

as witnessed in the monumental *Rosa Ursina*. He chose the name *Ursine Rose* to honor the book's patron, Paolo Gordano, Duke of Orsini, whose family insigne featured a bear (from which the name Orsini derived) and a wild rose, which, as an elegant medallion, is generously sprinkled through the illustrations in the book. The subtitle ("Or the sun dotted by the surprising phenomenon of its faculae and spots, by the German Swabian Christopher Scheiner, of the Society of Jesus") (Fig. 1) explicitly describes the content of the volume and reveals Scheiner's particular interest in the photospheric faculae. The book includes scattered sunspot observations that were made during the full 18 years of the author's interest in the solar surface. In it he determined the rotation period of the sun as between 26 and 27 days (an average over latitude) and found the inclination angle of the solar axis to be between 6° and 8°—as compared to the accepted, modern value of 7°15'. He also noted that higher-latitude spots rotated more slowly.

11. J. M. Beckers, *Astrophys. J.*, in press.
12. J. A. Eddy, in *The Solar Output and Its Variation*, O. R. White, Ed. (Univ. of Colorado Press, Boulder, 1977).
13. Original copies of the *Rosa Ursina* used in this study are in the Houghton Library of Harvard University and in the George E. Hale collection at the Hale Observatories, Pasadena, Calif. We are indebted to O. Gingerich for assistance in securing photographic copies of the Scheiner data, and to J. Beckers, R. Noyes, and O. R. White for helpful comments. The work of J.A.E. was supported by National Aeronautics and Space Administration contract NAS5-3950, the Environmental Research Laboratories of the National Oceanic and Atmospheric Administration, and the Langley-Abbott program of the Smithsonian Astrophysical Observatory. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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Sedimentary Polycyclic Aromatic Hydrocarbons: The Historical Record

Abstract. *Polycyclic aromatic hydrocarbons in three sections of a dated sediment core from Buzzards Bay, Massachusetts, have been analyzed by gas chromatographic mass spectrometry. This historical information suggests that sedimentary polycyclic aromatic hydrocarbons, at least at this location, result primarily from the anthropogenic combustion of fossil fuels.*

The presence of complex mixtures of polycyclic aromatic hydrocarbons (PAH) and their alkyl homologs in soils and sediments from the New England region has been well established (1-3). In all cases, the qualitative distributions of the unsubstituted PAH and the relative abundances of the alkyl homologs within a given PAH series have been very similar (4). Before the geochemical significance of these findings can be determined, however, a detailed understanding of the sources of PAH in these recent sediments must be developed.

At present, there is a consensus that these PAH mixtures are not produced biologically (3, 5) but rather that they result from the deposition of combustion-generated airborne particulate matter (3, 4, 6). There is, however, no consensus on whether these particulates are natural (2, 3) or anthropogenic (4, 6). This is an

important question. If the source were natural (forest fires, for example), man would have been exposed, for much of his history, to a burden of carcinogenic PAH to which he may well have developed a certain tolerance. On the other hand, if the source were man's activities, this tolerance probably would not exist since the level of environmental PAH would have been continuously increasing.

Semiquantitative measurements of the alkyl homolog distributions tend to suggest that sedimentary PAH could not result from anthropogenic airborne particulates (3). These data, however, are not conclusive because mechanisms which could modify the homolog distribution after the particulates have been deposited have not yet been taken into account (4, 6).

Other experimental information per-

taining to the source of these PAH has been the recent finding of complex mixtures of azaarenes in sediments from Buzzards Bay (7). These investigators assume that azaarenes are produced by the incomplete combustion of plant material, and thus by inference that the PAH in these sediments are also produced by the combustion of plant material such as in a forest fire.

Still another experimental approach is to search for a historical record of PAH in the environment. Man's inputs of DDT (8), lead (9), and trace metals (10) have been recorded in the recent sedimentary record. Obviously, man's patterns of utilization of fossil fuels have also changed considerably over time, and, if the anthropogenic combustion sources of PAH are substantially larger than natural sources, this change should be reflected in the sedimentary record. We report here the analysis of PAH in three sections of a dated sediment core in an attempt to establish a historical record of PAH production and deposition.

The core sample was obtained from Buzzards Bay, Massachusetts (station P, 41°29.0'N, 70°52.5'W, 17-m depth), from an area where measurements of ²¹⁰Pb (11), ¹³⁷Cs, ²³⁹Pu, and ²⁴⁰Pu (12) provide a means of estimating the sedimentation rate. [An earlier study (13) of alkanes, cycloalkanes, and phenanthrenes in another sediment core from this location showed a trend of decreasing concentrations between the upper 2 cm and 54 to 58 cm, which pointed toward fossil fuel combustion as the principal source of hydrocarbons in these surface sediments.] The core was collected in August 1975 with a sphincter corer 21 cm in diameter and 1 m long (14). Three sections of the core were used for this study: the top 4 cm (1970), 20 to 24 cm (1900), and 38 to 42 cm (1850). There was no sulfide present in the top 8 cm. An oxic, bioturbation zone of about 4 cm was indicated by the ²¹⁰Pb depth

Table 1. Concentrations of PAH (dry weight basis) and distributions of alkyl homologs in three sections of a sediment core taken from Buzzards Bay. The estimated errors in the PAH concentrations are ± 20 percent. The relative abundances of PAH are expressed as a percentage of the total unsubstituted PAH (values in parentheses). The bioturbation zone is 4 cm (11); thus the error in the dates is ± 15 years.

Year of deposition	Depth (cm)	PAH concentration (ppb) and relative abundance					Homolog distribution		
		Phenanthrene	Fluoranthene	Pyrene	C ₁₈ H ₁₂ *	C ₂₀ H ₁₂ †	Total‡	Slope§	Standard deviation
1970	0-4	53 (7)	130 (16)	120 (15)	160 (20)	340 (43)	800	-1500	± 500
1900	20-24	42 (5)	130 (15)	120 (14)	200 (23)	380 (44)	870	-1400	± 600
1850	38-42	8 (13)	11 (17)	7 (11)	12 (19)	26 (41)	64	-1800	± 300

*Compounds of the formula C₁₈H₁₂, including chrysene, benzantracenes, and triphenylene. †Compounds of the formula C₂₀H₁₂, including benzofluoranthenes and benzopyrenes. ‡Total unsubstituted PAH concentration, dry weight basis. §Slope of a least-squares line fitted to the average abundance (composed over the C₁₆H₁₀, C₁₈H₁₂, and C₂₀H₁₂ species) of the various alkyl homologs (normalized to 10⁴ for the unsubstituted species) versus the number of alkyl carbon atoms. For details on this type of data presentation, see (1-4). ||Standard deviation of the slope of the homolog distribution.

profile and benthic ecology studies (11, 15).

The wet sediments were Soxhlet-extracted with methanol for 24 hours and then with methanol-benzene (2 : 3) for another 24 hours. The PAH were isolated from these extracts by partitioning with cyclohexane-nitromethane followed by silicic acid chromatography (16) and subjected to gas chromatographic mass spectrometry (17). For quantitation we used selected ion monitoring, with a dwell time of 250 msec. By selecting the molecular ions of some 15 to 20 PAH and comparing the integrated response with standards, we were able to measure subnanogram quantities of PAH.

We obtained the alkyl homolog distributions by scanning the mass-to-charge ratio (m/e) from 150 to 350 in 4 seconds while distilling the sample mixture from the direct introduction probe. The areas of the individual mass chromatograms corresponding to the molecular ions of the alkyl-substituted PAH were integrated and normalized relative to the unsubstituted species.

The absolute and relative concentrations of the unsubstituted PAH species and the relative abundances of the alkyl homologs in the three sections from this

core are given in Table 1. Two outstanding features of these data can be noted:

1) Over the last 125 years, the PAH distribution has remained qualitatively constant. For example, pyrene has comprised 11 to 15 percent of the total unsubstituted PAH regardless of the age of the core, and the distributions of alkyl homologs are virtually identical (within experimental error) for all three sections.

2) The absolute concentrations of PAH in the sections for 1970 and 1900 are similar but greatly exceed those in the section for 1850. These data suggest that the nature of the source has been constant since 1850 (giving similar qualitative PAH distributions) but that the intensity of this source increased considerably between 1850 and 1900 and has not changed much since (18).

What could this source be? All evidence points to combustion. Since this conclusion has already been presented (2-4, 6, 7), we will simply say that the PAH data in this Buzzards Bay core are also consistent with a combustion source. Is the combustion source natural or anthropogenic? What fuel was burned?

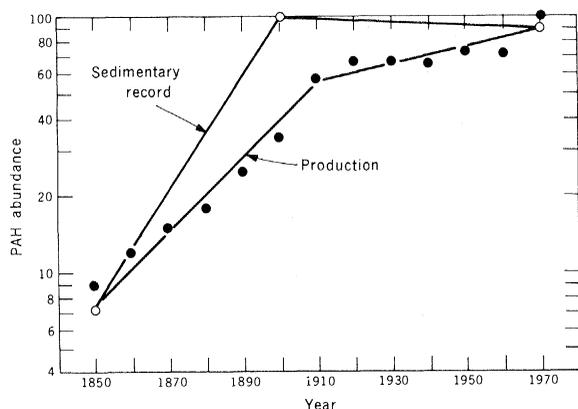


Fig. 1. Total relative unsubstituted PAH abundance observed in three dated sections of a sediment core from Buzzards Bay, Massachusetts (open circles), and calculated PAH production (closed circles) as a function of time.

Table 2. Energy produced from various fuels (19) and associated PAH production as a function of year.

Year	Energy (in 10^{15} Btu)					PAH		
	Coal	Wood	Oil	Hydro-electric	Gas	Nuclear	Arbitrary	Normalized
1850	0.22	2.1					2.3	9
1860	0.52	2.7					3.2	12
1870	1.0	2.9					3.9	15
1880	2.0	2.8					4.8	18
1890	4.0	2.5	0.15		0.25		6.6	25
1900	7.0	2.0	0.25	0.25	0.25		9.1	34
1910	13	1.8	1.0	0.58	0.58		15.2	57
1920	15	1.6	2.7	0.78	0.78		17.7	67
1930	14	1.4	5.8	0.76	1.9		17.7	67
1940	13	1.3	7.8	0.90	2.7		17.4	66
1950	13	1.2	13	1.6	6.0		19.4	73
1960	10	1.0	20	1.7	13		19.0	72
1970	14	0.84	29	2.6	23	0.21	26.4	100

First, it seems reasonable to dismiss natural sources such as forest fires. These sources should have been roughly constant in intensity over the period from 1850 to 1970. Thus, such sources would not account for the sedimentary increase in PAH concentration observed between 1850 and 1900.

Anthropogenic combustion, of course, has increased continuously over this period, but it has not leveled off since 1900 as has the sedimentary PAH concentration. The pattern of fuel usage has, however, changed considerably over this time period (19). Table 2 gives the total amount of energy obtained from various fuels for the period from 1850 to 1970. The annual relative release of PAH resulting from this energy production is also given in Table 2. We calculated these PAH abundances from the fuel usage by applying a conversion factor specific to each fuel. Energy production based on the use of nuclear fuel, hydroelectric power, and natural gas is assumed to produce no PAH (20); coal and wood are assumed to produce equal amounts of PAH per Btu (1 Btu = 1055 joules). Oil, unlike coal, has been used mostly as a transportation fuel, with about 60 percent of the oil used in this sector of energy consumption (19). We have assumed that transportation sources produce negligible PAH relative to stationary sources (20), and thus oil would produce 40 percent of the PAH produced by coal and wood when considered on a total Btu basis (21). Let us consider the year 1930 as an example. We get PAH production, in arbitrary units, by adding 14 (coal), 1.4 (wood), and 40 percent of 5.8 (oil) to get 17.7 units, which is then normalized against the 1970 value. These values have been plotted in Fig. 1 along with the relative total unsubstituted PAH concentrations.

It is clear from Fig. 1 that PAH production increased at a steady rate (about 3 percent per year) until 1910 when it leveled off. This production information is in agreement with the sedimentary PAH record. The agreement between these two trends is particularly gratifying in view of the fact that the sedimentary data have an uncertainty of ± 15 years in the dates of deposition and ± 20 percent in the PAH abundance values and in view of the simplicity of the model that was used to calculate the historical PAH production values.

From these data on depth distribution, we conclude that the combustion of fossil fuels has been the primary source of PAH in this Buzzards Bay depositional environment. There may well be a low-

level background of PAH from natural sources, but it seems clear that the major source of PAH in the present surface sediment at this location is anthropogenic combustion. A more detailed investigation of the depth distribution of PAH in sediments from a variety of depositional environments, near and remote from urban areas, is needed to confirm this conclusion. For example, studies of PAH in anoxic, rapidly depositing, near-shore, marine or lake sediments would be ideal because these locations would not be subjected to the uncertainties in reconstructing historical records which are introduced into sediments with bioturbated surface layers (22).

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- The gas chromatography was carried out on a stainless steel column 183 by 0.32 cm, with 3 percent OV-17. The temperature was programmed from 70° to 300°C at 8°C per minute. Gas chromatographic mass spectrometry was carried out on a quadrupole mass spectrometer (Hewlett-Packard 5982A) with a data system (Hewlett-Packard 5933A).
- This depth distribution cannot be the result of biodegradation of PAH in the deeper section. This zone was highly anoxic, and PAH are preserved under such conditions [T. B. Shelton and J. V. Hunter, *J. Water Pollut. Control Fed.* **47**, 2256 (1975)]. The PAH distribution cannot result from large changes in the sedimentation rate because this rate has been constant over the period from 1850 to 1970; this conclusion is based on ²¹⁰Pb data (1) and on the lack of visually noticeable discontinuities in the core.

19. H. C. Hottel and J. B. Howard, *New Energy Technology* (MIT Press, Cambridge, Mass., 1971), p. 4.

20. *Particulate Polycyclic Organic Matter* (National Academy of Sciences, Washington, D.C., 1972), pp. 13-35.

21. Coal, wood, and oil produce similar qualitative distributions of PAH, and these distributions are similar to those seen in this sediment. See (16) for detailed analyses of the PAH produced by these fuels.

22. K. K. Bertine and E. D. Goldberg, *Environ. Sci.*

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Pulmonary Metabolism During Diving: Conditioning Blood for the Brain

Abstract. During experimental diving by the awake Weddell seal, blood glucose concentration falls consistently. A large fraction of the glucose consumed from the central circulating blood appears as lactate. During diving, the lung utilizes blood lactate in preference to blood glucose as a source of both carbon and energy, and it is able to release glucose into pulmonary venous blood to supplement the supply available for brain metabolism.

Although the role of the lung in gas exchange was defined more than 100 years ago by Magnus (1), many of its metabolic functions in the living organism remain obscure in part because arteriovenous (AV) metabolic gradients across the lung are diluted by the large pulmonary blood flow (2). However, we repeatedly measured AV metabolic differences across the lungs of a diving mammal. Although the lung ceases to be a significant gas-exchange organ during diving, it remains perfused by the entire cardiac output, while the 70 to 90 percent fall in cardiac output during diving (3) should increase the measurable pulmonary AV metabolite concentration differences. In our

studies of experimental diving by the awake Antarctic Weddell seal (*Leptonychotes weddelli*), a species that can dive for more than an hour (4), we observed a decrease in glucose concentrations in systemic and pulmonary artery blood and an increase in lactate concentrations; at the same time, pulmonary AV differences of blood lactate and glucose were reciprocal. As all the enzymes necessary for lactate use and for glucose formation were present in fresh seal lung tissue, our study suggests that lactate is used by the lungs as a preferred substrate and that the lungs may supplement the circulating blood supply of glucose for the brain.

Weddell seals were captured at Turtle Rock on the Ross Island fast ice. Adult seals weighing 450 to 500 kg were herded into a large wooden box and hauled on a sled to the McMurdo Eklund Biological Laboratory. Here, the seal was tranquilized (intramuscular ketamine hydrochloride, 2 mg per kilogram of body weight); the box was positioned with a forklift, and the animal was transferred to a mobile operating table. During surgery (5), anesthesia was maintained by the spontaneous breathing of halothane in oxygen.

A large drop in glucose concentration was consistently seen during short- and long-term dives (Table 1) in samples of whole blood taken either from the pulmonary artery (mixed venous) or the aorta (6, 7). We believe that a notable fraction of the glucose used was being fermented for two reasons. (i) If all the glucose used were being fully oxidized metabolic rates would be far higher than expected (8) and P_{O_2} would drop further than observed (Fig. 1). (ii) Even in dives

Table 1. Relationship between the decrease in glucose concentration in systemic arterial blood and the rise in lactate concentration. Whenever two dives were studied, we allowed the seal to recover completely from the first before beginning the second. In all cases, from half to all of the glucose utilized appeared as blood lactate. As the seals were awake and varied in condition and degree of stress, no close correlation between diving time and glucose utilization was expected or evident.

Seal	Diving length (min)	Change in glucose concentration (μ mole/ml)	Change in lactate concentration (μ mole/ml)
1	5	-0.6	+0.5
2			
Dive 1	10	-1.5	+1.3
Dive 2	22	-1.0	+1.7
3			
Dive 1	20	-1.0	+1.1
Dive 2	25	-1.5	+1.5
4			
Dive 1	26	-0.9	+0.8
Dive 2	46	-1.0	+2.5