

## EVOLUTION AND MULTIDISCIPLINARY FRONTIERS OF $^{14}\text{C}$ AEROSOL SCIENCE<sup>1</sup>

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**ABSTRACT.** A review is given of some critical events in the development of radiocarbon aerosol science, and the profound influence of radiocarbon accelerator mass spectrometry (AMS) on its current applications and future prospects. The birth of this discipline occurred shortly after the initial development of  $^{14}\text{C}$  dating. Unlike dating, which is founded on the continual decay of  $^{14}\text{C}$  and the resulting full range of  $^{14}\text{C}/^{12}\text{C}$  ratios in once-living matter,  $^{14}\text{C}$  applications to atmospheric aerosol research relate primarily to the determination of mixing ratios of fossil and biomass components. Such determinations have come to have major importance in work ranging from the resolution of woodburning and motor vehicle components of urban particulate pollution, to the apportionment of radiation-forcing (black) particulate carbon from natural wildfires and anthropogenic regional plumes. The development of this area has paralleled that of AMS itself, with the one or the other alternately serving as the driving force, in a sort of counterpoint. The remarkable million-fold improvement in sensitivity made possible by AMS has become critical in meeting rapidly emerging societal concerns with the origins and effects of individual carbonaceous species on health and climate.

### INTRODUCTION

Shortly after Libby's initial work on radiocarbon dating, Jim Arnold, and later Hans Suess, had the idea to apply natural  $^{14}\text{C}$  to the apportionment of fossil and biomass combustion aerosol ("soot") which was afflicting several US cities. The first such experiment by Clayton, Arnold, and Patty (Clayton et al. 1955) took place just seven years after Libby's basic experiments that led to  $^{14}\text{C}$  dating. The stimulus was the need to determine the fossil carbon impact on serious levels of particulate urban pollution, equivalent to  $35 \mu\text{g C m}^{-3}$  in Pasadena, California at the time. The sampling efforts were heroic: nearly a week of continuous sampling was required to filter about a quarter of a million cubic meters of air, collecting approximately 42 g of aerosol to provide 8.5 g of carbon for measurement by liquid scintillation counting. The results foreshadowed what has been seen in many subsequent urban studies: the aerosol carbon was primarily, but not exclusively, from fossil sources (fraction of modern,  $f_M = 0.26 \pm 0.02$ ). (Note that all uncertainties are combined standard uncertainties, unless otherwise indicated.)

Work performed five years later by Lodge, Bien, and Suess (Lodge et al. 1960) had a similar grand scale: 3.8 g aerosol carbon were collected and decay counted with acetylene gas proportional counting. This research went beyond the earlier study, in that individual chemical fractions were measured; it was the first example of aerosol  $^{14}\text{C}$  speciation. Results were similar, however, showing that the urban carbonaceous particles were largely fossil in origin. More recent work in US cities has given some insight into current sources of the non-fossil (biomass carbon) component, ascribing a significant portion to commercial "meat cooking" (Hildemann et al. 1994) or, during winter, to residential wood combustion (Cooper et al. 1981).

Progress in the ensuing years has been enormous, primarily for 2 reasons: 1) gains in sensitivity, first with the development of miniature gas proportional counters for  $^{14}\text{C}$  in aerosol carbon at the  $\mu\text{g}$  level, followed by accelerator mass spectrometry (AMS) with an intrinsic mg level capability, and 2) increased concern about the health consequences of carbonaceous aerosols, their impact on visibility, and more recently, the potential effects on climate from the radiation forcing behavior of "black carbon" or soot arising from fossil and biomass fuel combustion. For all of these reasons it becomes

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important to identify sources and apportion aerosol carbon, even at the molecular level (individual compounds). This gives rise to a new dimension in  $^{14}\text{C}$  atmospheric and geochemistry, where we seek to determine the spatial and temporal distribution of  $^{14}\text{C}$  in individual compounds and chemical fractions— i.e.  $^{14}\text{C}$  speciation. This lay, of course, at one of the frontiers of modern AMS.

### EARLY “LOW-LEVEL” ATMOSPHERIC STUDIES

After a lapse of about two decades,  $^{14}\text{C}$  measurements were applied anew to atmospheric aerosol research, this time in the US cities of Los Angeles and Salt Lake City, and in the Utah desert. There had been a dramatic reduction in sample size, however. In this case only 5–10 mg of carbon was required, as the measurement was performed with miniature (5 mL) high purity quartz gas proportional counters. (See Figure 2 for low-level counting [*llc*] information, and Currie et al. [1983, 1998a] for characteristics of the miniature gas counting system. Note that a very recent change to “active” anticoincidence shielding in our laboratory has reduced the background by about a factor of 3 [G Klouda, personal communication 1998], such that the limiting factor has become Poisson counting statistics.) The *thousand-fold gain* in sensitivity marked the turning point for  $^{14}\text{C}$  aerosol research, in that daily and even diurnal sampling of fine particle (respirable) carbonaceous aerosol became practicable. Results for the urban samples were similar to those of Pasadena (approximately 60–70% fossil carbon), but the desert aerosol was essentially “living” (only 10% fossil carbon). Interestingly, these data were reported at the very first AMS conference, AMS-1, in Rochester, New York (Currie 1978).

During the next decade important urban results were obtained with both low-level gas counting of 5–10 mg (C) samples and AMS on 0.1–2. mg (C) samples. Noteworthy examples of the former were the first multivariate time series field studies, which took place in Oregon (Cooper et al. 1981) and in Norway (Ramdahl et al. 1984), where simultaneous data on  $^{14}\text{C}$  and chemical species were obtained on a series of fine particle (<2.5  $\mu\text{m}$ ) aerosol samples for the purpose of apportioning multiple sources of combustion aerosol. The multivariate time series character of the data provided the key to further dissecting (discriminating, apportioning) the fossil and biomass source contributions into individual source components, such as motor vehicle emissions, fuel oil combustion, and field (grass) and slash (timber) burning, through such techniques as chemical mass balance and factor analysis (Currie 1992).

To illustrate, the latter study took place in the small town of Elverum, Norway (approximately 10,000 inhabitants), where average wintertime aerosol carbon and polycyclic aromatic hydrocarbon (PAH) pollution levels of 20  $\mu\text{g m}^{-3}$  and 158  $\text{ng m}^{-3}$ , respectively, were comparable to those of Oslo (approximately 400,000 inhabitants), presumably due in large part to the use of wood fuel as a secondary heat source. This was the first study to combine time series data for  $^{14}\text{C}$ , chemical elements, PAH, mutagenicity, and meteorology. It showed that, on average, 65% of the aerosol carbon came from woodburning. This work led also to the development of a multivariate isotopic-chemical “urban signature” allowing the discrimination of long-range transport aerosol from the urban background aerosol. This is shown in Figure 1 (see Color Plate 1), which represents an optimal (principal component) two-dimensional projection for the subset of samples identified as long range transport [sample-10] or as belonging to the urban cluster (Currie 1992). It is seen that the two-dimensional representation gives a reasonably complete view of the entire seven-dimensional variable space, since it preserves most of the original information (95% of the variance). The multivariate (approximately bivariate) urban signature is indicated by the elongated, dashed ellipse. As shown by the Pb and  $^{14}\text{C}$  projections on the principal component biplot, the signature is approximately bi-polar, reflecting the varying mix of motor vehicle (Pb) and woodburning ( $^{14}\text{C}$ ) contributions to the urban

aerosol. The pattern for the long range transport aerosol sample [sample-10], having tracers found in coal fly ash, is almost totally resolved from that of the urban aerosol samples. Note that the multivariate signatures represent a powerful generalization of the “element ratio” technique that has been applied to identify source regions in cases of long range pollution (Rahn and McCaffrey 1980). It is expected that the multivariate signature developed in this work will serve as a prototype for future investigations of regional and global aerosol where such signatures may be used for the unique identification of local and regional aerosol sources. A critical example relates to the identification of source regions for remote aerosol, such as the “black carbon” transported to polar regions, as discussed in the penultimate section of this article.

The most extensive, early <sup>14</sup>C aerosol study utilizing AMS was the *Integrated Air Cancer Project* (IACP), organized by the US Environmental Protection Agency (EPA) (Lewtas et al. 1988). This was a multi-city investigation of aerosol mutagenic activity as related to motor vehicle and residential woodburning sources. Notable AMS related outcomes included one of the first examples of <sup>14</sup>C speciation in urban ambient aerosol (<sup>14</sup>C in elemental carbon [EC] and polycyclic aromatic hydrocarbon [PAH] chemical fractions), and the impact of the bivariate (<sup>12</sup>C, <sup>14</sup>C) chemical processing blank on the validity of some of the aerosol data. (See the discussion in the following section.) The IACP involved diurnal sampling (07.00–19.00, 19.00–07.00) during approximately two months in the winter in Raleigh, North Carolina and Albuquerque, New Mexico (1984–1985), Boise, Idaho (1985–1986), and Roanoke, Virginia (1986–1987). Typical sample sizes for AMS were 300–500 μg carbon. For a subset of samples <sup>14</sup>C speciation was applied, showing the elemental carbon fraction to be generally more fossil in character (41%) than the total extracted organic matter (18%) (midranges, Albuquerque; Klouda et al. 1988). The combination of <sup>14</sup>C and mutagenicity testing on the extracted organic matter showed that, on average, the concentration of carbonaceous aerosol from woodburning (16 μg C m<sup>-3</sup>) was approximately twice that from motor vehicles, but that the mutagenic potency of the latter (3.4 rev mg<sup>-1</sup> aerosol) was greater by about a factor of 4 (Currie et al. 1989, and references therein). Using PM10 particulate matter samples collected in the Boise phase of the IACP, Benner and coworkers demonstrated the ability of dimethylphenanthrene isomers to distinguish residential wood combustion from mobile source emissions; excellent correlation was obtained with <sup>14</sup>C data derived from the same field samples (Benner et al. 1995).

#### THE TRANSITION FROM MG-LEVEL BETA COUNTING (AND AMS) TO μg-LEVEL AMS

A comparative study of the fundamental limiting factors for AMS and low-level β counting for environmental <sup>14</sup>C research showed that: 1) for AMS, the isotopic-chemical blank constitutes the most important limitation, outweighing the machine background by 1 to 2 orders of magnitude, but 2) for β counting, the situation is reversed, with the typical blank being quite negligible compared to the counter background (Currie et al. 1989). (See Figure 2, where limits are expressed in terms of modern carbon equivalent mass.) The study showed also that the nominal AMS sample size of 1 mg C was 100–1000 times larger than the blank, so that the prospect of “μg AMS” for environmental <sup>14</sup>C was quite real, *provided that* the overall blank could be brought under control.

This matter, control of the isotopic-chemical blank for aerosol <sup>14</sup>C research at the microgram level, has been one of the foci of the Atmospheric Chemistry Group at NIST, in cooperation with colleagues at the AMS facilities at the University of Arizona (NSF-Arizona AMS Facility), the Woods Hole Oceanographic Institution (National Ocean Sciences AMS Facility), and the University of Vienna (Vienna Environmental Research Accelerator). The potential benefit of “μg AMS” is enormous, because the resulting *additional* thousand-fold reduction in sample size is critical for expanding the frontiers of atmospheric aerosol research to the assay of <sup>14</sup>C in EC and individual organic

tracers and toxic compounds, such as certain of the PAH. The capability is vital for research on the regional transport and historical (ice core) record of fossil and biomass combustion aerosol in environmentally sensitive regions, such as the Arctic, where EC concentrations in snow/ice may be as little as  $1 \mu\text{g kg}^{-1}$ .

The inherent AMS capabilities and target preparation blanks resulting from NIST collaborative work with the previously mentioned AMS facilities have been reported at previous international AMS and  $^{14}\text{C}$  conferences based on  $^{14}\text{C}$  measurements using the NIST Fe-C “bead” type target (Verkouteren et al. 1987; Klinedinst et al. 1994; Weissenböck et al. 1998). Although it has been possible to constrain chemical blanks to approximately  $2 \mu\text{g}$  carbon or less, there have been difficulties with  $^{12}\text{C}^-$  ion current magnitude and stability when the total carbon content of the bead dropped below approximately  $10 \mu\text{g}$  carbon. This has been a special problem when vigorous chemical processing (e.g. for isolating elemental carbon) may have introduced trace levels of electronegative impurities. Other laboratories, utilizing “graphite” targets, have been generally successful in measuring samples containing less than  $100 \mu\text{g}$  carbon, but  $20 \mu\text{g}$  is the typical lower limit (Vogel et al. 1987, 1989; Pearson et al. 1998). More recent efforts to overcome the  $10 \mu\text{g}$  barrier using “dilution AMS” with on-line purity monitoring appear to be successful for pre-combustion samples containing as little as  $1\text{--}2 \mu\text{g}$  carbon (Currie et al. 2000a).

## Aerosol $^{14}\text{C}$ : the transition from *llc* to AMS

(limiting factors, micrograms modern carbon)

### Miniature gas counters [*llc*]

Poisson limit: 2400 [1984 data]  
Background: 5000  
Blank: 40

### Accelerator Mass Spectrometry

Poisson limit: 1.0 [1998 data]  
Background 0.2  
Blank 2.0+

Bivariate blank: Integrated  
Air Cancer Project (AMS)

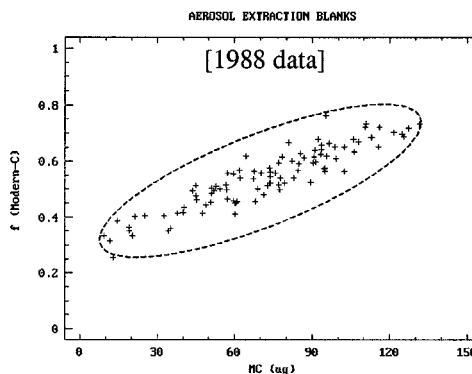


Figure 2 For aerosol research the minimum amount of modern carbon required for AMS measurement is about 3 orders of magnitude smaller than that needed for miniature counter decay counting (*llc*) (Currie et al. 1989). The switch in the fundamental limiting factor, from detector background to the isotopic-chemical blank, has a profound effect. Although a blank of approximately  $2 \mu\text{g}$  carbon can be achieved for the combustion-target preparation process, wide-ranging bivariate blanks may arise in aerosol sampling and sample preparation steps in a complicated field study, as shown in the plot. The points within the ellipse were generated for Monte Carlo error propagation, to simulate the actual distribution of blanks seen in one phase of the Integrated Air Cancer Project (Lewtas et al. 1988).

The isotopic-chemical blank for the *overall (aerosol) measurement process* is another matter. One must pay strict attention to the fossil and biomass carbon blanks introduced at each step, from aerosol sampling to chemical extraction and purification. The impact of this larger blank issue is indicated in the plot (inset) in Figure 2. This shows the covariation of  $f_M$  and carbon mass over a wide range for organic extraction blanks during one phase (Roanoke, Virginia) of the Integrated Air Cancer Project, where the typical blank and total sample carbon masses were approximately 70  $\mu\text{g}$  and 400  $\mu\text{g}$ , respectively. Although the processing blank was subsequently much improved, this large bivariate blank had an enormous impact on an entire set of Roanoke aerosol samples, especially with respect to the magnitude and nature of the final uncertainty bounds. Not only must the correlated behavior be taken into account in blank “error propagation”, but also the non-normality introduced by the non-linear blank correction function. This leads to poorly conditioned and asymmetric uncertainty intervals when the blank mass fraction becomes too large (Currie et al. 1994).

### DUAL ISOTOPIC CHARACTERIZATION: APPORTIONMENT AND FRACTIONATION ISSUES

An additional degree of source discrimination/apportionment capability for atmospheric aerosols is given when both  $^{13}\text{C}$  and  $^{14}\text{C}$  are utilized. The two isotope ratios that characterize the  $^{13}\text{C}$ - $^{14}\text{C}$  plane make possible the resolution of up to three sources or end members, as in Figure 3. If four or more end members are likely, the solution is indeterminate. For example, if  $\text{C}_4$  plants, such as sugar cane or tropical grasses, had also been possible sources, it would have been necessary to include a fourth biomass  $^{13}\text{C}$  value of about  $-10\text{‰}$  (Cachier 1989). For an illustration of the  $^{13}\text{C}$ - $^{14}\text{C}$  signatures of a broad range carbon isotopic reference materials, see Figure 16 in Currie (1992).

The particular example given in Figure 3 is that of the prototypical NIST Urban Particle Standard Reference Material (SRM 1649a) [U] that was originally collected in Washington, DC (1976–1977) to serve as an aerosol organic *chemical* standard. This material is becoming increasingly used, also, as a carbon isotopic reference material by atmospheric and marine scientists. Of special interest, with the advent of GC/AMS and other  $^{14}\text{C}$  speciation techniques, is the utilization of the SRM in research on the isotopic composition of individual compounds and classes of compounds (see also Figure 4 in Color Plate 1). A second SRM serves as one of the end member reference points. The point marked [D] in the plot indicates the  $^{13}\text{C}$ - $^{14}\text{C}$  composition of the diesel “soot” standard reference material, SRM 1650. (Note that the apportionment of “U” into pine, oak, and diesel end members is intended to illustrate the *principle* of dual isotopic source apportionment. It should not be taken literally for this specific material, for which there could be a host of fossil and biomass carbon sources in the Washington, DC urban area.)

A special issue related to Figure 3 is the isotopic and chemical fractionation that accompanies incomplete combustion. That is the reason for the comment about the extra  $^{13}\text{C}$  dispersion for the oak and pine end members. A report of a detailed laboratory combustion study of this phenomenon has recently appeared (Currie et al. 1999a). In contrast, isotopic fractionation associated with photosynthesis is enzyme catalyzed. For  $\text{C}_3$  plants (Calvin-Benson cycle), the first stable product following carboxylation with the enzyme ribulose-1,5-diphosphate carboxylase is a three-carbon compound; for  $\text{C}_4$  plants (Hatch-Slack cycle), the first stable product following carboxylation with the enzyme phosphoenol-pyruvate carboxylase is a four-carbon acid (Deines 1980).

Dual isotopic characterization of carbonaceous materials has recently taken on another role of practical, economic importance—namely the  $^{13}\text{C}$ - $^{14}\text{C}$  “fingerprinting” of industrial feedstocks and commercial products. A case in point is the authentication of a new industrial copolymer derived from a particular class of biomass feedstocks, where its compositional uniqueness is established by its loca-

**$^{13}\text{C}$ - $^{14}\text{C}$  Plane:** Apportionment of urban particle SRM 1649a [U] into assumed fossil [D, diesel soot SRM 1650] and biomass [pine, oak] end members

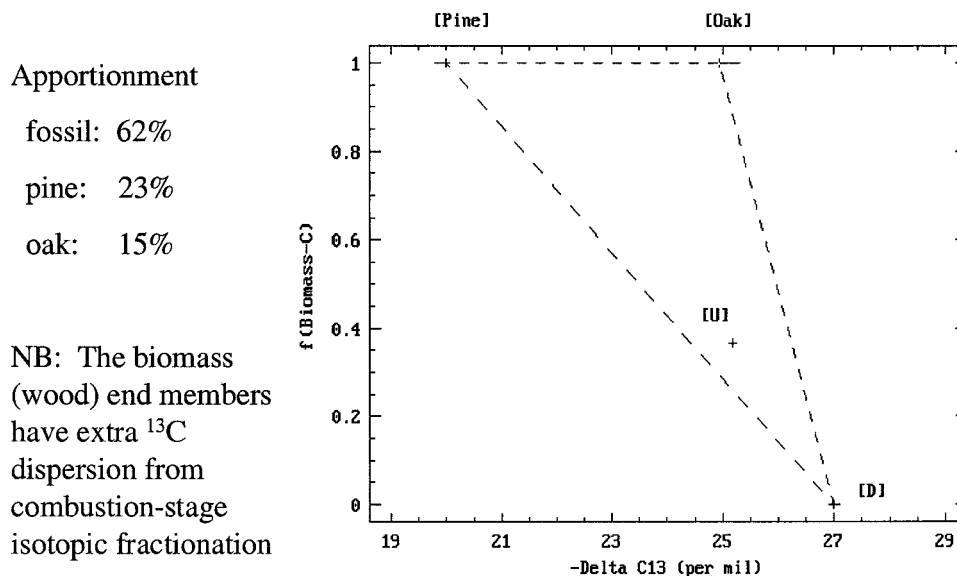


Figure 3 Plot showing the apportionment of the total carbon of urban dust standard reference material, SRM 1649a [U] into diesel [D], Pine and Oak end members. This figure contrasts with Figure 1 in that the goal here is end member apportionment rather than discrimination. The extra  $^{13}\text{C}$  dispersion noted for the pine and oak members yields an added uncertainty component to the apportionment estimates.

tion in the  $^{13}\text{C}$ - $^{14}\text{C}$  plane (Currie et al. 2000b). One consequence of such applications, having significant legal and economic ramifications, is the critical need for a range of carbon isotope reference materials that span the relevant two-dimensional “fingerprint” regions to provide defensible quality assurance for dual isotopic measurements of such industrial materials.

#### **$^{14}\text{C}$ SPECIATION; AND A SPECIAL ATMOSPHERIC REFERENCE MATERIAL**

Figure 4 shows two manifestations of the urban particle standard reference material (SRM 1649a) which was prepared specifically as a quality assurance material for the measurement of organic species in atmospheric aerosol samples, and which in recent years has been characterized for carbon isotopes in selected chemical fractions (NIST 2000). The SRM, *per se*, has been available for many years in bulk form (rear of photo). Within the last few years prototype aerosol filter samples (front of photo) have been prepared by redistributing the bulk SRM on 47 mm quartz and polycarbonate aerosol filters, to serve ultimately as carbonaceous particle filter reference samples (Klouda et al. 1996). This is especially important for aerosol carbon measurements that are based on optical and thermal-optical methods (Huntzicker et al. 1982).

It is the norm for ambient atmospheric aerosol to be isotopically heterogeneous—i.e. to have different  $^{14}\text{C}/^{12}\text{C}$  ratios for different chemical fractions. This reflects, of course, the differing chemical compositions of aerosol from fossil and biomass combustion (or emission) sources. The extent of

the <sup>14</sup>C isotopic diversity of SRM 1649a is shown in Figure 4 both for classes of organic species and for individual compounds. There, it is seen that the aliphatic components are derived almost entirely from fossil sources, presumably in this case (Washington, DC) motor vehicle emissions, whereas the polar organic fraction has a rather significant biomass contribution, such as might be derived from the incomplete combustion of wood or other biopolymers.

In keeping with the focus on fossil-biomass apportionment of carbonaceous aerosol, the data in Figure 4 are presented in terms of the (living) biomass carbon percentage composition. The fossil carbon composition is then complementary. If interest centers on a biomass component that represents a range of years, such as woodburning soot, adjustments may be made for its lifespan (Currie et al. 1989). The SRM *reference* values (not shown), however, are expressed as fraction (or percentage) of modern carbon,  $f_M$ . Two corrections are needed to convert from fraction of modern to fraction of (living) biomass: 1) correction for <sup>14</sup>C decay from sampling date to  $f_M$  reference date, and 2) correction for the time-dependent enhancement of biospheric <sup>14</sup>C due to atmospheric nuclear testing. The first correction is generally quite small, given the 5730-yr physical half-life; the second can be substantial, since the <sup>14</sup>C/<sup>12</sup>C ratio in atmospheric CO<sub>2</sub> approximately doubled during the mid-1960s. For SRM 1649a  $f_M$  values referenced to 1998, with an average sampling date of 1976.5, the correction is approximately  $(1.003/1.35)=0.743$ —i.e. the biomass carbon fraction (referenced to the date of sampling) equals 0.743 times  $f_M$  (referenced to 1998). For example, new data for total carbon <sup>14</sup>C in SRM 1649a (NIST 2000; Currie et al. 1999b), show an average  $f_M$  (1998) value of 0.509, so the corresponding biomass fraction is  $(0.509)(0.743)=0.378$ .<sup>2</sup>

Two matters deserve special noting: 1) “Elemental carbon” is one of the most important species in atmospheric aerosol science, yet it is one of the most problematic from the perspective of metrology; hence, the parenthetical result given in Figure 4. There are major interlaboratory comparisons (chemical and isotopic) underway at present in efforts to reach consensus on this matter (Currie et al. 1999b). The value quoted comes one such interlaboratory effort involving the University of California Irvine (C Masiello), NIST (L Currie et al.), and the University of Arizona (D Donahue et al.), for which  $f_M$  equals  $0.153 \pm 0.002$  (Poisson standard uncertainty), and 2) The results for fluoranthene and benzo(*ghi*)perylene are also very recent data, linked to baseline resolved GC/AMS (Currie et al. 1999a). A more extensive view of the latter is given in Figure 5, which gives a comparison of the multivariate statistical route for individual compound “dating” to direct, pure compound isolation for AMS <sup>14</sup>C measurement, in this case by “off-line” GC/AMS (Eglinton et al. 1996; Currie et al. 1997).

Figure 5 gives further insight into <sup>14</sup>C speciation in aerosol PAH. The diagram at the left comes from a multivariate urban field study that showed benzo(*ghi*)perylene to be highly correlated with the motor vehicle (fossil emissions) tracer Pb, with a quantitative estimate of 92% fossil carbon, based on multiple regression (MR). The panel at the right of the figure shows six PAH fractions isolated from the SRM by preparative capillary gas chromatography for <sup>14</sup>C measurement by AMS. The result immediately below this panel shows the benzo(*ghi*)perylene, again, to be primarily fossil. Both the MR result and this one suffered from substantial uncertainties, however; the former, because of the limited number of samples and the error amplification (variance inflation) that typifies most multivariate source resolution studies; the latter, because of imperfect isolation of the PAH

<sup>2</sup>Recent information indicates that SRM 1649a was sampled during 1976–1977 rather than 1973, the assumed sampling date for SRM 1649a in Currie et al. (1997, 1999a). Because the <sup>14</sup>C/<sup>12</sup>C ratio in atmospheric CO<sub>2</sub> was about 6% higher in 1973, the computed biomass carbon fractions in these references should be increased by a factor of 1.06 (Note that at the time of these earlier publications, only the early, relatively imprecise total <sup>14</sup>C value,  $f_M=0.61$ , was available.)

from the underlying “unresolved complex mixture” (ucm) seen in the bottom chromatographic trace of the material in the waste trap.

The baseline resolved result at the bottom right of Figure 5 ( $94 \pm 1\%$  fossil), is a very recent datum that was achieved by the offline GC/AMS technique where the influence of the baseline was essentially eliminated through the special pre-purification technique of PAH ring size fractionation (Wise et al. 1977; Pearson et al. 1997). Two very important conclusions derive from this work. First, compound-specific techniques such as on-line GC/AMS cannot give high quality results unless the individual compounds meet the baseline resolved criterion; unresolved material that is co-eluted is directly analogous to the isotopic-chemical process blank discussed earlier in connection with Integrated Air Cancer Project. Second, the baseline resolved result for benzo(*ghi*)perylene shows that this compound, which has been broadly accepted as unique tracer for fossil fuel combustion aerosol, has a small but definite biomass carbon component in this urban particle SRM. The latter conclusion is consistent with the observed production of this compound during the flaming phase of the laboratory combustion of pine (but not oak; Currie et al. 1999a).

### EMERGENCE OF $^{14}\text{C}$ SPECIATED, NATURAL-MATRIX REFERENCE MATERIALS

The Urban Dust reference material discussed in the preceding section foreshadows a major, new trend in  $^{14}\text{C}$  reference materials, as the need for procedural quality assurance and isotopic-chemical traceability expands to new horizons. This has been brought about, in part, by the importance of isotopic speciation in a host of scientific disciplines and environmental compartments. One of the driving forces, for example, is the importance of quantitative apportionment of the incomplete combustion tracers, “black carbon” and PAH in the bio- and geosciences (atmospheric, soil, marine, cryospheric,...) (Currie et al. 1999b).<sup>3</sup> An equally important driving force is the emerging capability of “dating” extremely small ( $\mu\text{gC}$ ) samples and especially the “chemical” AMS revolution that holds the possibility of on-line isotopic-chemical characterization of individual compounds, using techniques such as GC/AMS (Shibata 1999). Already,  $^{13}\text{C}$  and  $^{14}\text{C}$  speciated reference data are being generated for representative sediment materials, for the benefit of the marine chemistry community (Masiello et al. 1999).

The solid foundation for this new trend toward  $^{13}\text{C}$  and  $^{14}\text{C}$  speciated reference materials, in appropriate natural matrices, has been established through several, very important international exercises using  $^{14}\text{C}$  reference materials specially selected to be representative of the types actually radiocarbon dated, such as wood, peat, cellulose, limestone, etc. (Scott et al. 1998). Reference materials growing out of these intercomparison exercises have taken their place beside the basic  $^{14}\text{C}$  dating oxalic acid standards (SRMs 4990B and 4990C). Lessons learned from these earlier exercises showed also the extreme importance of providing adequate supplies of homogeneous and representative, natural matrix reference materials. As noted in the discussion accompanying Figure 3, *dual* isotopic characterization of such materials serves the critical quality assurance function of “qualifying” the  $^{13}\text{C}$ - $^{14}\text{C}$  plane in the context of authentication of industrial and commercial products (Currie et al. 2000a).

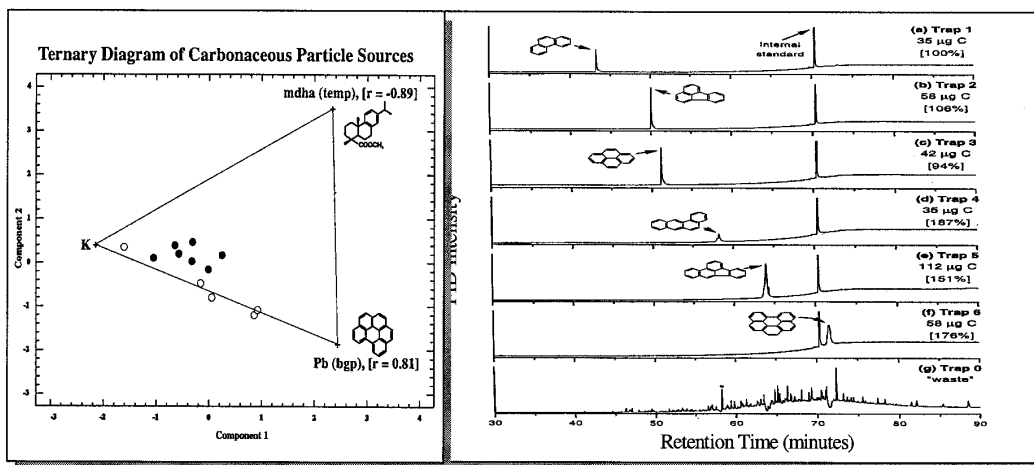
<sup>3</sup>Chemical as well as isotopic-chemical speciation has considerable importance in biogeochemical applications. The “black carbon,” for example is of great concern because of its radiation scattering and absorption properties (visibility, climate); and detailed chemical characteristics of the PAH have important implications for biological effects and for inferences concerning petrogenic vs. pyrogenic origins. The breadth of concern for suitable, multidisciplinary reference materials expressed at the Black Carbon Symposium led to the formation of the *International Steering Committee for the Development of Black Carbon Reference Materials*, with an early mission to identify and characterize (chemically, isotopically) natural matrix reference materials that are suitable for the atmospheric, soil, and marine sciences (Black Carbon 1999).



## Benzo(ghi)Perylene -- Fossil Carbon Speciation

statistical (multivariate)

direct (GC/AMS)



**B(ghi)P:**

**B(ghi)P:** 92 (+8, -17) % fossil

1) Above [trap-6]: 90 (+10, -7) % fossil

2) Baseline resolved: 94±1 % fossil

Figure 5 Fossil/biomass carbon apportionment at the molecular level (benzo(ghi)perylene). This figure contrasts multivariate statistical vs. direct (GC/AMS) modes for “dating” trace organic compounds in atmospheric aerosol, and shows the sensitivity of the latter to the “ucm” blank (Currie et al. 1997). *The diagram on the left*, derived from a large field study with day (o) and night (•) sampling, indicates a strong association between fossil motor vehicle emissions (with Pb as surrogate) and benzo(ghi)perylene. The numerical result below comes from multiple regression with Pb and K as regressors. *The diagram on the right* shows the isolation of several PAH by preparative scale capillary gas chromatography, which preceded AMS on individual molecular fractions of the SRM 1649a. A principal observation is that the initial <sup>14</sup>C result for benzo(ghi)perylene has a large uncertainty, due to the large “unresolved complex mixture” (ucm) of unknown isotopic composition that coeluted and was recovered in trap-6, the B(ghi)P trap. The vastly improved result showing 94 ± 1% fossil carbon was achieved through an improved purification technique involving the isolation of PAH ring size fractions (Wise et al. 1977; Pearson et al. 1997; Currie et al. 1999a).

### A MULTIDISCIPLINARY CASE STUDY; IMPLICATIONS FOR FUTURE RESEARCH

We conclude with highlights from research presented in part at the 1997 International <sup>14</sup>C Conference in Groningen (Currie et al. 1998b). This work extends the multivariate aspect of modern <sup>14</sup>C aerosol research to multidisciplinary science. In this case the objective was to study the long range transport of dust and combustion aerosol from boreal wildfires to remote regions such as Greenland. The study captures central features of large-scale atmospheric contaminant investigations, ranging from source region identification, to long range transport, to aerosol arrival and deposition at receptor sites. Key elements include: fire count data, transport “observations” via UV and IR satellite imagery plus air mass trajectory analysis, and receptor site sampling followed by multicomponent chemical and isotopic analysis—with a focus on elemental or “black carbon” (EC), because of its radiative properties. As indicated in Figure 6 (see Color Plate 2), information drawn from these several disciplines showed conclusively the causal relation between the boreal wildfires in central Can-

ada and the singular enhancement of biomass burning aerosol carbon at Summit, Greenland on 5 August 1994.

The next direction in the  $^{14}\text{C}$  aerosol research is focused on the recovery of the history of aerosol carbon, as captured in polar snow and ice cores. The more recent history is linked to the excavation of samples from snowpits, as illustrated in the photograph from Summit, Greenland (Figure 7 in Color Plate 2). Besides time series data on isotopic and chemical tracers of fire, such as elemental carbon and the PAH, we have the opportunity to investigate individual particles, using extremely powerful microanalysis tools. One such example is the woodburning char particle shown in Figure 7. This was recovered from a depth of 114 cm in a 1996 snowpit, in the vicinity of a 1994 fire horizon (Currie et al. 1998b). The future of such research is extremely promising, having the potential to improve our understanding of: 1) the processes involved in the transport of carbonaceous aerosol and its incorporation in snow crystals and eventually ice cores, and 2) the history of fossil and biomass burning as recorded in atmospheric aerosols trapped in the ice cores.

### CONCLUSION AND OUTLOOK

The advances in AMS that are making possible the measurement of  $^{14}\text{C}$  at the microgram level, and the link with chemical science making possible compound-specific and continuous flow  $^{13}\text{C}$  and  $^{14}\text{C}$  measurements will enormously enhance our ability to expand isotopic carbonaceous aerosol research to regimes that are remote in time and space. In the Greenland snow, for example, the concentrations of elemental carbon are commonly in the neighborhood of  $1\ \mu\text{g}$  per kg of snow, so the improved sensitivity is vital. Among the special challenges are low-level  $^{14}\text{C}$  speciation in chemical tracers of fire (e.g. PAH and EC), and improved understanding of isotopic and molecular fractionation in incomplete combustion, including some surprising differences between laboratory and field experiments (Currie et al. 1999a). Also, as the quantity of sampled material gets larger, and the  $^{14}\text{C}$  detection limit, smaller, increased effort will be needed to understand and control the chemical and isotopic blank. Similarly, the full benefit of on-line GC/AMS will require creative approaches to achieve baseline resolved peaks. An accompanying challenge, as samples become smaller, and applications, increasingly multidisciplinary, is the provision of appropriate, natural matrix isotopic-chemical reference materials. Finally, with expanded AMS capabilities and highly interdisciplinary approaches, we see the local and urban  $^{14}\text{C}$  aerosol researches of the past taking on a regional and even global character, allowing us to better understand the impact of carbonaceous aerosol sources on our planet.

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principal components biplot, derived from cluster and biplot data in §3.4.2 of Currie (1992); Figure 4: photo of SRM 1649a filter reference samples, courtesy of George Klouda, NIST; Figure 5: adapted from Figures 6–7 of Currie et al. (1997); Figures 6–7: (snowpit photo) adapted from Figures 1–2 of Currie et al. (1998b); Figure 7: (SEM image, X-ray spectrum) courtesy of John Kessler, NIST.

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