 \pm 0.8	0.36 \pm 0.06	2.7 \pm 2.2	1.4 \pm 0.6	0.27 \pm 0.12	5.2 \pm 3.1
Inorganic	1.7 \pm 0.3	2.7 \pm 0.5	0.6 \pm 0.2	6.1 \pm 1.4	3.7 \pm 1.0	1.6 \pm 0.6
Iron						
Particulate	820 \pm 47	28 \pm 4	29 \pm 5	35 \pm 7	8.2 \pm 1.2	4.3 \pm 1.1
Organic	3.7 \pm 1.5	0.60 \pm 0.33	6.2 \pm 4.3	5.1 \pm 2.3	3.8 \pm 0.8	1.3 \pm 0.6
Inorganic	2.8 \pm 0.4	1.4 \pm 0.2	2.0 \pm 0.3	17 \pm 8	12 \pm 1	1.4 \pm 0.7
Copper						
Particulate	7.2 \pm 2.3	0.20 \pm 0.09	36 \pm 18	1.3 \pm 0.4	0.26 \pm 0.11	5.0 \pm 2.7
Organic	5.6 \pm 0.5	0.19 \pm 0.11	29 \pm 17	1.6 \pm 1.0	0.11 \pm 0.04	15 \pm 11
Inorganic	3.4 \pm 0.4	3.3 \pm 0.3	1.0 \pm 0.2	1.5 \pm 0.6	1.3 \pm 0.4	1.2 \pm 0.6
Nickel						
Particulate	11 \pm 3.0	0.2 \pm 0.1	50 \pm 30	13 \pm 5	2.1 \pm 0.3	6.2 \pm 2.5
Organic	4.9 \pm 2.6	0.48 \pm 0.33	10 \pm 8.7	5.0 \pm 0.6	1.8 \pm 0.7	2.8 \pm 1.1
Inorganic	11 \pm 4.0	14 \pm 1.0	0.8 \pm 0.3	21 \pm 5	16 \pm 2	1.3 \pm 0.3

* The enrichment factor is equal to the surface concentration divided by the subsurface concentration. † NA, hydrocarbons not detected because of limited sample. ‡ PCB's expressed as Aroclor 1254.

scribes our efforts to determine the distribution of fatty acids, hydrocarbons, chlorinated hydrocarbons, and trace metals in samples from Narragansett Bay, Rhode Island.

Several surface microlayer samples were collected near the mouth of the west passage of Narragansett Bay (41°30'20"N, 71°23'30"W; 41°34'30"N, 71°23'W). The area is designated class SA (Rhode Island Department of Health) and is free of industrial and municipal effluents and major ship traffic. Samples for trace metal analysis were collected on a polyethylene screen (75 by 75 cm, 20 mesh) mounted on a Plexiglas frame. After the screen had been rinsed in seawater several times, it was submerged in the water and then passed back up through the water surface with the screen approximately parallel to the water surface. The frame was allowed to drain for 10 seconds, and then the screen was drained for 60 seconds into a polyethylene container through a polyethylene funnel. This collector samples the top 100 to 150 μm of the water surface (3). Polyethylene gloves were worn throughout the collection, and great care was taken to ensure that the sample was not contaminated by the collection boat (an aluminum rowboat) or the individuals doing the collecting.

Samples for organic analysis were collected on a 16-mesh circular stain-

less steel screen, 30 cm in diameter, in a manner similar to that used for trace metal sampling. The screen was drained into a Teflon bottle through a glass funnel. Subsurface samples were collected by submerging a Teflon bottle approximately 20 cm below the water surface and then removing the cap (polyethylene gloves were worn during this collection). Sample collection was limited to periods when wind conditions were less than 12 to 15 knots (22 to 28 km/hour) and wave heights were less than 3 feet (91 cm). The collection time was approximately 1½ to 2 hours per station.

Surface microlayer samples for organic analysis were acidified and extracted with chloroform after the addition of fatty acid and hydrocarbon internal standards (4). The chloroform extract was evaporated under reduced pressure, dissolved in a mixture of benzene and methanol (1:1), and divided into two equal portions for lipid and chlorinated hydrocarbon analysis.

The sample for lipid analysis was saponified and then methylated to convert total fatty acids (free and esterified) into methyl esters (5). The methyl esters and hydrocarbons were isolated and purified by preparative thin-layer chromatography. Qualitative and quantitative analyses were carried out with a gas chromatograph (Hewlett-Packard model 700) equipped with a flame ion-

ization detector. The samples were analyzed on polar (diethylene glycol succinate or free fatty acid phase) and nonpolar (Apiezon L) columns, and relative retention times were compared to those of authentic fatty acid and *n*-alkane hydrocarbon standards. In addition, the fatty acids were analyzed on these columns after hydrogenation. Quantitative results were obtained by comparing the areas of naturally occurring component peaks to the area of the internal standards. The results obtained on standard mixtures of fatty acids and *n*-alkanes were in agreement with the stated composition data with a relative error of less than 5 and 8 percent, respectively, for major components (> 10 percent of the total mixture).

The sample used for chlorinated hydrocarbon analysis was separated into a polychlorinated biphenyl (PCB) and a pesticide fraction on a silicic acid column. The fractions were analyzed on a gas chromatograph (Tracor model 220) equipped with two ⁶³Ni electron-capture detectors and two electrometers. The samples were analyzed on two different nonpolar columns (OV-17/QF-1 and SE-30/QG-1), and the relative retention times were compared to those in authentic Aroclor and pesticide standards.

Surface microlayer samples for trace metal analysis were filtered through Millipore HA filters (47 mm, 0.45 μm)

in an in-line closed filtering system constructed entirely of polyethylene and polypropylene. The collected particulate material appeared to be largely biogenic. The "particulate" sample and filter were dissolved in a mixture of perchloric and nitric acid for subsequent atomic absorption (AA) analysis. The filtrate from the particulate sample was extracted with chloroform. The chloroform, along with any interfacial material, was filtered through a Millipore HA filter (24 mm, 0.45 μm) to remove the interfacial material. The chloroform extract was concentrated in a rotary evaporator, and the final few milliliters were transferred to the 24-mm filter and evaporated. The "organic" phase on the filter was then processed in the same manner as the "particulate" sample for AA analysis. After filtration and chloroform extraction, the remaining aqueous portion of the sample was acidified and buffered to a pH of 3.0. The solution was then extracted with a 5 percent (by weight) solution of diethyldithiocarbamic acid into methyl isobutyl ketone. This "inorganic" phase was analyzed directly by AA. All AA analyses were performed with an atomic absorption spectrophotometer (Perkin-Elmer model 303) with standards prepared in a seawater matrix.

We have collected several surface microlayer samples in Narragansett Bay and analyzed them for trace metals, lipids, and chlorinated hydrocarbons. The results of the analysis of two of these surface slicks and subsurface waters are presented in Table 1. Sample 1 was collected in a heavy frothy surface slick and showed enrichment factors in the surface microlayer relative to those in the subsurface water ranging from 3 to 50 for fatty acids, PCB's, and "particulate" and "organic" trace metals. Sample 2, from a less pronounced slick, had lower enrichment factors varying from slightly over 1 to 15. With the exception of iron in sample 1, no enrichment was found for trace metals in the "inorganic" phase for these or other surface microlayer samples collected in Narragansett Bay. In general, the fatty acids were normal saturated and mono-unsaturated acids and ranged from 12 to 20 carbons in chain length. Only three hydrocarbons were detected in these samples, and they were tentatively identified as having carbon numbers of $\text{C}_{21.0}$, $\text{C}_{22.5}$, and $\text{C}_{24.0}$ relative to *n*-alkanes on an Apiezon L column. The only chlorinated hydrocarbons found

were PCB's which were measured as Aroclor 1254.

An enrichment factor given in Table 1 for any of these substances in the top 100 to 150 μm of the water surface suggests a much greater enrichment in the film material itself. If the film layer is monomolecular, as has been suggested (1), it should have a thickness of about 2×10^{-3} μm . If the film thickness is estimated conservatively as five molecular layers (10^{-2} μm) and all the chemical enrichment is in this layer, the actual concentration in the film would be 1.5×10^4 times the concentration in the top 150 μm . In sample 1, where the enrichment of PCB's in the top 100 to 150 μm is 28, the PCB concentration would be ~ 60 parts per million, which would represent an enrichment of 4×10^4 in the film layer itself. The effects of the high concentrations of chlorinated hydrocarbons, lipids, and heavy metals on the diversity and species composition of the bacteria, phytoplankton, and zooplankton living in the surface microlayer are unknown.

Pollutants present in the surface microlayer of the coastal zone may easily be introduced into the atmosphere for subsequent transport to open ocean waters. The surface of the ocean is a major source of atmospheric particulate matter. The primary production mechanism for these particles is the breaking of bubbles, which ejects particles both from a central jet and from the ruptured bubble film cap (6). There is evi-

dence that these particles are chemically more representative of the surface microlayer than the bulk water underneath (7), and thus this study suggests that the particles may be considerably enriched in pollutants if they are generated in highly polluted nearshore areas.

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Cloud Seeding Experiments: Lack of Bias in Florida Series

Abstract. *There has been concern about the possibility of selection bias in cloud seeding experiments. Covariates and experimental design have been used to obtain an estimate of this bias. The results indicate that there was no selection bias in the Caribbean and Florida series of cloud seeding experiments.*

Stigler (1) has made the general point that selection bias may be introduced when suitable experimental subjects arrive sequentially; he referred in particular to the cloud seeding experiments in Florida. We present evidence here that such a bias is not detectable in the experiments over the Caribbean Sea (2) in 1965 and over Florida (3) in 1968 and 1970. These references should be consulted for a description of the experimental details. In addition, we wish to make a suggestion about what to do in some experimental situations where selection bias has not been (or

cannot be) eliminated by some appropriate design.

In planning the Caribbean cumulus experiments, careful attention was given to the design. This included consultations with experts in experimental design, one of whom, W. J. Youden (now deceased), prepared the randomization scheme. These experiments represent the first time that a numerical model of cumulus dynamics was used to make predictions of cloud growth and to provide a measure of "seedability" of selected clouds. The power of the experiments was greatly increased by in-