

degradation of the underlying permafrost.

Two areas—one covered with ice-rafted sediments and one without—were instrumented with thermal probes placed at the surface, at 6 cm and at 13 cm; the temperature was recorded four times a day with a telethermometer (Yellow Springs). For five consecutive days of measurement, starting on 18 June and ending on 22 June 1973, the soil under the ice-rafted sediments was consistently warmer than the nearby vegetation-covered soil, probably because of the dark color of the ice-rafted sediments and their lack of insulating vegetation. On 19 June 1973, at 0840, the two sites showed maximum differences as follows: the temperature of the ice-rafted sediments exceeded the temperature at the corresponding depth for the vegetation-covered soil by 3.5°C at the surface, by 6.5°C at the 6-cm depth, and by 4.0°C at the 13-cm depth. Hence, the warmer soil would induce differential thawing that should lead to thermokarst development.

Once a pond has been initiated, repeated freezing of ice to the bottom and subsequent flooding would tend to lift the ice cover with its adhering sediments, further deepening the pond; indirect evidence in support of this process are the vertical and apparently sheared edges of ponds and lakes. This process stops when the lakes are too deep to freeze to the bottom. However, shallow portions of deep lakes and shallow channels of the Noatak Delta can still contribute ice-rafted sediments. As mentioned above, the process outlined depends on the occurrence of floods. Conversations with the local Eskimos and with Buck Maxson, a pilot from Kotzebue, established that a severe storm occurred during November 1972, a storm the likes of which had not been recorded for some 20 years, flooding the Noatak Delta, rafting numerous ice floes, and leaving them stranded after the waters had receded. This was further confirmed by ERTS-1 (Earth Resources Technology Satellite) mission images (70 1313-21585-7-01 and 1314-22043-07-01) taken on 1 and 2 June 1973, which documented these effects. Some floes stranded at this time were responsible for the sediment patches I observed during the summer of 1973 after the ice had melted. Numerous sediment patches of similar origin were also observed along the west coast of Alaska between Kotzebue and

Point Hope (5). Since many lakes whose shorelines have the characteristic shape of ice floes were observed in the western part of the delta, it is conceivable that similar floods could have been the initiating cause of these lakes and that other deltas and tidal marshes of the Arctic also can be affected by the same process. Although this evolutionary process for the formation of deltaic lakes has not been observed in its entirety, it supports the view that landscapes are often formed by catastrophic events, in this case by storms rather than by slow, everyday processes.

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Polycyclic Aromatic Hydrocarbons in Soils and Recent Sediments

Abstract. Soils and recent marine sediments contain a complex polycyclic aromatic hydrocarbon assemblage. There is a high degree of similarity in the molecular weight distribution of the many series of alkyl homologs of these aromatic hydrocarbons, and this distribution varies little over a wide range of depositional environments. The evidence suggests that these hydrocarbons are formed in natural fires, are dispersed and mixed by air transport, and are eventually deposited into surface sediments. The analytical, geochemical, and environmental implications of these findings are discussed.

Polycyclic aromatic hydrocarbons (PAH) occur commonly in soils and young marine sediments (1). Until recently it had been thought that this sedimentary PAH fraction consisted of a limited number of unsubstituted hydrocarbons, but newer analyses with greater analytical resolution have now demonstrated a far greater compositional complexity and the presence of extended series of alkyl homologs (2, 3). Thus, the marine sediments of Buzzards Bay, Massachusetts, contain, in addition to the previously known parent hydrocarbons, homologs extending to at least C₁₂ and extended series of naphthenologs and thienologs.

The discovery of these complex PAH assemblages in recent sediments has considerable geochemical and environmental significance. In order to study the regional variability of the PAH fraction and to obtain clues on its origin, we have analyzed samples that cover depositional and chemical environments ranging from continental and coastal soils to marsh and subtidal marine deposits, and from high to low oxidation-reduction potentials (4).

- ### References and Notes
1. J.-C. Dionne, *Z. Geomorphol. Neue Folge* 3, 131 (1972).
 2. "Thermokarst" is defined as: "karst-like topographic features produced by the melting of ground-ice and the subsequent settling or caving of the ground" [S. W. Muller, *Permafrost or Permanently Frozen Ground and Related Engineering Problems* (J. W. Edwards, Ann Arbor, Michigan, 1947), p. 223].
 3. D. Huggins, personal communication.
 4. Munsell Color Notation, Munsell Color Company, Inc., Baltimore; color determined under moist field conditions.
 5. J. Walters, personal communication.
 6. I thank J. Walters and the other members of the Noatak River Project for assistance while in the field; I thank A. L. Washburn, C. Bull, and D. M. Anderson for reading and commenting on the manuscript. This research was sponsored by the Center for Northern Studies under contract with U.S. Department of the Interior, National Park Service. Contribution No. 4 of the Center for Northern Studies, Wolcott, Vermont.

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We used the method of Giger and Blumer (2) in the sampling and initial work-up; this involves solvent extraction, separation by adsorption and gel permeation chromatography, and charge transfer complexation. The purified aromatic concentrate is separated by chromatography on alumina. In order to determine the molecular weight distribution within several PAH series, we collect in a single fraction, after the elution of most bicyclic aromatics, all the tri- and tetracyclic compounds (anthracenes, phenanthrenes, pyrenes, fluoranthenes, chrysenes, triphenylenes, benzanthracenes, and others). To assure complete recovery of the most strongly retained four-ring compounds, elution is continued into the pentacyclic fraction.

This tri- and tetracyclic concentrate is then subjected to mass spectral probe distillation. While the probe warms up, first through indirect heating from the source and then through programming, spectra are collected at 12 eV until the sample is completely exhausted. The intensities of the molecular ions are integrated over the course of the distil-

Table 1. Homologous polycyclic aromatic hydrocarbons in soils and recent sediments.

Possible sources	Comments
Fossil hydrocarbons	Unlikely except where documented by molecular weight distribution
Weathering	No major outcrops of sediments in our area
Seepage, spills	No contribution to soils in our area
Biosynthesis	Questionable in view of the extreme complexity and similarity over the wide range of depositional environment
Early diagenesis	Questionable in view of the wide range of source material and depositional environment; should favor a high degree of alkyl-substitution
Pyrolysis	Possible, parent hydrocarbon favored at high pyrolysis temperature
In situ	Unlikely in view of the wide range of depositional environments
"Urban air particulates"	Questionable; existing analyses suggest a paucity of alkyl homologs
Forest fires	Possible but unproven; low-temperature pyrolysis could yield homology; air transport on carbon might preserve similarity over a wide area

lation, and the abundances are normalized to the predominant species within each series of equal hydrogen deficiency. The resulting homolog plots (Fig. 1) provide a reproducible measure of the molecular weight distribution within numerically corresponding series. Each point on the curve may represent contributions from many isomers of unknown structure and unknown relative abundance.

These analyses serve to characterize the recent sedimentary PAH fraction: The molecular weight distribution within all homologous PAH series is consistent; the patterns of Fig. 1 for the chrysene, triphenylene, and benzanthracene series (molecular weight, 228) are closely duplicated by the other series. In each series the unsubstituted hydrocarbons predominate, and for each additional alkyl carbon atom there is a nearly twofold decrease in the total concentration of the isomeric homologs. The molecular weight distribution appears to be independent of the depositional environment; moreover, it differs markedly from that of crude oil and ancient sediments, which resemble the pattern for South Louisiana crude oil (Fig. 1).

These findings provide clues to the origin of the recent sedimentary PAH fraction. In principle, many sources might be involved, each characterized by its own typical compositional pattern. However, the consistency in the PAH distribution among our samples suggests a predominant single mode of origin. The alternate assumption of a uniform contribution from different sources appears less plausible in view of the wide range of depositional and chemical environments covered by our analyses.

The possible sources of the PAH assemblage in soils and sediments are compiled in Table 1. Fossil fuels and ancient rocks are rich in polycyclic

aromatics. Yet, they could not be the predominant source of the recent sedimentary PAH fraction because of the considerable compositional differences. Also, an even contribution from fossil fuels over our entire sample range is unlikely.

It has been suggested that PAH are formed by organisms. However, this is still a matter of vigorous and unresolved controversy (5). The assumption of a biosynthetic origin for the recent sedimentary PAH would imply the synthesis of a complex hydrocarbon assemblage of constant composition by a wide variety of organisms, independent of environmental conditions. It is

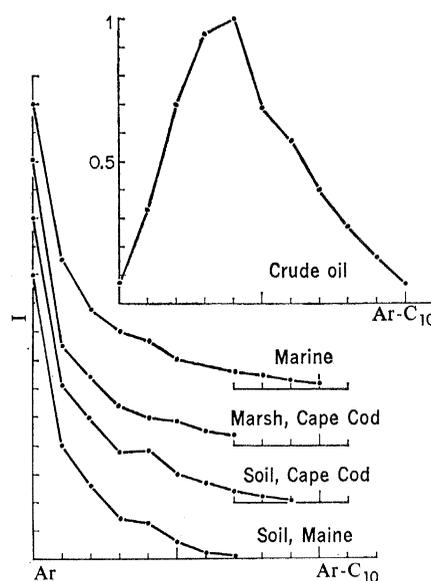


Fig. 1. Relative abundance of the unsubstituted aromatic hydrocarbons and their C_1 to C_{10} alkyl homologs in the overlapping chrysene, triphenylene, and benz[*a*]anthracene series in a crude oil and recent sediments (4); *Ar*, unsubstituted hydrocarbons; molecular weight, 228; *I*, integrated intensities of the molecular ions during mass spectral probe distillation, normalized to the predominant peak. The homolog plots of the recent sediments are vertically displaced by equal increments.

difficult to reconcile this idea with the established principle of biosynthetic selectivity and the known dependence of plant and animal products on species contribution and environmental conditions. Therefore, we question the importance of biosynthesis as a primary source of the entire sedimentary PAH fraction, without entirely ruling out the biochemical origin of some PAH.

The thermal formation of PAH is better understood; this mode of formation is energetically favored, and the rate of transformation and the composition of the final product depend on the transformation temperature. Low temperatures favor alkylated products; thus, sedimentary diagenesis at low to intermediate temperatures produces the highly alkylated PAH assemblages of petroleum. An even higher degree of alkylation would result from the early, nonbiochemical transformation of sedimentary organic matter at environmental temperatures. Such extensive alkylation is not revealed by our analyses. This suggests, together with the constant sample composition over a wide depositional range, that early diagenesis is not the primary source of the recent sedimentary PAH fraction. Similarly, the fact that subtidal marine samples, which are not directly exposed to fires, contain PAH assemblages resembling those of soils rules out the in situ pyrolysis as the primary source of these hydrocarbons.

Aromatic hydrocarbons are formed at elevated temperatures by incomplete combustion, and they are present in polluted air. Consistent with the high formation temperature is the paucity of alkyl derivatives, for example, in urban air particulates (6), where only C_1 to C_3 homologs are found, with the C_2 and C_3 homologs far less plentiful than the C_1 homologs. This finding suggests that air pollutants are not the primary source of the sedimentary PAH fraction, unless future analyses should demonstrate a greater compositional complexity.

Large quantities of PAH are formed in forest and prairie fires. Combustion products from these sources are distributed widely through the environment. Thus, Smith *et al.* (7) interpret the carbon particles with recognizable wood texture, which they discovered in marine sediments, as material derived from natural fires in the temperate zones of the continents. In view of the wide range of combustion temperatures involved in forest and prairie fires, more alkylated derivatives should be

formed there than in the high-temperature processes discussed here. In the cooling gas mass over the fires, freshly formed active carbon particles would readily scavenge the aromatic hydrocarbons and would protect them from photooxidation during extended air transport. Tropospheric mixing could account for the relative compositional uniformity of the sedimentary PAH fraction and for the fact that its composition is independent of that of the biota and the chemical conditions in the sedimentary environment.

Therefore, we suggest that natural fires form, and that air currents disperse, a complex PAH assemblage that eventually accumulates in soils and recent sediments. This hypothesis is open to tests, for instance, through the analysis of air samples or of sediment cores that predate the industrial revolution.

Our findings have analytical, geochemical, and environmental implications. The sedimentary PAH fraction is far more complex than was previously recognized. In fact, a complete resolution into individual components and their quantitative determination is difficult, if not often impossible (8). Regardless of the detailed mode of origin, the sedimentary PAH fraction may be accompanied by other classes of organic compounds, equally complex. This would imply that our present insight into the composition of nonbiological sedimentary organic compounds may be more limited, and our analytical capabilities more restricted, than generally accepted.

Our analyses demonstrate that the sedimentary PAH fraction contains, in addition to the already recognized carcinogens (benzo[*a*]pyrene and benz[*a*]anthracene), other, not previously recognized carcinogens (dibenzothiophene, methylchrysenes, and others) and a wealth of other polycyclic compounds that may comprise many biologically active compounds. Therefore, we need to reexamine the environmental toxicology of the sedimentary PAH fraction. Finally, our interpretation would imply that carcinogenic and mutagenic hydrocarbons occurred on the earth's surface during geologic time spans. This raises the question of whether these compounds might have contributed significantly to the processes of natural selection and mutation, and to the evolution of species.

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4. Experimental details and additional data are presented elsewhere (M. Blumer and W. W. Youngblood, *Geochim. Cosmochim. Acta*, in press). Samples may be identified as follows. (i) South Louisiana "crude oil": standard sample, provided by J. W. Anderson, Texas A & M University; (ii) "marine": surface sediment at station A of Giger and Blumer (2); (iii) "marsh, Cape Cod": surface sample, Little Sippewissett marsh, tidal, Falmouth, Massachusetts;

setts; (iv) "soil, Cape Cod": surface soil from a hummock within Little Sippewissett marsh, oaks predominate; and (v) "soil, Maine": coniferous forest, North Anson, Maine.

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Chemotherapeutic Drugs Increase Killing of Tumor Cells by Antibody and Complement

Abstract. *When the ascitic forms of two antigenically distinct guinea pig hepatomas induced by diethylnitrosamine are treated in vitro with chemotherapeutic drugs, their sensitivity to killing by xenogeneic antibody plus guinea pig complement increases. The effect is dependent on drug dose, is reversible, and does not appear to be due to increased antigen expression or fixation of the early acting components of guinea pig complement.*

The variation in sensitivity of different types of nucleated cells to the cytotoxic action of antibody and complement has generally been ascribed to differences in antigen concentration (1), immunoglobulin class (2), source of complement (3, 4), and phase growth of cells (5). Data from our laboratory showed that cells of two antigenically distinct guinea pig hepatomas induced by diethylnitrosamine (designated line 1 and line 10) were resistant to the cytotoxic action of specific rabbit antibodies to tumor and guinea pig complement. In addition, cells of line 10, but not of line 1, were resistant to 19S antibody to Forssman antigen and guinea pig complement. However, both tumor cell lines sensitized with either specific antibody to tumor or 19S antibody to Forssman antigen were susceptible to killing by human complement (4). Variable susceptibility to antibody and complement could not be ascribed to differences in antigen concentration, to antibody class, or to lack of fixation of C4 (the fourth component of complement) and C3 (4).

We have reported that cells of line 10 could be killed by antibody and guinea pig complement if the cells were first treated with actinomycin D, mitomycin C, puromycin, or hydroxyurea (6). Other investigators have shown that treatment of cultured human lymphoid cells with puromycin or cycloheximide increased their sensitivity to

HL-A alloantibody and complement (7). Actinomycin D was not effective. We now report that line-1 and line-10 tumor cells can be killed by antibody and guinea pig complement if the cells are first treated with drugs used in the treatment of cancer.

The ascitic forms of line 1 and line 10 were used in our experiments (8). Ascitic fluids were collected 6 to 8 days after intraperitoneal injection of 3×10^6 cells. Ascites tumor cells (60×10^6) were freed of erythrocytes by lysing them with 5.0 ml of tris-NH₄Cl (9), washed twice with barbital-buffered saline containing 1 g of gelatin (10), and resuspended in RPMI 1640 containing 15 percent calf serum (11). All centrifugations were at 200g for 5 minutes at room temperature.

Line-1 or line-10 tumor cells (2.5×10^6) were added to 5.0 ml of tissue culture medium (RPMI 1640 containing 15 percent fetal calf serum) containing one of the following compounds: 5-fluorouracil (Roche, lot 0776-0843); cytosine arabinoside (NCI, Cancer Therapy Evaluation Branch, NSC-63878); 6-mercaptopurine (NCI, NSC-755); vincristine sulfate (NCI, NSC-67674); methotrexate (NCI, NSC740); cyclophosphamide (Meade Johnson); adriamycin (NCI, NSC123127); or azacytidine (NCI, NSC102816). Control suspensions were prepared concurrently with tissue culture medium alone. After incubation for 17 hours at 37°C