RADIOCARBON "DATING" OF INDIVIDUAL CHEMICAL COMPOUNDS IN ATMOSPHERIC AEROSOL: FIRST RESULTS COMPARING DIRECT ISOTOPIC AND MULTIVARIATE STATISTICAL APPORTIONMENT OF SPECIFIC POLYCYCLIC AROMATIC HYDROCARBONS

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The ability to measure tiny amounts of radiocarbon (^{14}C) has revolutionized our ability to apportion fossil and biogenic sources of trace carbonaceous gases and aerosols. Because of the impacts of these species on visibility, human health, and climate, accurate assessment of anthropogenic and natural sources is mandatory both for understanding the atmospheric carbon system, and for making informed decisions about that portion which may be subject to control. The chemical complexity of carbonaceous aerosol, however, presents a challenge in the interpretation of average isotopic composition. Therefore, it has long been interesting to consider ways to "date" special classes of compounds, or better still, individual compounds of particular concern. One such class comprises the polycyclic aromatic hydrocarbons (PAH), produced at trace levels (ppm) in combustion processes, such as biomass burning. The PAH hold special interest because of compound-specific genotoxicity and because of the potential for individual PAH or abundance patterns of PAH to serve a "molecular markers" for ambient aerosol sources. Prior to the work reported here, such inferences relied on indirect, multivariate statistical techniques.

The new work demonstrated, for the first time, the ability to measure ^{14}C in individual, trace organic compounds in atmospheric aerosol. It utilized a special, well characterized sample collected in Washington, D.C.: "urban dust" Standard Reference Material (SRM 1649). Following extraction, individual PAH were isolated using a two-stage process involving semi-preparative liquid chromatography and preparative capillary gas chromatography, which cycles the sample stream hundreds of times through a series of traps. This process generated "datable" quantities of selected PAH which were subsequently converted to targets for ^{14}C accelerator mass spectrometry, performed at Lawrence Livermore National Laboratory. Results showed considerable isotopic heterogeneity reflecting varying source contributions to different chemical fractions. The polar organic fraction, for example, had a significant biogenic component (60% fossil), whereas the aliphatic portion was almost totally derived from fossil sources (98% fossil). Among the PAH compounds dated, one—benzo(*ghi*)perylene—held special interest because previous multivariate statistical analysis of urban aerosol indicated that it might be a useful tracer for soot generated by motor vehicles. Preliminary analysis of the ^{14}C data for this compound (87% fossil carbon) generally supported the statistical result.

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RELEASE OF SEQUESTERED ^{14}C DEPLETED CO_2 DURING THE GROWING SEASON NEAR THE ARCTIC CIRCLE: A REGIONAL ^{14}C EFFECT

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Previously, we measured $\Delta^{14}C$ in annual tree rings of white spruce (AD 1870–1885) from the Grand View site, Mackenzie River area of the Northwest Territory of Canada near the Arctic Circle (67°N, 130°W). We found no anomalous 11-yr ^{14}C cycle as previously reported. However, we found a 2.6

± 0.9‰ (1σ) depression of $\Delta^{14}C$ relative to the Olympic Peninsula. We find a 3.2‰ average depression of $\Delta^{14}C$ for single-year Douglas fir samples from the Olympic Peninsula relative to Douglas fir from the Santa Catalina Mountains near Tucson (32°26′N, 110°47′W; elev. 2740 m). This implies a *ca.* 5.8‰ average anomaly between the Tucson mountains and Grand View site areas. Expressed in years, this would result in a *ca.* 48-yr discrepancy in ages from the two sites.

We ascribed the relative suppression of $\Delta^{14}C$ near the Arctic Circle to the release of ^{14}C depleted CO_2 as thawing occurs during the May–August growing season. This is similar to the release of radon that occurs during spring thaws resulting in the tagging of air masses with anomalous amounts of radon.

In order to further study this regional effect, we extended our measurements back to AD 1861. The measured depression was a little greater than previously measured, 3.1 ± 1‰ (1σ) rather than 2.6 ± 0.9‰ (1σ), primarily resulting from an anomalous warming from AD 1867–1869 determined by dendroclimatology involving tree-ring density. The inverse correlation between $\Delta^{14}C$ and temperature is r = 0.63, implying that *ca.* 40% of the relationship can be explained by increased thawing during warmer growing seasons. If this is correct, measurement of $\Delta^{14}C$ in annual tree rings from Arctic regions may provide an additional paleoclimate technique.

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SUPERNOVA: PRIME PROBLEM OF PALEOASTROPHYSICS

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Galileo constructed his first telescope in 1609. Prior to that, astronomers had been limited to naked-eye observations of light reaching Earth from the cosmos. Instruments have evolved to record virtually the entire electromagnetic spectrum plus protons, electrons and other particles arriving at Earth from objects distant in time and space. However, until recently the instrumental record has been limited to radiation arriving at Earth since Galileo. Cosmogenic isotope research expands the astrophysical record into the distant past limited only by the half-lives of the cosmogenic isotopes.

Cosmogenic isotopes are produced by cosmic rays and cosmic rays are of primarily galactic origin, generated by supernova explosions. If a supernova explosion were to occur near enough to the Earth, it would be observed as an increase in the cosmic ray flux, leaving a record in increased concentration of cosmogenic isotopes in natural archives. Hard γ-rays would arrive after the visible light and produce ^{14}C. The 8‰ ^{14}C pulse recorded in tree rings in the third year after light arrived from SN 1006 AD probably signals the arrival of the hard γ-rays from that event. If so, the total γ-ray energy from SN 1006 AD is ~10^{50} ergs. No measurable increase in ^{14}C has been observed for the Tycho and Kepler supernovae and would not be expected because of their greater distance from Earth.

The ^{10}Be increase in the Vostok ice core at *ca.* 35 kyr is a candidate for arrival of a supernova shock wave at Earth. An event at approximately the same time has been observed in the GISP ice cores and in ocean sediment cores from the Gulf of California and Adriatic Sea. We believe the supernova hypothesis is correct because the increase in production rate is too great to be explained by zero geomagnetic field intensity. Geomagnetic field lines are almost vertical at Vostok and a Maunder type