New Rules for AAAS–Newcomb Cleveland Prize

The AAAS–Newcomb Cleveland Prize, which previously honored research papers presented at AAAS annual meetings, will henceforth be awarded annually to the author of an outstanding paper published from September through August in the Reports section of *Science*. The first competition year under the new rules starts with the 3 September 1976 issue of *Science* and ends with that of 26 August 1977. The value of the prize has been raised from $2000 to $5000; the winner also receives a bronze medal.

To be eligible, a paper must be a first-time presentation (other than to a departmental seminar or colloquium) of previously unpublished results of the author's own research. Reference to pertinent earlier work by the author may be included to give perspective.

Throughout the year, readers are invited to nominate papers appearing in the Reports section. Nominations must be typed, and the following information provided: the title of the paper, issue in which it is published, author's name, and a brief statement of justification for nomination. Nominations should be submitted to the AAAS–Newcomb Cleveland Prize, AAAS, 1515 Massachusetts Avenue, NW, Washington, D.C. 20005. Final selection will rest with a panel of scientists appointed by the Board of Directors.

The award will be presented at a session of the annual meeting at which the winner will be invited to present a scientific paper reviewing the field related to the prize-winning research. The review paper will subsequently be published in *Science*. In cases of multiple authorship, the prize will be divided equally between or among the authors; the senior author will be invited to speak at the annual meeting.

Reports

Azaarenes in Recent Marine Sediments

Abstract. *Chemical fractionation and mass spectral probe distillation reveal the presence in recent marine sediments of a complex assemblage of nitrogen-containing aromatic compounds. These azaarenes range from three- to eight-membered rings, with homologs containing up to eight alkyl carbons. In their composition, and presumably in their origin in natural fires, they resemble the aromatic hydrocarbons found in the same sediments. The analytical, geochemical, and environmental implications of these findings are discussed.*

Soils and recent marine sediments contain a complex assemblage of polycyclic aromatic hydrocarbons (PAH) together with thienologs and extended series of alkyl and cycloalkyl derivatives (*1*, *2*). Nitrogen analogs of the PAH had not been discovered in these samples. If the PAH are formed pyrolytically, as has been suggested (*2*), they should of course be accompanied by similarly complex assemblages of azaarenes.

Recently we have discovered a rich source of azaarenes and of their alkyl analogs in curtisite and idrialite (*3*), two fossil hydrocarbon minerals thought to be formed from plant material by pyrolysis in deeply buried sediments. These minerals are hydrocarbon mixtures pure enough to require little chemical separation before mass spectral analysis. The fact that these minerals require so little preliminary treatment led us to suspect that any azaarenes that might be present in recent sediments at low concentrations may have been overlooked because they were lost during the extensive prefractionation.

A reexamination of our earlier mass spectra revealed an excess intensity at the $M + 1$ ion of the principal PAH components, over and above that expected from the isotope contributions alone. This, of course, is also the position of the intense molecular ions of the aza analogs of the individual arenes. We now have tested and modified our analytical procedure for optimum recovery of the azaarenes, using 1-azapyrene as a reference compound.

The work-up presented here follows the method of Giger and Blumer (*1*) for sampling, extraction, and initial separation by gel permeation chromatography on Sephadex LH-20. However, the removal of elemental sulfur on active copper is avoided, since it leads to some loss of aza compounds. The eluate from gel permeation is chromatographed from pentane on acidic silica gel (8 ml, containing 3 percent 1*N* HCl). A pentane eluate is discarded, and the arenes are collected in two fractions (benzene and benzene with 2 percent methanol, 20 ml each). The bases are then recovered with 35 ml of methanol containing 3 percent concentrated aqueous ammonia. This eluate is partitioned between water and benzene; the organic layer is dried over anhydrous sodium sulfate, evaporated, and chromatographed on a bed of alumina packed over silica gel (4 ml each, both with 3 percent water). Eluates of pentane and methylene chloride (20 ml each) are discarded, and the azaarenes are eluted in two fractions (methylene chloride with 10 and 40 percent methanol, 20 ml each). These last eluates are combined, dried, and redissolved in benzene containing 20 mg of picric acid. After evaporation at room temperature in a rotary evaporator, the solids are washed three times with 2 ml of pentane; the washings are discarded. The remaining solids are dissolved in benzene and washed in a separatory funnel three times with 5 percent aqueous ammonia. The benzene layer is washed with water, dried, evaporated, and chromatographed over alumina (5 ml with 1 percent water). A 10-ml pentane fraction is discarded, and the azaarenes are eluted with 40 ml of pentane containing 60 percent methylene chloride.

The azaarene fraction is weighed and fractionally distilled from a capillary with a restricted opening (*4*) into the source of a mass spectrometer (Finnigan 3200) operated at 12 ev. Individual spectra, acquired on a Finnigan model 6000 data system, are inspected for the presence, appearance, and disappearance of homologous aza series. Because of the changing vapor composition during the distillation, individual spectra do not represent the true composition of the total samples. However, successive addition of all spectra that contain appreciable aza components reconstructs a spectrum that is representative of the total sample composition.

Few azaarenes and alkyl derivatives of

Table 1. Homologous series of azaarenes in recent sediments. Relative abundance of series: $229 > 253 > 279 \geq 203 > 179 > 303 > 277 > 327 > 353 > 351 > 329 > 376$. Weight of total aza fraction (dry weight of sediment): 0.14 mg/kg (Buzzards Bay, Massachusetts); 0.22 mg/kg (marsh, Wild Harbor River, North Falmouth, Massachusetts).

Initial mass	Extent of series	Representative structures
179	To C_7	Azaanthracene, azaphenanthrene
203	To C_7	Azafluoranthene, azapyrene, azabenzofluorene
229	To C_6	Azabenzanthracene, azachrysene, azatriphenylene
253	To C_6	Azabenzofluoranthene, azabenzopyrenes, azaperylene
277	To C_6	Azaanthanthrene, azabenzoperylene
279	To C_5	Azadibenzanthracene, azapicene
303	To C_6	Azadibenzofluoranthene
327	To C_3	Azabenzanthanthrene, azadibenzoperylene
329	To C_3	Azabenzopicene
351	To C_3	Azabenzocoronene
353	To C_3	Azatribenzofluoranthene
377	To C_1	Azadibenzanthanthrene, azatribenzoperylene

high molecular weight are known, and reference compounds and spectra are generally unavailable. In spite of this lack, a conclusive identification is possible through an analytical procedure based on the different chemical and physical properties of this class of compounds. In our separation, the materials giving rise to odd mass peaks in the mass spectra remain with azapyrene through selective retention on Sephadex LH-20, acid-base fractionation, picric acid adduction, and adsorption chromatography. Further confirmation comes from the retention of a high spectral intensity at low ionization voltage, a behavior that agrees with that of arenes and known azaarenes. Also, in their evaporation temperatures and distillation patterns our materials follow closely the behavior of the PAH series.

The analytical work-up resolves extraneous components of the sediment extracts from the azaarenes without splitting this group of components into separate fractions. In this manner, a representative picture of the composition of the sediment samples is retained.

The mass spectra of the aza concentrates from two stations in Buzzards Bay, Massachusetts, and from a coastal marsh adjacent to the same estuary are virtually identical and exhibit an array of odd mass peaks which we attribute to unsubstituted three- to eight-ring azaarenes and extended series of their alkyl homologs (Fig. 1 and Table 1). With the exception of a positive shift by one mass unit, the spectra are closely similar to those of the PAH series in marine and marsh sediments from the same general area (*1*, *2*). In view of the lack of reference materials, quantitative estimates of the weights for individual components cannot be given; however, the total weight of the aza fraction is one to two orders of magnitude lower than that of the PAH fraction.

Blumer and Youngblood have suggested that the sedimentary PAH fraction in soils and sediments from the northeastern United States represents material that was formed pyrolytically in forest and prairie fires, dispersed and mixed by air transport, and eventually deposited in surface sediments (*2*). The findings presented here add support to this interpretation. Azaarenes of lower molecular weight are well-known products of pyrolysis, and their heavier analogs can be expected to form during the partial combustion of nitrogen-containing plant material. In the pyrolysis of plants, where the moderate amount of nitrogen is distributed between aromatic rings, few rings with two nitrogen atoms should be formed. Correspondingly, none were found at the limit of our analytical sensitivity.

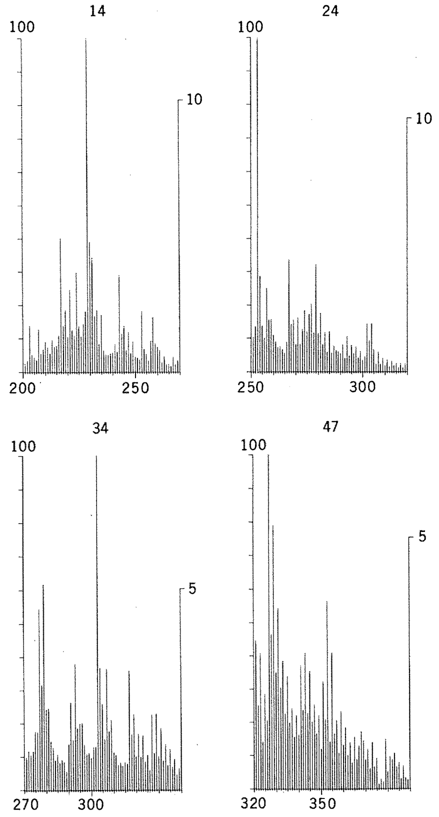

Fig. 1. Azaarenes in sediments of a coastal marsh on Buzzards Bay, Massachusetts. Probe distillation of the total azaarene fraction yields 50 mass spectra, with appreciable odd mass ions in spectra 4 through 47. Addition and normalization of four consecutive groups of 10 to 13 spectra each show the fractional distillation, extending from low to high ring numbers. Evident are aza analogs of the following arenes: phenanthrene, pyrene, and chrysenes (spectra 4 through 14); benzopyrenes and isomers (spectra 15 through 24); benzoperylene, picene, and dibenzofluoranthene (spectra 25 through 34); and hepta- and octacyclic arenes (spectra 35 through 47).

Other PAH sources, from industry, domestic heating, or automotive traffic, may be more important than the natural background in some areas. Processed petroleum fuels (for example, gasoline and fuel oil) have a low nitrogen content by comparison with plant material. Therefore, they should give rise to a PAH mixture with a low aza contribution. Accordingly, the analysis of a soot from an automotive engine demonstrated a rich PAH assemblage but no detectable azaarenes. Thus, compositional features of environmental aromatic compounds, such as the nitrogen distribution in rings or the molecular weight distribution in PAH series (*5*), provide clues to the origin of these compounds.

The discovery of complex homologous azaarene series further complicates the picture of the polycyclic aromatic components of recent sediments; it lends strength to our argument that we are still far removed from a true assessment of environmental organic chemistry (*6*). This, of course, is a critical limitation if we are concerned about the biological effects of environmental chemicals, whether they be natural or synthetic.

The biological activity of some azaarenes of lower molecular weight is well documented (*7*), and it often exceeds that of the PAH analogs. In contrast, the toxicology of the heavier azaarenes and of their alkyl derivatives is unexplored. The anticipated global distribution of these newly discovered series makes it necessary to investigate their importance as environmental carcinogens and mutagens.

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8. This work was supported by the Office of Naval Research (NOO-14-66 contract CO-241) and the National Science Foundation (grant DES 74-22781). Contribution Number 3673 of the Woods Hole Oceanographic Institution.

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Biological Consequences of the 1975 El Niño

Abstract. *The weak El Niño event of 1975 had a clearly defined effect on the biological productivity of the southeastern tropical Pacific. During February and March 1975, warm (27°C) water of low salinity (33.5 parts per thousand) and low nutrient content extended south across the equator east of the Galápagos Islands, replacing the nutrient-rich water normally supplied by equatorial upwelling. Equatorial primary production was less than 0.2 gram of carbon per square meter per day, one-fifth of the normal value. At the maximum development of the 1975 event, the coastal region of Peru continued to have strong nearshore upwelling with primary production values greater than 2.5 grams of carbon per square meter per day, although the zone of high production was confined to a 250-kilometer-wide band, one-half its normal width. The biological effects of the 1975 event were short-lived; in April and May 1975 the equatorial region had begun to reestablish its normal levels of primary production.*

El Niño conditions are characterized by invasions of anomalously warm, nutrient-depleted water into the coastal regions of Ecuador and Peru. Under normal conditions these coastal waters are strongly influenced by the cold, nutrient-rich water that reaches the surface by coastal upwelling. This water supports high primary production and the world's largest anchovy fishery. Onset of severe El Niño conditions usually has disastrous effects on the yield from this fishery.

Quinn (*1*) predicted that "weak" El Niño conditions would develop in the eastern tropical Pacific during the early months of 1975. Wyrtki *et al.* (*2*) presented the physical features of the observed El Niño conditions, which occurred as predicted. East of the Galápagos Islands, in February and March 1975, warm (27°C), low-salinity [33.5 parts per thousand (ppt)] water extended south across the equator as far as 4°S, and the Galápagos Equatorial Front was almost 500 km south of its usual position. Severe reductions in offshore primary production were also observed in February and March, although primary production along the coast of Peru was comparable to normal, non–El Niño conditions. In this report we describe the observed primary production during and after the 1975 El Niño in the equatorial and coastal upwelling regions and comment on the potential influence of the 1975 event on the Peruvian anchovy.

The data reported here were collected during two successive cruises (11 February to 31 March and 17 April to 27 May) of the R.V. *Moana Wave* along the cruise track shown in Fig. 1A (*3*). Primary production was measured by the modified carbon-14 method of Steeman-Nielsen [(*4*); see also (*5*)], with samples incubated for 24 hours under natural light in neutral-density filters, which simulate light intensity at the depths of sample collection (depths at which incident radiation was 100, 50, 25, 10, and 1 percent of surface radiation). Productivity values were then integrated over the depth of the euphotic zone. The data are expressed as grams of carbon assimilated per square meter of ocean surface per day. Nutrients were analyzed with a modified Technicon AutoAnalyzer II, and data are reported in micromoles per kilogram of seawater.

Table 1. Dominant phytoplankton in the coastal surface waters of Peru in March and April 1966 and February and March 1975. Values for 1966 are from Ryther *et al.* [table 1 in (*11*)]; those for 1975 are mean values for two coastal stations (ranges are given in parentheses).

Species	Abundance (cell/ml)	
	1966	1975
Asterionella japonica	21	22 (0–45)
Chaetoceros compressus		62 (0–123)
Chaetoceros curvisetus		68 (62–73)
Chaetoceros debilis	312	
Chaetoceros lorenzianus	67	42 (0–84)
Chaetoceros socialis	26	308 (168–448)
Leptocylindrus danicus		65 (6–123)
Nitzschia delicatissima	2	11 (6–17)
Nitzschia seriata	22	
Schroederella delicatula	12	146 (84–207)
Skeletonema costatum	4	247 (34–459)
Thalassiosira sp.		879 (868–890)
Coccolithus huxleyi	2	

Wyrtki *et al.* (*2*) discussed the intrusion of warm, low-salinity water (27°C, less than 33 ppt) across the equator east of the Galápagos Islands. The normal pattern of equatorial primary production was drastically altered by this warm-water intrusion (Fig. 1A). During the February-March interval, only one station in the equatorial zone had production greater than 0.25 g m^{-2} day^{-1}, while most stations had productivity values an order of magnitude lower than normal (Fig. 1C).

Primary production values in the Peruvian coastal region were as high as normal ones in February and March 1975 (Fig. 1, A and C), but the productivity was confined to a narrower zone than in the non–El Niño years for which we have data. In February and March 1975, the contour representing 0.5 g m^{-2} day^{-1} was no farther than 250 km from the coast, while the same contour extended 500 km from the coast in 1968 (*6*). In 1966, all the productivity measurements within 250 km of the coast were greater than 1.0 g m^{-2} day^{-1}.

Equatorial primary production returned to near-normal levels during April and May 1975, as seen in Fig. 1B. The 0.5 g m^{-2} day^{-1} contour extended 400 km off the coast, and primary production increased two- to fivefold across the equatorial region.

Results from previous oceanographic expeditions to the southeastern tropical Pacific have established the pattern of primary production in non–El Niño years. Figure 1C shows contours of primary production from cruises in 1966 and 1968 (*7*). Note the wide band of higher production along the equator west of the Galápagos Islands. Owen and Zeitzschel (*6*) reported similar results from a survey of a larger region of the eastern tropical Pacific. They found that integrated production values along the equatorial zone ranged from 0.3 to 0.5 g m^{-2} day^{-1} in February and March 1968 [see figure 1 in (*6*)] west of the Galápagos.

It is not clear what factors were limiting primary production in the offshore, nonequatorial region south of the Galápagos and west of Peru during the 1975 El Niño conditions. Nutrients were present in excess in the surface waters (NO_3^- greater than 5.0 μmole/kg), yet the small standing stock of phytoplankton showed