Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States

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[1] Fine particulate matter collected at two urban, four near-urban, and six remote sites throughout the United States were analyzed for total carbon (TC) and radiocarbon (^{14}C). Samples were collected at most sites for both a summer and winter season. The radiocarbon was used to partition the TC into fossil and contemporary fractions. On average, contemporary carbon composed about half of the carbon at the urban, $\sim$70–97% at near-urban, and 82–100% at remote sites. At Phoenix, Arizona, and Seattle, Washington, one monitor was located within the urban center and one outside to assess the urban excess over background concentrations. During the summer the urban and rural sites had similar contemporary carbon concentrations. However, during the winter the urban sites had more than twice the contemporary carbon measured at the neighboring sites, indicating anthropogenic contributions to the contemporary carbon. The urban fossil carbon was 4–20 times larger than the neighboring rural sites for both seasons. Organic (OC) and elemental carbon (EC) from TOR analysis were available. These and the radiocarbon data were used to estimate characteristic fossil and contemporary EC/TC ratios for the winter and summer seasons. These ratios were applied to carbon data from the Interagency Monitoring of Protected Visual Environments network to estimate the fraction of contemporary carbon at mostly rural sites throughout the United States. In addition, the ratios were used to develop a semiquantitative, lower bound estimate of secondary organic carbon (SOC) contribution to fossil and contemporary carbon. SOC accounted for more than one-third of the fossil and contemporary carbon.

1. Introduction

[2] Carbonaceous aerosols are a major component of the particulate matter (PM) less than 2.5 microns (PM$_{2.5}$) [*Hegg et al.*, 1997; *Malm et al.*, 2004]. In the United States the annual PM$_{2.5}$ total carbon (TC) concentrations range from less than 1 μg/m^3 in the rural West, to 3 μg/m^3 in the rural Northwest and Southeast, and over 4 μg/m^3 in many urban centers (Figure 1). Carbon compounds are also the largest component of PM$_{2.5}$ at many rural sites in the western United States and urban centers throughout the United States [*Malm et al.*, 2004; *DeBell et al.*, 2006], and the carbon mass fraction is increasing as sulfate aerosols continue to decrease [*Malm et al.*, 2002; *Husain et al.*, 2004; *Brewer and Adlhoch*, 2005]. The high carbon concentrations and their efficient scattering and absorption of visible and infrared radiation make them a key factor in atmospheric transparency and the balance of solar radiation [*Adams et al.*, 1990; *Malm et al.*, 1994; *Hegg et al.*, 1997; *Jacobson*, 2001a, 2001b]. Carbonaceous emissions from wood burning and fossil fuel combustion also have possible health effects [*Lewis et al.*, 1988; *Salvi et al.*, 1999; *Pope and Dockery*, 2006].

[3] Carbonaceous aerosols arise from a wide array of sources including combustion of fossil fuels, meat cooking, deep frying, and biomass burning [*Bond et al.*, 2004]. Secondary organic carbon (SOC) produced from biogenic and combustion volatile organic compounds (VOCs) can also contribute to organic aerosols. The diverse carbon sources and atmospheric processing result in a complex mixture of compounds with widely differing reactivities, volatilities, and other properties, leading to difficulties in sampling and analysis [*Eatough et al.*, 1989; *Hering et al.*, 1990; *Rogge et al.*, 1993]. This in turn results in an incompletely characterized mixture, complicating the mod-

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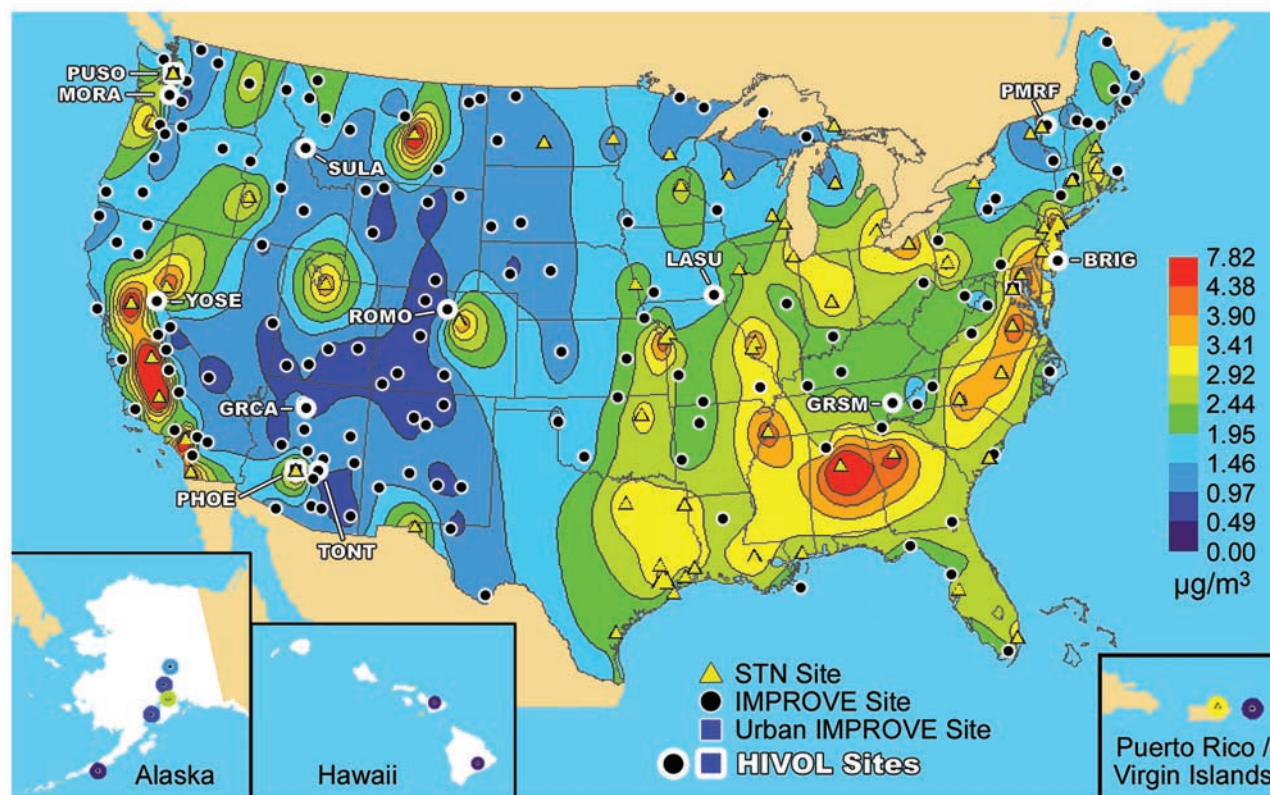
Figure 1. Total particulate carbon (OC + EC) at rural and urban locations from the IMPROVE and STN networks averaged over the years 2000–2004 [*DeBell et al.*, 2006]. IMPROVE sites with collocated Hi-Vol samplers used in the radiocarbon field study are labeled for correspondence with Table 1. The data are spatially interpolated using a Kriging algorithm to help visualize spatial patterns in the data.

eling of ambient concentrations and determination of the contributions from their sources.

[4] The distinction most commonly drawn within the carbonaceous component is one between organic (OC) and elemental (EC) fractions, based on thermal optical reflectance (TOR) or thermal optical transmittance (TOT). These techniques measure the evolution of carbon vapors and changes in sample reflectance or transmittance during a programmed cycle of sample heating and oxidation [*Chow et al.*, 1993; *Birch and Cary*, 1996; *Chow et al.*, 2007a]. Thermal optical methods accurately measure the TC concentrations, but the distinction between OC and EC is operationally defined, depending on the sensitivity to the temperature analysis, the atmosphere, and the optical monitoring [*Chow et al.*, 2001, 2004, 2005; *Currie et al.*, 2002]. These analysis techniques are cost-effective and precise at low filter mass loadings, making them suitable for routine monitoring networks. A TOR carbon analysis is currently being used in the Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring network [*Malm et al.*, 1994] to determine the carbon concentrations in 24-h PM$_{2.5}$ samples collected at ~160 monitoring sites in mostly rural and remote areas of the United States (Figure 1). A TOT carbon analysis is being used in the Speciation Trends Network (STN) to determine the carbon concentration in 24-h PM$_{2.5}$ samples at over 250 sites primarily located in urban and suburban settings [*Flanagan et al.*, 2006]. The temperature profile used in the STN TOT

analysis is different from that used in IMPROVE and networks in other countries [*Watson et al.*, 2005]. Intercomparisons of the IMPROVE TOR and STN TOT carbon analyses on ambient samples [*Chow et al.*, 2001] and filter samples created from reference material [*Klouda et al.*, 2005] have shown that both methods produce similar TC concentrations, but EC by IMPROVE TOR is systematically higher than EC by STN TOT, leading to higher EC/TC. The discrepancies in the IMPROVE and STN carbon analyses will be minimized for samples acquired after 2007 as the IMPROVE_A protocol [*Chow et al.*, 2007a] will be implemented in the STN [*Environmental Protection Agency*, 2006].

[5] The fraction of OC and EC in the primary emission is source dependent, and OC/EC/TC ratios have been used to infer the contributions of biomass burning, primary urban emissions, and SOC [e.g., *Turpin et al.*, 1991; *Cabada et al.*, 2004; *Malm et al.*, 2004]. However, there are large variations in the ratios within the same source categories [e.g., *Gillies and Gertler*, 2000], so the results are semiquantitative in nature. One means of refining these results is to combine the carbon thermal profiles with other aerosol properties and constituents in receptor models to estimate the contributions from source types such as mobile sources and biomass burning [*Lewis et al.*, 2003; *Kim et al.*, 2004]. These results often suffer from large errors and ill-defined source categories due to collinearities in the data.

[6] The source apportionment of the carbon fraction has been improved using specific organic marker species [*Schauer et al.*, 1996; *Chow and Watson*, 2002; *Zheng et al.*, 2002; *Chow et al.*, 2007b]. With such approaches, marker compounds are associated with different source types, and the abundances of these species in the ambient samples are used to infer contributions from each profiled source. While compound-specific analysis has proven its value in a variety of atmospheric chemistry studies, numerous source profiles are often needed to apportion PM mass and chemical concentrations to sources. Only ~30% or less of the total organic mass in ambient samples has been associated with identifiable chemical compounds [*Rogge et al.*, 1993]. In addition, organic compounds can be formed or degraded in the atmosphere due to chemical reactions, causing the source profiles to change over time.

[7] Isotopic abundances can also serve as source markers. Radiocarbon (^{14}C) is present at a small but approximately constant level in living (or contemporary) materials but is absent in fossil fuels, which are much older than the radiocarbon half-life of 5730 years. Radiocarbon also retains its identity throughout chemical transformations. Consequently, a radiocarbon measurement performed on a PM sample provides a means of quantitatively distinguishing between the relative contributions of fossil and contemporary carbon sources [*Cooper et al.*, 1981; *Hildemann et al.*, 1994], even if the measured PM was influenced by a directly emitted organic precursor gas. These carbon fractions are often referred to as fossil and biogenic carbon [*Lemire et al.*, 2002; *Lewis et al.*, 2004]. This analysis currently requires large samples and is too expensive to be used in routine monitoring networks but has been used to assess the fraction of fossil and biogenic carbon in a number of short-term studies throughout the world [*Endo et al.*, 2004; *Jordan et al.*, 2006; *Szidat et al.*, 2006].

[8] A variety of radiocarbon studies analyzing the fossil and contemporary content of particulate carbon in the United States have been conducted over the past 30 years. Most of these studies have focused on urban centers. An early study conducted in Portland and Eugene, Oregon, in 1977 and 1978 found that 45–95% of the carbon was contemporary on selected filters when biomass burning was thought to be a significant source of carbon [*Cooper et al.*, 1981]. In the Los Angeles basin the typical fraction contemporary was 20–43% in 1982 [*Hildemann et al.*, 1994] and 39% in a 1987 study [*Kaplan and Gordon*, 1994]. Similar results for Los Angles were also found by others [*Currie et al.*, 1983; *Berger et al.*, 1986]. In Houston, Texas, the fraction of contemporary carbon was 40% in September 1980 [*Dzubay et al.*, 1982] and 48% in August 2000 [*Lemire et al.*, 2002]. Samples collected in Albuquerque, New Mexico, in December 1985 were found to have a fraction contemporary of 40–84%, with 71% on average [*Sheffield et al.*, 1994]. A study in Phoenix, Arizona, and Puget Sound, Washington, estimated the fraction of contemporary carbon at ~50% for both a winter and summer season in 2004–2006 [*Bench et al.*, 2007]. In Denver, Colorado, the fractions contemporary were 25% on average during the 1996–1997 winter and 47% during the summer [*Klinedinst and Currie*, 1999]. In southeastern U.S. urban centers, the fractions of contemporary carbon were 30% in Birmingham, Alabama, 46% in Atlanta, Georgia, and 60% in Pensacola, Florida, during the winter of 2003–2004 [*Zheng et al.*, 2006]. Finally, a study in Nashville, Tennessee, during the summer of 1999 found the fraction of contemporary carbon varied from 51% to 73% and was 64% on average [*Lewis et al.*, 2004].

[9] Sampling of radiocarbon has also occurred in several rural areas near urban centers. At a heavily forested site near Houston, Texas, the fraction of contemporary carbon varied from 44% to 77% [*Lemire et al.*, 2002], near Tampa, Florida, it was ~70% [*Lewis and Stiles*, 2006], and south of Birmingham, Alabama, in Centerville, 72% of the carbon was contemporary. As part of a larger study, *Bench et al.* [2007] reported on the radiocarbon at three rural sites within 100 km of urban centers in New Jersey, Arizona, and Washington and found that the fractions contemporary varied from 70% to 97%, with an average of 80%.

[10] Sampling has also been conducted at remote sites. In Yosemite National Park, California, during the summer of 2002, the average fraction contemporary was 86% [*Bench and Herckes*, 2004], and from the *Bench et al.* [2007] study, contemporary carbon at the Grand Canyon National Park in Arizona, Rocky Mountain National Park in Colorado, and Sula, Montana, accounted for over 90% of TC. At the Great Smoky Mountains National Park in Tennessee, *Bench et al.* [2007] estimated the average fraction of contemporary carbon to be 90% in the summer and 82% in the winter, while *Tanner et al.* [2004] estimated that 71% of the PM_{10} carbon was contemporary for samples collected in the spring, summer, and fall seasons.

[11] These studies report on data collected over the past 30 years at different locations and times of years. In addition, they used different assumptions to derive the fraction of contemporary carbon from the radiocarbon data. Nonetheless, the multiple studies of the radiocarbon in the urban and rural areas of the United States provide a consistent set of results. Specifically, in the urban centers contemporary carbon accounts for a large fraction of TC, though often less than 50%. In the rural but near-urban areas, more than half of the carbon is contemporary, and the particulate carbon concentration in remote areas is primarily composed of contemporary carbon.

[12] The preponderance of contemporary carbon in ambient air is also consistent with current emission inventories. In a global emission inventory of primary particulate carbon from fossil and biogenic combustion sources, *Bond et al.* [2004] estimate that in North America combustion of fossil fuel accounts for ~22% of the primary particulate carbon. *Park et al.* [2006] suggest that this emission inventory underestimates anthropogenic carbon emissions by a factor of 2, which would increase the contribution of fossil fuel combustion to the primary particulate carbon. These results are qualitatively consistent with the radiocarbon results in that the majority of the primary carbon emissions are from contemporary carbon sources. In addition, on- and off-road mobile emissions for North America accounted for about 85% of the fossil PM carbon emissions, and the highest mobile source emission densities occur in urban areas (Environmental Protection Agency National Emission Inventory, available at http://www.epa.gov/ttn/chief/net/index.html). Therefore a higher fraction of urban PM is expected from the fossil carbon relative to the fraction at nonurban locations distant from major roadways.

Table 1. Radiocarbon Monitoring Sites and the Median Total Carbon (TC) Concentrations and Elemental Carbon (EC) to TC Ratios From Collocated IMPROVE Monitoring Sites for the 2000–2004 Time Period and for Each Radiocarbon Sampling Period[a]

| Site Name | Code | Site Type | 2000–2004 | | | | Radiocarbon Sampling Periods | | | |
| | | | TC, $\mu g/m^3$ | | EC/TC | | TC, $\mu g/m^3$ | | EC/TC | |
			Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
Brigantine, NJ[b]	BRIG	near urban	2.4 (0.87)	2.0 (0.82)	0.18 (0.04)	0.26 (0.03)	2.0 (0.67)	2.0 (0.63)	0.16 (0.03)	0.25 (0.03)
Proctor Maple, VT[b]	PMRF	rural	1.8 (0.78)	1.1 (0.4)	0.15 (0.03)	0.2 (0.03)	1.8 (0.56)	0.85 (0.33)	0.16 (0.03)	0.22 (0.04)
Great Smoky Mtn, TN[b]	GRSM	rural	2.3 (0.62)	1.4 (0.43)	0.16 (0.03)	0.21 (0.03)	2.1 (0.46)	1.7 (0.61)	0.14 (0.02)	0.22 (0.03)
Lake Sugema, IA[d]	LASU	near urban	1.8 (0.6)	1.2 (0.36)	0.19 (0.03)	0.2 (0.04)		1.3 (0.31)		**0.27 (0.04)**
Mount Rainier, WA[b]	MORA	near urban	1.8 (0.93)	0.58 (0.38)	0.2 (0.04)	0.2 (0.04)	1.9 (1.1)	**1.3 (0.93)**	0.16 (0.03)	0.23 (0.04)
Puget Sound, WA[b]	PUSO	urban	2.2 (0.91)	3.7 (1.7)	0.28 (0.07)	0.29 (0.06)	2.4 (1.1)	4.2 (1.6)	0.28 (0.06)	0.32 (0.04)
Grand Canyon, AZ[c]	GRCA	rural	0.81 (0.27)	0.23 (0.1)	0.14 (0.03)	0.22 (0.06)	0.78 (0.32)	0.2 (0.11)	0.16 (0.04)	0.22 (0.07)
Rocky Mountain, CO[d]	ROMO	rural	1.4 (0.43)	0.28 (0.11)	0.13 (0.02)	0.17 (0.06)	1.3 (0.57)	0.22 (0.07)	0.15 (0.02)	0.14 (0.05)
Sula, MT[e]	SULA	rural	1.7 (0.7)	0.27 (0.11)	0.09 (0.02)	0.16 (0.04)	1.2 (0.55)		**0.12 (0.02)**	
Tonto, AZ[c]	TONT	near urban	1.1 (0.3)	0.78 (0.22)	0.13 (0.03)	0.25 (0.05)	1.0 (0.27)	0.71 (0.26)	**0.17 (0.03)**	0.27 (0.04)
Phoenix, AZ[c]	PHOE	urban	2.2 (0.47)	6.9 (3.1)	0.24 (0.04)	0.25 (0.06)	2.3 (0.64)	7.3 (3.0)	0.25 (0.05)	**0.35 (0.04)**
Yosemite, CA[f]	YOSE	rural	2.1 (0.78)	0.33 (0.18)	0.12 (0.02)	0.16 (0.04)	**3.8 (1.5)**		0.1 (0.03)	

[a]The values in parentheses are the median absolute difference (MAD) of the distribution. MAD = median $|x - \text{median}(x)|$ where x represents either the TC concentrations or EC/TC values. Bold values in columns under radiocarbon sampling periods are more than 1 MAD from the 2000–2004 median TC or EC/TC.
[b]Radiocarbon samples collected from June 2004 to August 2004 and December 2004 to February 2005.
[c]Radiocarbon samples collected from June 2005 to August 2005 and December 2005 to February 2006.
[d]Radiocarbon samples collected from December 2005 to February 2006.
[e]Radiocarbon samples reported for June 2005 to August 2005.
[f]Radiocarbon samples collected from July 2002 to August 2002.

[13] Corroboration also comes from modeling studies. *Zheng et al.* [2006] found good agreement between fossil carbon fractions estimated by radiocarbon and the chemical mass balance receptor model at several sites in the southeastern United States. A modeling study conducted by *Park et al.* [2003], using 1998 emissions and meteorology but climatological average emissions for wildfire, estimated that 62% of the carbon in the western United States was from natural biogenic sources. However, in the eastern United States only 31% of the PM carbon was estimated to be of natural biogenic origin. These are lower bounds to the contributions of contemporary carbon, since the natural particulate carbon concentrations did not include anthropogenic contributions to contemporary carbon such as residential wood burning [*Park et al.*, 2003].

[14] The consistency of results across the radiocarbon studies and other modeling studies provides some confidence of the large contributions of contemporary carbon to the PM in the United States. However, the data are from a relatively few locations. Also, the contribution of natural and anthropogenic sources and SOC to the fossil and contemporary carbon fraction is less understood.

[15] In this work we further analyze the data of *Bench and Herckes* [2004] and *Bench et al.* [2007] to examine three issues. First, the differences between urban and rural concentrations are examined to assess the contributions of the urban areas to the fossil and contemporary carbon concentrations. Second, the radiocarbon data are integrated with OC and EC data from collocated IMPROVE monitoring sites to develop relationships between the fossil carbon fraction and the fraction of elemental carbon (EC/TC) during a winter and summer season. This relationship is used to derive characteristic EC/TC ratios for fossil and contemporary carbon. These ratios are then used to estimate the contemporary carbon fraction of the particulate carbon concentrations measured in IMPROVE to develop a national map of the contemporary carbon fraction at mostly rural sites in the conterminous United States. Last, the EC/TC ratios are used to develop a semiquantitative estimate of the contribution of SOC to the fossil and contemporary concentrations during the summer months.

2. Monitoring Networks, Sampling Periods, and Data Representativeness

[16] Radiocarbon data from two field studies were combined and used for the analyses. The first field campaign used Hi-Vol samplers to collect 6-d integrated $PM_{2.5}$ samples at 11 IMPROVE sites throughout the conterminous United States (see Figure 1 and Table 1). The sites were selected to represent geographically diverse areas and, as shown in Figure 1, included sites in two urban centers, five remote areas, and four rural locations that were within 100 km of an urban center at a similar elevation. Samples were collected at most sites for one summertime period from June to August and one wintertime period from December to February in 2004 through 2006. Table 1 lists the sample collection periods for each site. Nine to 13 valid samples were collected each season at each site and used in this analysis, except at Sula, Montana, which had five valid samples during the summer season. The Lake Sugema, Iowa, monitor did not operate during the summer sampling period, and the Sula, Montana, monitoring site had equipment failures during the winter sampling period and only two samples were collected. Consequently, the winter Sula, Montana, data are not discussed. *Bench et al.* [2007] report on and discuss the contemporary and fossil carbon concentrations from this network, except for the data collected at Lake Sugema and Sula.

[17] The second field study used a Hi-Vol sampler to collect 1- to 3-d integrated $PM_{2.5}$ samples at the IMPROVE monitoring site in Yosemite, California, from 14 July to

3 September 2002 [*Bench and Herckes*, 2004]. The samples were collected and analyzed using identical procedures as used by *Bench et al.* [2007].

[18] Sampling at these diverse sites during winter and summer seasons enabled the characterization of the $PM_{2.5}$ carbon influenced by different source categories and atmospheric processing. Table 1 reports the median and median absolute deviation from the median (MAD) of the $PM_{2.5}$ TC concentrations and EC/TC ratios measured in the IMPROVE program for each of the 12 IMPROVE sites used in the two radiocarbon field studies. The site-specific medians and MADs were calculated for all data collected from 2000 to 2004 and for the periods that $PM_{2.5}$ samples were collected for radiocarbon analysis (hereto referred to as radiocarbon sampling period). The comparison of the aggregated carbon values during the radiocarbon sampling periods and the 5-year aggregated values allows for the assessment of the representativeness of these sampling periods.

[19] The MAD was used in this assessment because it is a robust measure of the spread of the distribution around the data's median and is less influenced by high carbon concentrations, such as those resulting from the impact of biomass burning. Therefore MAD results in a narrower distribution compared to other measures such as the standard deviation and provides a more stringent comparison between the data collected during the radiocarbon sampling periods and all of 2000 to 2004.

[20] As shown in Table 1, there was large variability in the typical TC concentrations across the sites for the 2000–2004 data set, with the median summer TC varying by a factor of 3, from 0.8 $\mu g/m^3$ at Grand Canyon to 2.4 $\mu g/m^3$ at Brigantine. During the winter months, the median TC ranged from 0.23 $\mu g/m^3$ at Grand Canyon to 6.9 $\mu g/m^3$ at Phoenix. There were also differences in the seasonal variability of TC across the sites, with higher wintertime TC at the two urban sites, Phoenix and Puget Sound, and higher summertime TC at all other sites. Different EC/TC ratios are indications of differing source contributions and/or atmospheric processing of gaseous and particulate carbon compounds. During the summer months the EC/TC ratios varied from 0.09 to 0.16 at the rural sites to 0.13 to 0.2 at the near-urban sites and 0.24 to 0.28 at the two urban sites. The EC/TC ratios increased at all sites during the winter, and the differences between the rural, near-urban, and urban sites decreased.

[21] The median TC concentrations during the radiocarbon sampling periods are within 1 MAD of the 2000–2004 median concentrations for all sites, except during the summer at Yosemite and winter at Mount Rainier, where the TC concentrations were larger than typically found. The higher concentrations at Yosemite were due to smoke from wildfires in southern Oregon and in the Sierra Nevada mountains impacting Yosemite during most of the sampling period [*McMeeking et al.*, 2006].

[22] The EC/TC ratios during the radiocarbon sampling periods were also less than or near 1 MAD from the long-term median. The exceptions are during the winter sampling periods at Lake Sugema and Phoenix, where the EC/TC ratios were higher than typical. These results indicate that in general the TC concentrations and EC/TC ratios during the radiocarbon studies' sampling periods are similar to and representative of the typical values measured at the monitoring sites.

3. Measurement Methods

[23] Detailed descriptions of the sample collection, filter analysis procedures, and uncertainty analysis for radiocarbon are provided by *Bench and Herckes* [2004] and *Bench et al.* [2007]. All $PM_{2.5}$ samples were collected using Thermo Anderson total suspended particulate (TSP) Hi-Vol samplers with SA-231-F impactor plates. Samplers were operated at a volumetric flow of 68 m^3/h, collecting samples for 6 d from Tuesday to Monday on prefired Gellman QM-A quartz-fiber filters. Filter blanks were obtained from each site once a month by placing a quartz-fiber filter in the sampler for 10 min with the pump off. Sampling at Yosemite differed in that the sampler duration was 1 to 3 d as opposed to 6 d at the other sites.

[24] At the Lawrence Livermore National Laboratory (LLNL), 25 cm^2 filter punches were taken from the central region of each quartz filter that was analyzed for TC and radiocarbon. Each punch was sealed under vacuum with a CuO oxidizer in a quartz tube and combusted at 900°C. CO_2 from the combustion was cryogenically isolated from other combustion products and measured manometrically before conversion to graphite by hydrogen reduction using an iron catalyst. $^{14}C/C$ ratios in the graphite samples were measured by accelerator mass spectrometry (AMS). The data were reported as a fraction of the Modern radiocarbon standard (fraction Modern or F_M) [*Stuiver and Polach*, 1977]. Filter blanks were also analyzed for $^{14}C/C$ to correct the samples for positive organic artifacts [*Bench et al.*, 2007]. The F_M on the filter blanks was always smaller than the F_M on the exposed filters, so the correction always increased the aerosol F_M. The increase was typically less than 6%, but there was a greater than 30% increase for the winter samples at Rocky Mountain and Grand Canyon [*Bench et al.*, 2007].

[25] The fraction of modern carbon was calculated as $F_M = R_a/R_m$, where R_a is the $^{14}C/C$ ratio of a $PM_{2.5}$ aerosol sample and R_m is the $^{14}C/C$ ratio in contemporary carbon in 1950. Fossil carbon has $F_M = 0$ and contemporary carbon should have $F_M = 1$. However, due to above-ground nuclear testing in the 1950s and 1960s, the $^{14}C/C$ levels in the atmosphere increased, reaching a maximum in 1964 of 185% of pre-1950 levels. Since 1964 the $^{14}C/C$ levels have decreased, and from 1999 to 2003 the F_M of contemporary samples decreased from 1.11 to 1.07 [*Levin and Kromer*, 2004]. The F_M of contemporary samples has further decreased to around 1.05 in 2006. For this study, the F_M in the contemporary component was taken to be 1.08 ± 0.06. This value corresponds to the average F_M of contemporary material over the time period 1999–2005, with an uncertainty that corresponds to the difference between the maximum and minimum values over this time period. Therefore the fraction of contemporary carbon (F_c) in the aerosol samples was estimated using $F_c = F_M/(1.08 \pm 0.06)$ and the fraction of fossil carbon using $F_f = 1 - F_c$.

[26] A large source of contemporary carbon is from biomass burning. The carbon released by biomass burning may have been sequestered before 1999 and therefore has an F_M larger than 1.08. For example, the average F_M of

wood from 50-year-old trees is 1.3 [*Lewis et al.*, 2004]. In such cases, the F_c will be an overestimate.

[27] Analytical uncertainty in the TC mass and F_M measurements was examined using replicate analyses from eight filters [*Bench and Herckes*, 2004] that showed that both carbon mass and F_M were within the reported analytical measurement uncertainties. Collocated samplers were located in Phoenix, Arizona, during the winter sampling period. The observed difference in the TC from the comparison of the collocated samples was 8% but only 1.3% for the F_M [*Bench et al.*, 2007]. Bounding calculations were also conducted to test the sensitivity of F_c on the assumed F_M in the contemporary carbon and the filter blank correction. It was found that the results were robust and relatively insensitive to these factors [*Bench et al.*, 2007]. However, there were samples with F_c significantly greater than 1. This occurred at sites likely to be impacted by biomass burning and could be due to an underestimation of the radiocarbon content of contemporary material.

[28] After the initial analysis of the radiocarbon data was reported by *Bench et al.* [2007], samples from the Tonto, Phoenix, Puget Sound, and Mount Rainier monitoring sites were further analyzed for OC and EC by TOR, following the IMPROVE_A protocol at the Desert Research Institute [*Chow et al.*, 1993, 2007a]. Comparisons of TC from the manometric and TOR analyses showed high correlation with r = 0.97. However, TC by TOR was 25% lower. The difference was found to be due to inhomogeneous deposits on the quartz-fiber filters with the highest deposits at the center of the filter, where the filter punches for the AMS analysis were taken, and the lowest deposits in the corners of the filters, where the filter punches for the TOR analysis were taken. This inhomogeneity was identified by taking multiple punches from several filters and analyzing them by TOR. The inhomogeneity was not found in the replicate AMS analyses because all punches were taken closer to the center of the filters and any bias was within the uncertainty of the analysis. Owing to the inhomogeneity, the absolute radiocarbon and TC values are thought to be high by 10–15%; however, this does not affect fractional results such as F_c and F_f.

4. Results and Discussion

4.1. Seasonal Fossil and Contemporary Carbon Concentrations

[29] The seasonal concentrations of the fossil and contemporary carbon and the range in the individual samples are summarized in Figure 2. As shown, the summer contemporary carbon concentrations are rather uniform across the sites, ranging from 1.3 to 2.4 $\mu g/m^3$ at most sites. Yosemite measured an average summertime contemporary carbon concentration of 6.8 $\mu g/m^3$, due to smoke from wildfires, as noted earlier [*McMeeking et al.*, 2006]. There was more variability during the winter, with the average contemporary carbon concentrations ranging from less than 0.5 $\mu g/m^3$ at Rocky Mountain and Grand Canyon to 2.8 $\mu g/m^3$ at Puget Sound and 5.8 $\mu g/m^3$ at Phoenix. During both the winter and summer there was large variability among the individual samples, with the 6-d concentrations varying by a factor of 2–10 at a given site. The fossil carbon concentrations at the two urban sites were similar to the
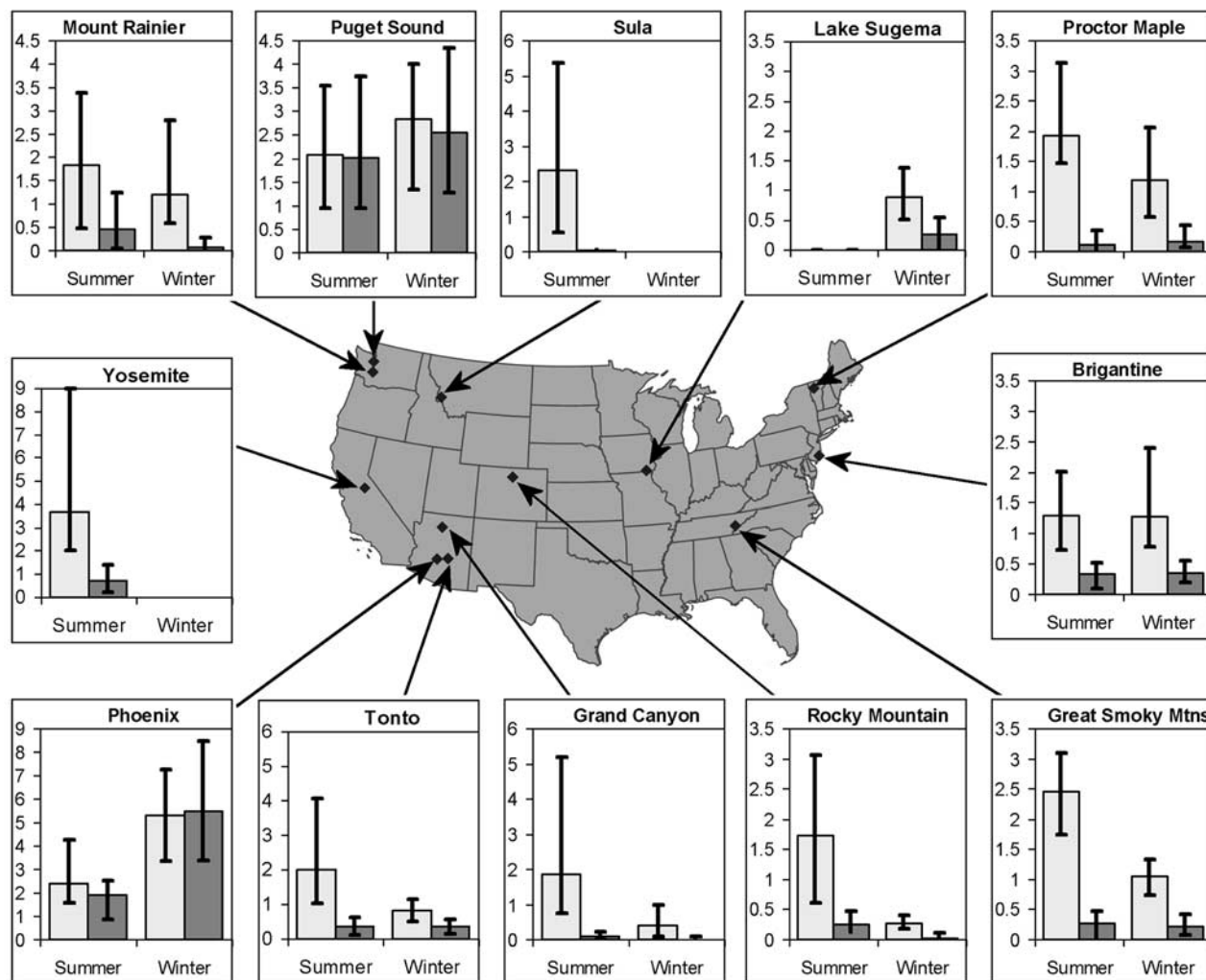
contemporary carbon concentrations during both the summer and winter. The fossil carbon at the other sites was less than the contemporary carbon, at concentrations <0.5 $\mu g/m^3$ for both seasons.

[30] At both urban sites, the winter fossil and contemporary carbon concentrations were larger than those for summer, with concentrations greater by a factor of 2 at Phoenix during the winter. At the near-urban site, Brigantine, the summer and winter concentrations are similar. At all other sites the contemporary carbon concentrations were larger during the summer than winter, by a factor of 1.5 at Mount Rainier to a factor of 6 at Rocky Mountain. The concentrations of fossil carbon at the rural western U.S. sites, Mount Rainier, Grand Canyon, and Rocky Mountain, were also larger during the summer. There was little to no difference between the summer and winter fossil concentrations at the three rural eastern U.S. sites and Tonto, Arizona.

[31] Figure 3 presents the average winter and summer fractions of TC that are contemporary and the range in the individual samples at each site. There is less site-to-site, sample-to-sample, and winter-to-summer variation than seen for the contemporary and fossil carbon concentrations. At the two urban sites, the fractions of contemporary carbon are about 50% during both seasons. The contemporary carbon fractions increase to ~80% at the four near-urban sites, Mount Rainier, Tonto, Lake Sugema, and Brigantine, except for the winter season at Mount Rainier and Tonto, which were 97% and 70%, respectively. At the rural sites, Yosemite, Grand Canyon, Sula, Rocky Mountain, Great Smoky Mountains, and Proctor Maple, the fraction of contemporary carbon varied from ~82% to 100%, with an average of 92%. The winter and summer contemporary carbon fractions were within 10% at all of the sites except at Mount Rainier, Tonto, and Phoenix, which were within 15–20% of each other.

4.2. Urban Excess Fossil and Contemporary Carbon

[32] As shown in Figure 1, TC concentrations at most urban sites were larger than at the neighboring rural sites. This is most pronounced in the western United States where the annual TC concentrations at urban monitors such as Denver, Colorado, Salt Lake City, Utah, and Phoenix, Arizona, are more than a factor of 2 larger than neighboring rural sites. If the concentrations at the rural sites represent the regional background concentrations that are transported into and through the urban area, then the increase in carbon concentrations, or urban excess, can be interpreted as the contribution of primary and secondary carbon from the urban sources. However, there are several complicating factors and the concentrations at near-urban sites may not represent the nonurban concentration in the urban area. First, urban areas tend to have higher temperatures and availability of oxidants, both of which could enhance SOC formation rates from the background organic gases transported into the urban area. In this case the urban excess would overestimate the contribution from urban sources. On the other hand, the increased temperatures could cause volatilization of some of the background organic aerosols, causing an underestimation of the contribution from the urban sources. Last, airmass transport between the urban and rural sites will occur, and on average the carbon

Figure 2. Average seasonal concentrations of contemporary (light gray bars) and fossil (dark gray bars) carbon at each monitoring site. The whiskers represent the range in the 6-d concentrations in each season.

concentrations at the rural sites will have contributions from the urban areas, resulting in an underestimation of the contribution from urban sources. Consequently, the urban excess will be thought of as a measure of the influence of the urban area on the total $PM_{2.5}$ carbon concentrations.

[33] The radiocarbon monitoring network had two urban/rural pairs of sites in which an urban excess could be examined. In the northwestern United States, the rural Mount Rainier site was located 88 km to the southeast of the urban Puget Sound site, and in the southwestern United States, the rural Tonto site was located 92 km east of the urban Phoenix site (Figure 2). Examination of back trajectories to Tonto and Mount Rainier showed that, during both the summer and winter seasons, transport frequently occurred between the urban and rural sites, though it occurred more often during the summer months. Therefore the rural sites are influenced by the urban emissions, and the rural concentrations will likely overestimate the regional background concentrations being transported into the urban areas. However, on average the urban influence on the neighboring rural sites should be small, since, as shown in Figure 1 and discussed by *Malm et al.* [2004], the Mount

Rainier and Tonto carbon concentrations are similar to more remote receptor sites farther from the urban centers.

[34] The fossil and contemporary carbon concentrations and urban excesses for the Puget Sound and Mount Rainier sites are presented in Figures 4 and 5. Owing to the inhomogeneity of the sample deposit, the concentrations and urban excesses are possibly overestimated by 10–15%. As shown in Figure 4, the average summer urban excess at Puget Sound for the contemporary carbon was small, 0.23 μg/m^3 or 11% of the contemporary carbon concentration, but the fossil carbon excess was 1.56 μg/m^3, 77% of the fossil carbon concentration. The summer contemporary carbon concentrations were also similar for the 6-d samples and were correlated at r = 0.8 (Figure 5). Although the Puget Sound fossil carbon concentrations were 4 times higher than at Mount Rainier, their concentrations were correlated with r = 0.7. During the winter, the average fossil carbon at Mount Rainier was near 0, but ~2.5 μg/m^3 at Puget Sound. The Puget Sound contemporary carbon concentrations were also more than twice that measured at Mount Rainier. In addition, the fossil and contemporary carbon at
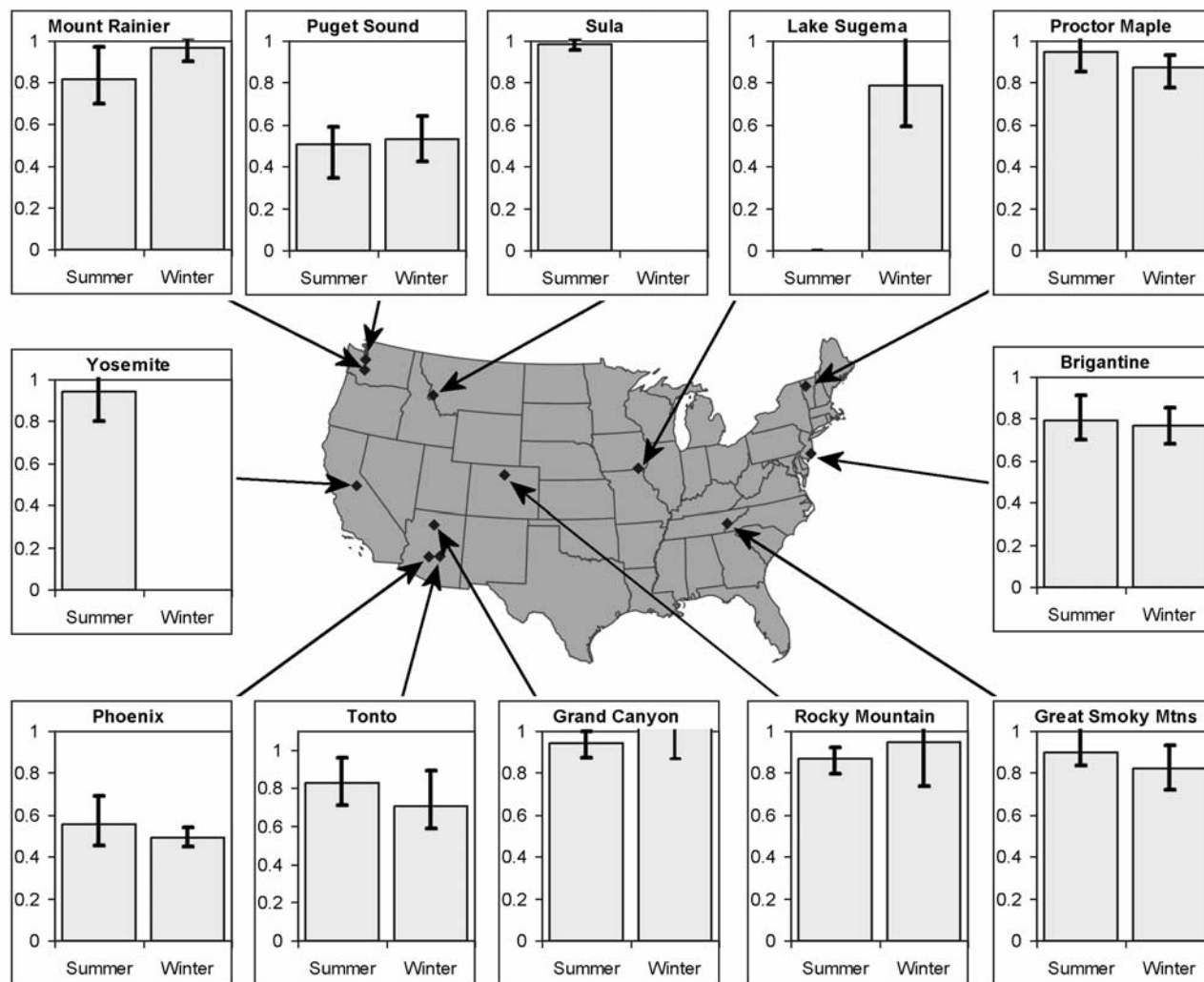
Figure 3. Seasonal average fraction contemporary carbon at each monitoring site. The whiskers represent the range in the 6-d fraction contemporary values in each season. The fraction contemporary is the ratio of average contemporary carbon to average total carbon.

Puget Sound and Mount Rainier were not correlated (Figure 5).

[35] The fossil and contemporary concentrations and urban excesses for the Phoenix and Tonto sites are presented in Figures 6 and 7. The Phoenix urban excess has a seasonal pattern similar to that for Puget Sound. During the summer the average contemporary urban excess was small at 0.42 $\mu g/m^3$ or 17% of the contemporary carbon concentration, while the fossil urban excess was 1.53 $\mu g/m^3$ or 81% of the fossil carbon concentration in Phoenix. During the winter, both fossil and contemporary carbon had large urban excesses of 5.1 $\mu g/m^3$ and 4.5 $\mu g/m^3$, respectively, which represents more than 80% of the Phoenix winter fossil and contemporary carbon. The Phoenix and Tonto fossil and contemporary carbon during both the summer and winter were not correlated.

[36] These results imply that most of the fossil carbon at Puget Sound and Phoenix was due to local sources during both winter and summer. This is expected, owing to higher local emissions from fossil-carbon-rich sources such as vehicle exhaust, relative to the rural sites. Receptor model-ing using aerosol concentrations collected in Phoenix from 1995 through 1998 attributed about 50% of the PM$_{2.5}$ to the carbon-rich mobile sources [*Ramadan et al.*, 2000; *Lewis et al.*, 2003]. In Seattle, Washington, mobile sources were estimated to contribute to 30–40% of the PM$_{2.5}$ during the 2000–2001 winter season [*Kim et al.*, 2004].

[37] The small difference and the high correlation in the summertime contemporary carbon between Puget Sound and Mount Rainier indicate that the two monitors were influenced by a similar set of regional sources and the urban area does not appreciably contribute to the contemporary carbon or enhance the formation of contemporary SOC. Two important sources of contemporary carbon are biogenic SOC and biomass burning. The Northwest is a heavily forested area with high emissions of turpenes (NOAA Emission Inventory Mapviewer, available at http://map.ngdc. noaa.gov/website/al/nei99_v3/viewer.htm), precursors to biogenic SOC, so biogenic SOC is a likely contributor and would have similar concentrations in the urban and near-urban sites. Examination of the satellite-derived fire products from the National Oceanic and Atmospheric
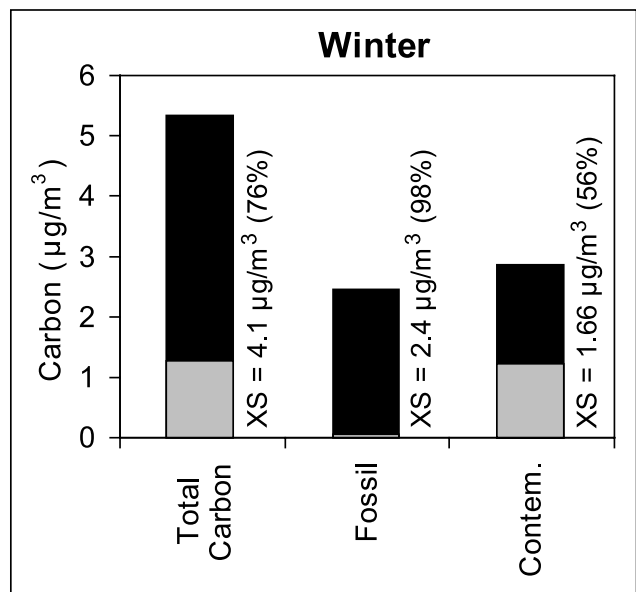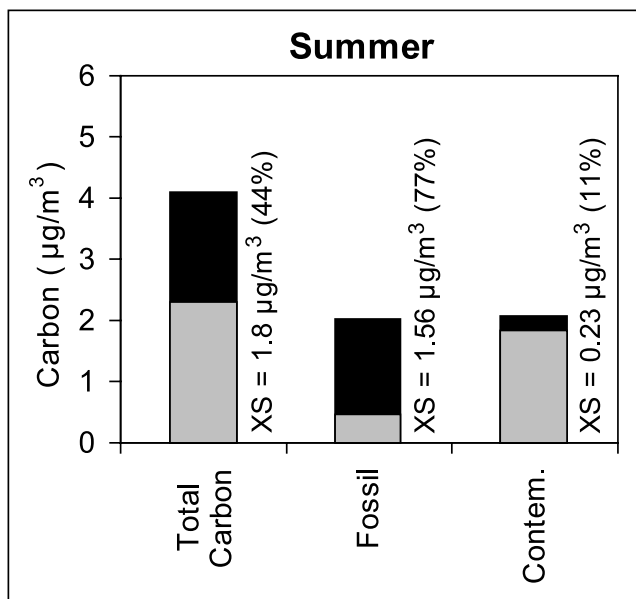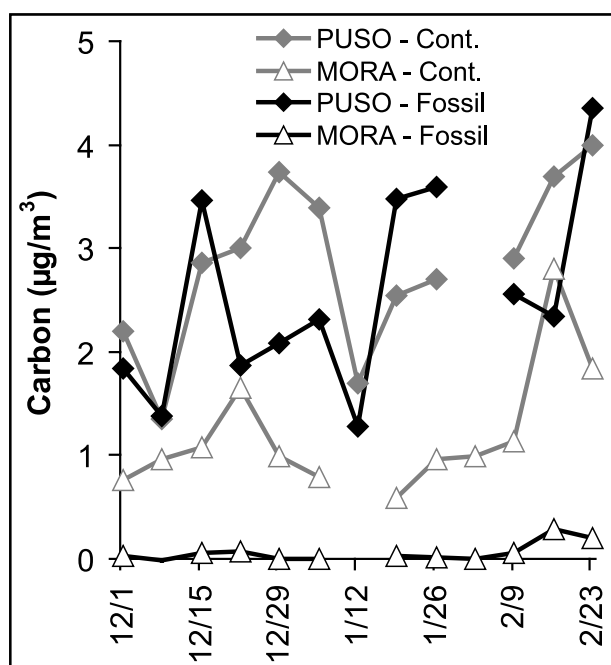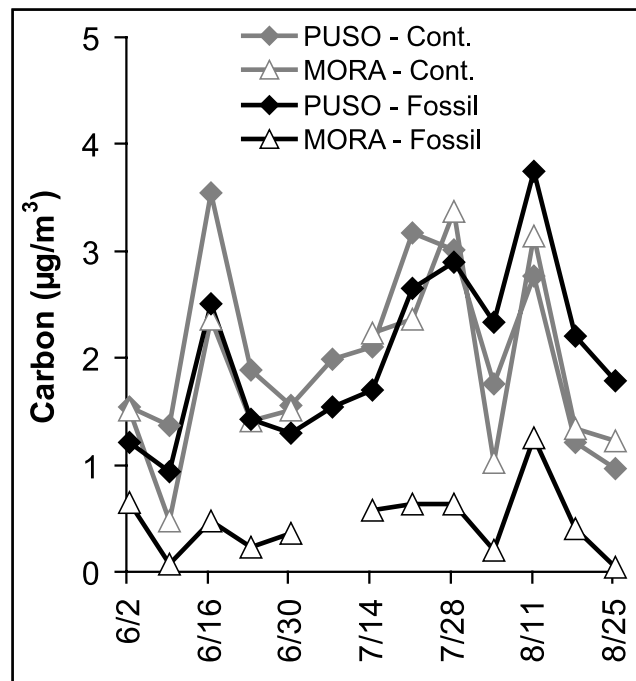
Figure 4. Comparison of the carbon concentrations between the urban Puget Sound and neighboring rural Mount Rainier monitoring sites. The gray bars are the concentrations at Mount Rainier and the black bars are the urban excess (XS = urban − rural).

Administration's (NOAA) Hazard Mapping System (HSM) (Satellite fire detections, available at http://www.ssd.noaa. gov/PS/FIRE/hms.html) identified few fires near the receptors. However, there were several large fires to the east, and the satellite fire products show smoke plumes from these fires impacting both receptors in late July and the middle of August.

[38] The Phoenix contemporary carbon excess was also small during the summer, but 6-d concentrations were not correlated. The lack of correlation was partly due to wildfires in the vicinity of Phoenix and Tonto during most of the summer sampling period. NOAA's HSM fire product (Sat-

ellite fire detections, available at http://www.ssd.noaa.gov/ PS/FIRE/hms.html) indicates that the most intense activity was from 29 June 2005 through 27 July 2005 when the highest contemporary carbon concentrations occurred. Biogenic VOC emissions also occur in Arizona, though at a much smaller rate than in the Northwest (http://www.epa. gov/asmdnerl/biogen.html).

[39] During the winter, the contemporary carbon urban excess was more than 50% at both Puget Sound and

Figure 5. Fossil and contemporary carbon concentrations at Puget Sound (PUSO) and Mount Rainier (MORA) for the (top) summer and (bottom) winter seasons.
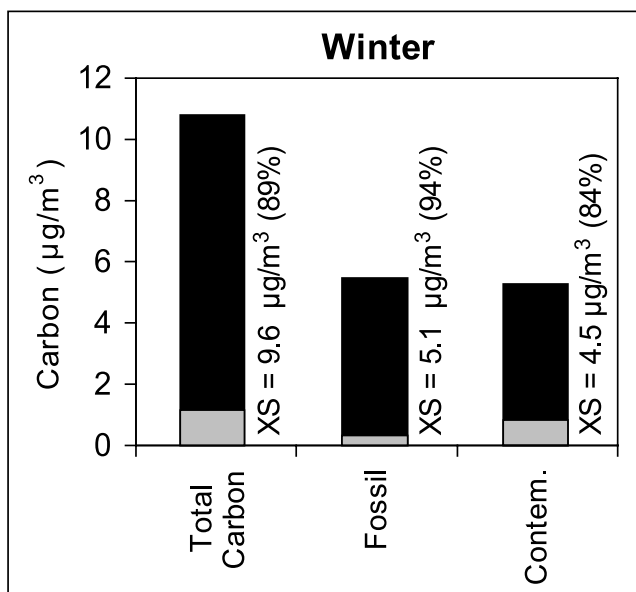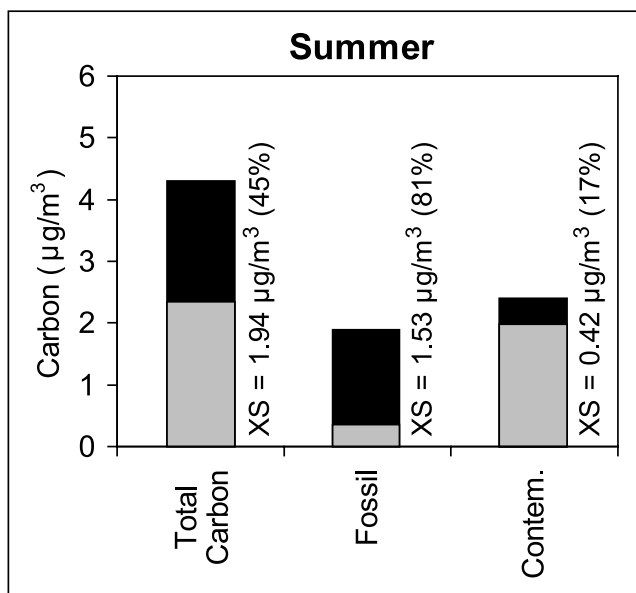
Figure 6. Comparison of the carbon concentrations between the urban Phoenix and neighboring rural Tonto monitoring sites. The gray bars are the concentrations at Tonto and the black bars are the urban excess (XS = urban − rural).

Phoenix. In addition, the winter contemporary carbon concentrations decreased at the rural sites compared to the summer but increased at the urban sites. The decrease at the rural sites can partly be attributed to little to no wildfire activity (Satellite fire detections, available at http://www.ssd.noaa.gov/PS/FIRE/hms.html) and reduced biogenic SOC [*Lack et al.*, 2004]. The increased contemporary carbon at the urban sites indicates increased contributions from anthropogenic sources. In Puget Sound, residential wood combustion (RWC) has been identified as a significant contributor to particulate carbon during the winter months. For example, *Kim et al.* [2004] estimate RWC

accounted for 45% of the measured PM$_{2.5}$ during the winter of 2000–2001. In Phoenix, receptor modeling estimated biomass burning during the winter months accounted for only ∼10% of the PM$_{2.5}$ concentrations [*Ramadan et al.*, 2000; *Lewis et al.*, 2003].

[40] RWC is not the only anthropogenic source of contemporary carbon. In a study conducted to understand the large fraction of contemporary carbon in Los Angeles,
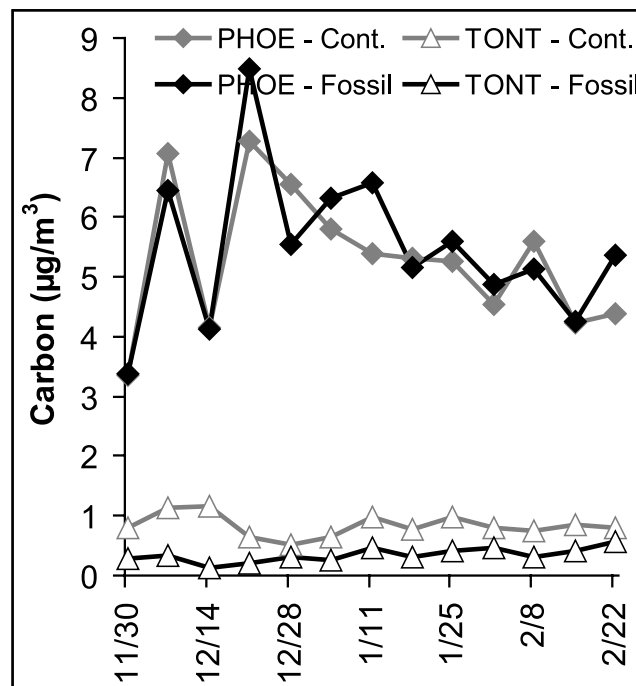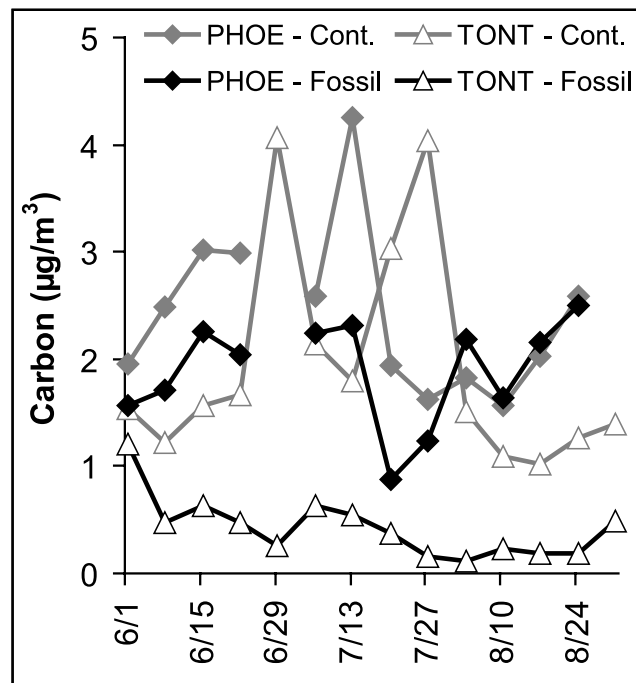
Figure 7. Fossil and contemporary carbon concentrations at Phoenix (PHOE) and Tonto (TONT) for the (top) summer and (bottom) winter seasons.
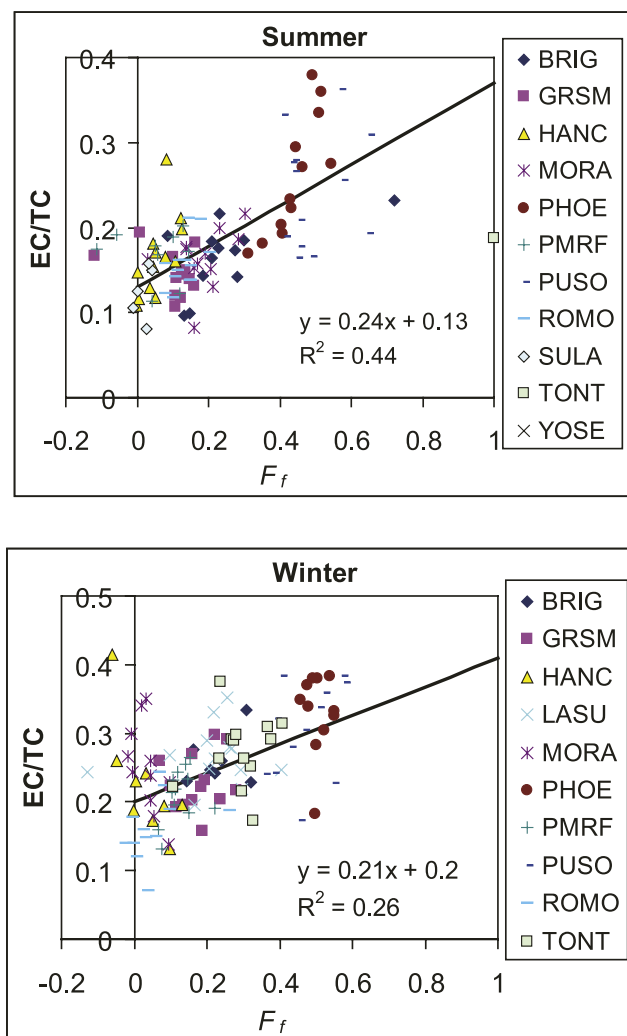
Figure 8. Scatterplot of the fraction of the fossil carbon (F_f) and EC/TC ratios for the 6-d sample periods. See Table 1 for site codes.

California, *Hildemann et al.* [1994] concluded that the contemporary carbon was largely due to anthropogenic sources from fireplaces, charcoal broilers, paved road dust, and cigarette smoke.

4.3. Relationship of Fossil and Elemental Carbon Concentrations

[41] OC aerosol is a mixture of primary and secondary fossil and contemporary carbon, while EC is assumed to be primary fossil or contemporary carbon. However, carbon concentrations are generally measured using thermal optical methods where the OC and EC split is operationally defined. Therefore EC concentrations can possibly contain contributions from SOC. For example, *Schauer et al.* [2003] analyzed laboratory-generated SOC using a TOT carbon analyzer and the IMPROVE temperature protocol and found that 2.2% ± 1% of the SOC was measured as EC. Circumstantial evidence of the contribution of SOC to measured EC in ambient samples was also found in a field study conducted in Yosemite, California, during 14 July through

5 September 2002. During this time period, even though the EC/TC ratio was relatively constant [*Malm et al.*, 2005], *Engling et al.* [2006] estimated the average contribution of SOC to OC varied from 21% to 82%, depending on the week. With the large relative increase in SOC, the EC/TC ratio was expected to decrease. The lack of a large decrease in the EC/TC could be due to SOC contributing to EC.

[42] The EC/TC ratios in emissions are source dependent, with fossil combustion typically having larger ratios than biomass combustion. These differences have been used to help distinguish between the contribution of mobile sources, biomass burning, and SOC to TC [*Turpin and Huntzicker*, 1991; *Chow and Watson*, 2002; *Lim and Turpin*, 2002; *Malm et al.*, 2004]. In several studies it has also been shown that the fraction fossil (F_f) increases with increasing EC/TC ratios [*Lemire et al.*, 2002; *Lewis et al.*, 2004; *Lewis and Stiles*, 2006]. The data collected in this study provide an opportunity to more fully explore and exploit the relationship between the EC and fossil carbon compositions over a number of different sites and for a winter and summer season.

[43] The EC/TC ratios were estimated from the carbon data collected at the collocated IMPROVE samplers. IMPROVE collects 24-h $PM_{2.5}$ samples every third day, so the two samples during each 6-d radiocarbon sample period were aggregated together. As shown in Figure 8, during both seasons the F_f increased with increasing EC/TC at similar rates, though the intercept (EC/TC = 0.2) during the winter is higher than the summer (EC/TC = 0.13). There is no discernable geographic difference in the relationship, with the EC/TC ratios and fraction fossil for all sites generally scattered around the ordinary least square (OLS) regression lines. However, the correlation is low with an r of 0.66 and 0.51 for the summer and winter, respectively.

[44] There are two sources of variability in the EC/TC to fossil carbon ratios in Figure 8. The first source is the variability in the EC/TC ratios from the different sources of fossil and contemporary carbon, as well as due to different atmospheric aging and contributions of SOC. The second source of variability is caused by differences in the $PM_{2.5}$ sample collection by the collocated Hi-Vol and IMPROVE samplers. Most important is the fact that the Hi-Vol measured a 6-d integrated sample and IMPROVE measured a 24-h sample every third day. This second uncertainty may be large. Comparisons of TC from the IMPROVE and Hi-Vol data had summer and winter r of 0.71 and 0.92, respectively, with the IMPROVE TC ~25% smaller than that from the Hi-Vol TC during both seasons. As noted, the difference is likely due to the inhomogeneity of the Hi-Vol samples. However, these correlations are lower than the correlation between the TC from the TOR and manometric analysis from the same Hi-Vol filters, which had an r = 0.97. This decreased precision is due to the additional uncertainty from the different samplers, operation, and sampling durations.

[45] To reduce the uncertainty and inherent variability, the radiocarbon and IMPROVE data were aggregated over each season for each site. The EC/TC ratios were calculated as the ratio of average EC and TC per the recommendation of *Chu* [2005]. As shown in Figure 9, the relationships have improved, with the r increasing to 0.84 for the summer and 0.93 for the winter. The strength in the linear relationship
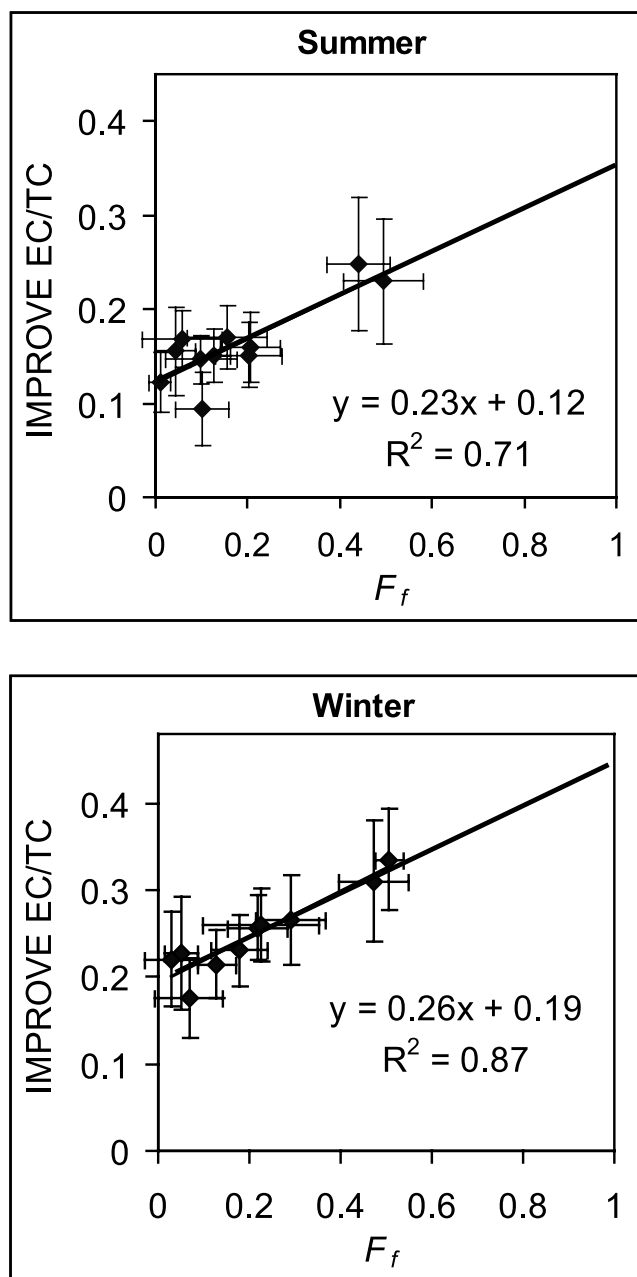
Figure 9. Scatterplot of the fraction of the fossil carbon (F_f) and EC/TC ratios for each site averaged over the summer and winter seasons. The whiskers are the standard deviations of the weekly data values.

between the EC/TC ratios and fossil/contemporary carbon content is surprising considering that the data were from urban and remote sites in different climatic regions across the United States.

[46] The linear relationship implies that the average EC/TC ratios for fossil and contemporary carbon are relatively constant across the sites. On the basis of this assumption, characteristic EC/TC ratios for fossil, $(EC/TC)_f$, and contemporary, $(EC/TC)_c$, carbon were derived by fitting a regression line through the data to estimate EC/TC ratios at $F_f = 1$ and $F_f = 0$, respectively. Several regression methods were applied to the data, including OLS, orthogonal, and Theil. All of the methods produced similar results, that is, within the standard error of the OLS regression. Therefore only the OLS regression results are presented and discussed. Table 2 presents the $(EC/TC)_f$ and $(EC/TC)_c$, their standard errors, and 95% confidence intervals estimated from the regression analysis. As shown, the standard errors in the ratios are relatively small with ~5% error in the winter ratios and ~10% for the summer ratios. The fossil and contemporary carbon EC/TC ratios were season-dependent, with significantly higher EC/TC ratios during the winter than summer. Part of the increased winter EC/TC is likely due to a decrease in the SOC contribution to total carbon. In addition, the mix of sources contributing to the carbon during the winter and summer will likely be different. For example, wildfires are a large contributor to carbon aerosol, and wildfire activity is at a minimum during the winter months [*Westerling et al.*, 2006].

[47] Although the relationship between the EC/TC and F_f in Figure 9 is good for both seasons, it is degraded in the summer compared to the winter season. One explanation for this is that there are additional geographical or site-to-site variations in the summer $(EC/TC)_f$ and $(EC/TC)_c$ that are masked by the characteristic values. The constant $(EC/TC)_c$ implies that all sites had similar relative contributions of SOC, which is questionable. Also, the EC/TC ratio of summertime contemporary sources impacting the monitoring sites can vary widely, even within the same source category. For example, the EC/TC from the flaming stage of wildfires is greater than EC/TC ratio from the smoldering stage [*Conny and Slater*, 2002; *Chakrabarty et al.*, 2006]. The linear relationship implies that these difference average out over a season. The good summertime relationship is also being driven by the high F_f (~0.5) at the two urban clusters and the low F_f (<0.21) at the nonurban sites. Therefore the summer $(EC/TC)_c$ is being defined by the nonurban data. Owing to these factors, the summer relationship may change as more data from different locations become available. With additional data, it may also be possible to derive region-specific EC/TC ratios.

4.3.1. Evaluation of the Fossil and Contemporary Carbon EC/TC Ratios

[48] Fossil and contemporary carbon EC/TC ratios can also be estimated from sources profiles of primary emissions and from ambient samples analyzed by TOR. The majority of primary fossil carbon aerosol is from mobile sources. *Gillies and Gertler* [2000] summarized over 200 source

Table 2. Summer and Winter Characteristic EC/TC Ratios for Contemporary and Fossil Carbon

	Summer			Winter		
	EC/TC	Standard Error	95% Confidence Interval	EC/TC	Standard Error	95% Confidence Interval
Contemporary carbon	0.12	0.011	0.024	0.19	0.0095	0.022
Fossil carbon	0.35	0.039	0.088	0.46	0.028	0.066

Table 3. Summary of Primary EC/TC Ratios From Mobile Sources Compiled by *Gillies and Gertler* [2000]

	Number of Profiles	Mean	Standard Deviation	Minimum	Maximum
Light duty gas vehicle[a]	109	0.34	0.22	0.02	0.94
Diesel[a]	39	0.61	0.25	0.01	0.91
Mixed ambient samples[b]	64	0.40	0.14	0.1	0.79

[a]Included data from SPECIATE, DRI, CE-CERT and NFRAQS.
[b]Included data from DRI.

profiles from light-duty gasoline vehicles (LDGV), diesel vehicles, and a mix of LDGV and diesel vehicles. The profiles were from the Environmental Protection Agency's (EPA) SPECIATE database [*Environmental Protection Agency*, 1999], the Desert Research Instituted (DRI) source profile database [*Gillies and Gertler*, 2000], the Northern Front Range Air Quality Study (NFRAQS) [*Fujita et al.*, 1998; *Watson et al.*, 1998], and source profiles developed by the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside [*Norbeck et al.*, 1998]. The source profiles included a wide variety of vehicles under different operating conditions and states of maintenance. As shown in Table 3, there was a broad range of EC/TC for LDGV and diesel, with EC accounting for ~2% to ~90% of the measured carbon. The EC/TC averages ± standard deviations were 0.34 ± 0.22 and 0.61 ± 0.25 for LDGV and diesel, respectively. The DRI database also contained source profiles from 64 mobile-source-dominated ambient samples. The benefit of these source profiles is that they contain contributions from a real-world distribution of vehicles. However, they also likely contain contributions from non-mobile sources. The average EC/TC ratio from these results was 0.4 ± 0.14, which is between the average LDGV and diesel ratios, with a narrower distribution.

[49] Table 4 summarizes the primary EC/TC ratios from the U.S. EPA's SPECIATE 3.2 and 4.0 databases for the combustion of biogenic material. This includes profiles for burning mixed vegetation, agricultural fields, prescribed fires, RWB, and meat cooking, which are major sources of primary contemporary carbon in urban and rural areas. A compilation of biomass burning source profiles of grass/savanna and temperate and tropical forests [*Reid et al.*, 2005] was also included. Other potential sources of contemporary carbon such as road dust, vegetative detritus, and cigarette smoke have generally been found to have small contributions to TC [e.g., *Hildemann et al.*, 1994; *Zheng et al.*, 2006] and were not included. As shown, the variability of the EC/TC ratios in individual source profiles is large, varying from 0 to 0.86. The average of the composite EC/TC ratios across the studies is 0.13, with a standard deviation of 0.11.

[50] The fossil and contemporary carbon EC/TC ratios can also be estimated from the range of EC/TC values from the IMPROVE TOR data. Figure 10 presents the scatterplots of EC and TC from all 164 IMPROVE rural sites and 13 urban sites for the winter and summer season during June 2004 through February 2006. The rural and urban sites were located throughout the United States (Figure 1). The

well-defined or hard edges, such as the upper edges for the winter and summer urban EC and TC data, can be indications of contributions from a single source type [*Henry*, 1997]. Edges with more variability, such as the lower edge for the winter rural EC and TC data, are indications of contributions from more than one source type. The 90th and 10th percentiles of the EC/TC ratios were used to estimate the slope of these edges, and the 82th and 98th and 2nd and 18th percentiles were used as a measure of their variability. The results are presented in Table 5.

[51] The urban sites have large contributions from fossil carbon sources, and EC/TC for fossil carbon is typically larger than for contemporary carbon. Therefore the 90th percentile of the urban EC/TC is interpreted as the characteristic $(EC/TC)_f$ with values of 0.41 and 0.44 for the summer and winter, respectively. Since the wintertime OC in urban areas is thought to be mostly primary in origin [*Chu and Macias*, 1981; *Strader et al.*, 1999; *Chu et al.*, 2004], the winter $(EC/TC)_f$ is assumed to be representative of primary emissions. The similarity between the winter and summer values indicates that the summer $(EC/TC)_f$ is also representative of primary emissions, since large contributions of SOC would likely further decrease this ratio below the winter values.

[52] The $(EC/TC)_c$ is estimated by the lower edge of the scatter at the rural sites, based on the fact that contemporary carbon is the largest contributor to the rural sites and the $(EC/TC)_c$ is smaller than for fossil carbon. However, these are also likely to have contributions from SOC, particularly during the summer months, and should be considered as ratios for contemporary and SOC-dominated carbon concentrations. SOC contribution is also suggested in Figure 10, where the lower edges of the rural EC and TC data are less

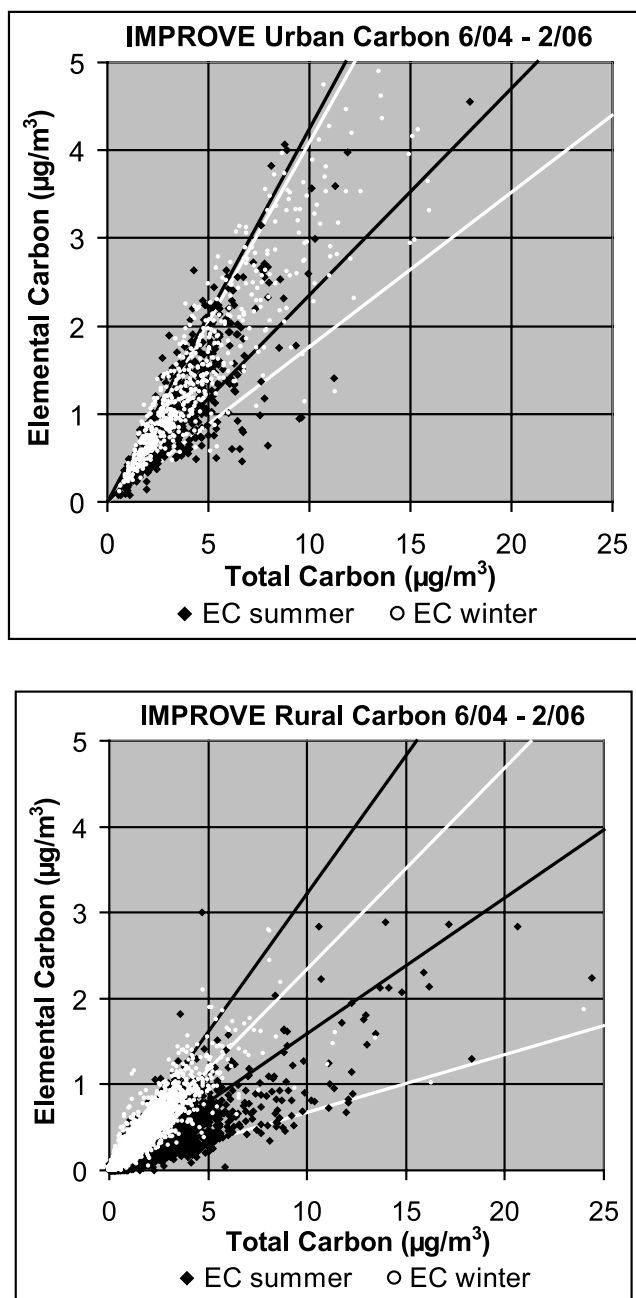**Table 4.** Summary of Primary EC/TC Ratios From Biogenic (Contemporary) Combustion Sources

	EC/TC	Standard Deviation	Minimum	Maximum
U.S. EPA SPECIATE 3.2- Composite Values[a]				
Residential wood combustion	0.21	0.10	0.056	0.46
Slash burning	0.14	0.088	0.018	0.34
Agricultural field burning	0.14	0.047	0.14	0.23
Forest prescribed burning - broadcast conifer	0.096	0.062[b]	–	–
Meat cooking	0	–	–	–
U.S. EPA SPECIATE 4.0[a]				
All cooking	0.069	0.056	0.004	0.18
Burning	0.22	0.18	0.028	0.86
Reid et al. [2005][a]				
Mixed vegetation burning	0.14	0.1	0.04	0.38
Overall composite	0.13[c]	0.12[d]	0	.86

[a]The EC/TC ratios are the reported composite values. The standard deviation and minimum and maximum EC/TC ratios are derived from the reported results from individual studies in the SPECIATE database.
[b]Estimated from the reported uncertainties in the SPECIATE 3.2 database.
[c]The average EC/TC ratio from all source profiles in the table.
[d]The overall composite standard deviation was calculated by modeling each source profile as a normal distribution using the mean and standard deviation reported in the table. All profiles were given equal weight in the aggregation. Meat cooking was not included since a standard deviation was not available.

Figure 10. Scatterplot of the total carbon and elemental carbon concentrations measured at the 13 urban and 164 rural IMPROVE monitoring sites.

Table 4 are used for the contemporary carbon ratios. The overall composite contemporary EC/TC and its standard deviation were derived by aggregating the contemporary carbon source profiles in Table 4. No attempt was made to weight the profiles by their assumed contributions to the different sites since this information is not available.

[54] As shown, there is good correspondence between the $(EC/TC)_f$ across the three methods for both seasons, with all three methods within 5–15% of each other. This is within the estimated range of EC/TC values for each method. There is more variability in the comparison of the $(EC/TC)_c$. During the winter, the average $(EC/TC)_c$ from the radiocarbon is 20% and 60% greater than the estimate from the TOR data and source profiles, respectively, and is near or above their upper range. The radiocarbon $(EC/TC)_c$ is also above or at the upper end of the range of $(EC/TC)_c$ estimated from the source profiles and TOR data. During the summer, the average $(EC/TC)_c$ estimated by the radiocarbon is about equal to the average values from the source profiles and twice the ratio estimated from the TOR data.
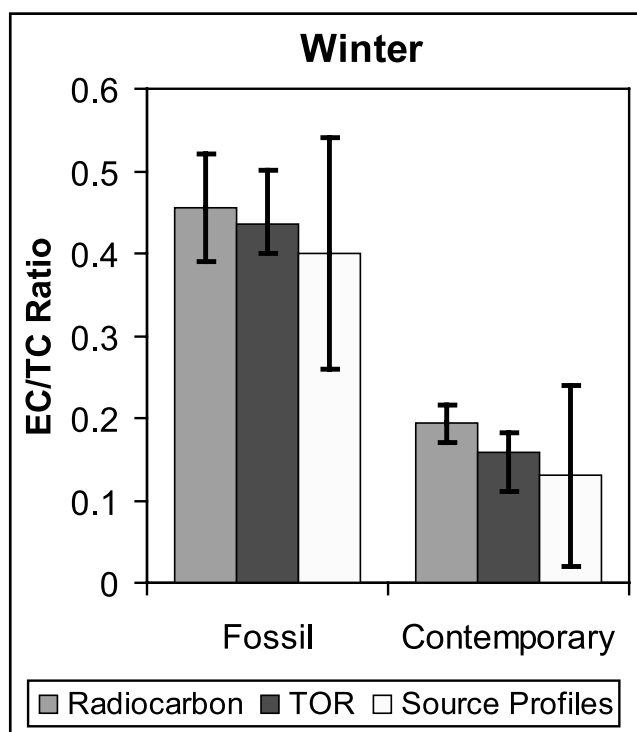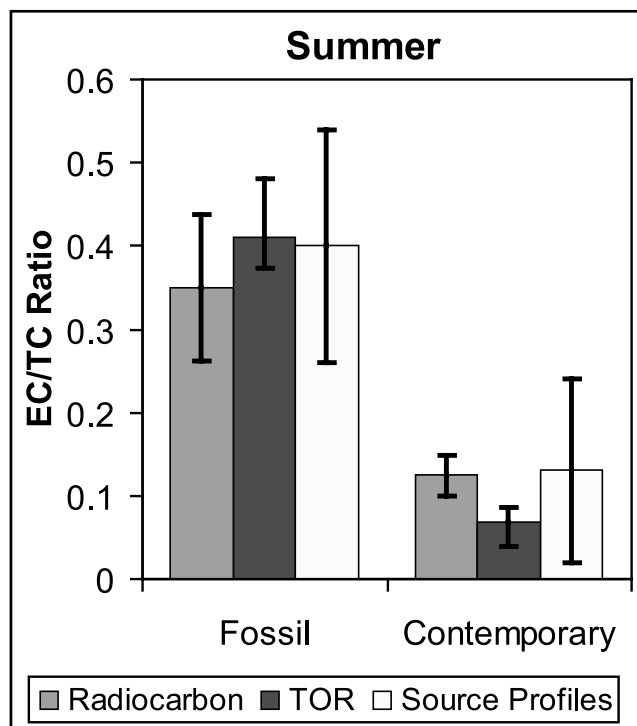
[55] The comparison of the fossil and contemporary EC/TC ratios is somewhat confounded by the different contributions of SOC to TC in the three methods. SOC formation is at a minimum during the winter months, so the fossil and contemporary EC/TC ratios from all three methods are mostly primary carbon and should be directly comparable. Therefore these results indicate that the winter radiocarbon $(EC/TC)_f$ is consistent across the methods, but the winter $(EC/TC)_c$ estimated from the radiocarbon data is higher than the other two methods.

[56] During the summer, the EC/TC ratios from the radiocarbon data will most likely be influenced by SOC, but the ratios from the measured source profiles are meant to only reflect primary particulate emissions. The EC/TC ratios from the TOR data will also be influenced by SOC, but, as previously discussed, this is thought to be small for the fossil ratios but large for the summer contemporary ratios. The summer radiocarbon $(EC/TC)_c$ is larger than the estimate from the TOR data, but the summer radiocarbon $(EC/TC)_f$ is generally smaller than the estimate from the TOR. This is consistent with the assumed varying contributions of SOC. The source profiles have a broad range of $(EC/TC)_f$ and $(EC/TC)_c$ and the summer radiocarbon ratios are within these ranges. Therefore these results indicate that the summer radiocarbon ratios are consistent with the other two methods.

well defined compared to the upper edges for the urban data. As shown in Table 5, the estimated contemporary carbon EC/TC ratio is 0.16 in winter and is 0.07 in summer.

[53] In Figure 11, the fossil and contemporary EC/TC ratios derived from the radiocarbon data are compared to the range of EC/TC ratios estimated from the measured source profiles and the analysis of EC and TC data. The error bars for the radiocarbon EC/TC ratios are the 95% confidence intervals in Table 2. The measured source profiles for fossil carbon and error bars are from the mixed ambient samples and standard deviations for mobile sources in Table 3, while the overall composite EC/TC and its standard deviation in

Table 5. Percentiles of the EC/TC Ratios for Urban and Rural Monitoring Sites in the IMPROVE Network[a]

Percentile	90th	82nd–98th	10th	2nd–18th
		Rural		
Winter	0.32	0.29–0.41	0.16	0.11–0.18
Summer	0.23	0.2–0.3	0.07	0.04–0.09
		Urban		
Winter	0.44	0.4–0.5	0.24	0.17–0.26
Summer	0.41	0.37–0.48	0.18	0.11–0.21

[a]The percentiles were calculated for a winter (December, January, February) season and summer (June, July, August) season using IMPROVE carbon data from June 2004 to February 2006.

Summary

Summer

Winter

Figure 11. Characteristic fossil and contemporary EC/TC ratios derived from the radiocarbon compared to the EC/TC ratios estimated from source profiles and EC and TC measurements. The fossil EC/TC from the source profiles is only for mobile sources.

[57] All three methods are indirect measures of the ambient $(EC/TC)_f$ and $(EC/TC)_c$. Ideally, one would directly measure the fractions fossil and contemporary in the EC and OC fractions of the particulate carbon. *Szidat et al.* [2006]

have done this for samples collected in Zurich, Switzerland, during 12 August to 8 September 2002 and 17 February to 26 March 2003. They found a high correlation between fossil OC and fossil EC with r = 0.9 and OC/EC = 1.47 ± 0.08 or $(EC/TC)_f = 0.41$. This is between the summer (EC/TC)$_f$ of 0.35 and winter $(EC/TC)_f = 0.46$ found in this study. The correspondence is encouraging, but *Szidat et al.* [2006] used a different thermal technique from TOR for separating the EC and OC fractions. It is not known how the OC/EC split between the two methods differs and what impact this has on the results.

4.4. Fraction Contemporary Carbon at IMPROVE Monitoring Sites

[58] The OLS regression line in Figure 9 relates EC/TC to the F_f and can be written as

$$(EC/TC) = \left[(EC/TC)_f - (EC/TC)_c \right] * F_f + (EC/TC)_c \quad (1)$$

where $(EC/TC)_c$ and $(EC/TC)_f$ are the characteristic EC/TC ratios for contemporary and fossil carbon. Solving equation (1) for the F_f, F_c can be written in terms of the EC/TC ratios:

$$F_c = \left(1 - F_f \right) = \frac{(EC/TC)_f - (EC/TC)}{(EC/TC)_f - (EC/TC)_c} \quad (2)$$

[59] Equation (2) and the $(EC/TC)_c$ and $(EC/TC)_f$ ratios derived from the radiocarbon data were used to partition the IMPROVE carbon concentrations into fossil and contemporary fractions for the summer (June–August) and winter (December–February) seasons using carbon data from December 2004 through February 2006. Equation (2) is unconstrained and F_c can be less than 0 and greater than 1. This is due to errors in the estimates of $(EC/TC)_c$ and $(EC/TC)_f$ and measured EC/TC. In this analysis there were no negative values, but values greater than 1 did occur. All values greater than 1 were set equal to 1. As previously discussed, the radiocarbon-derived $(EC/TC)_c$ appears to be high compared to other estimates. If the $(EC/TC)_c$ is overestimated, then the calculated F_c will be overestimated and F_f underestimated.

[60] The results and their uncertainties are presented in Figure 12 as isopleth maps. These maps were created by spatially interpolating the F_c at each site using a Kriging algorithm. The spatial interpolation is to help visualize the spatial patterns in the data and is not meant to estimate the F_c between the sites. For example, the Kriging method has artificially spread the low F_c at the two urban sites in Atlanta, Georgia, and Birmingham, Alabama, to the surrounding rural areas. The uncertainties in Figure 12 were estimated from the propagation of $(EC/TC)_f$ and $(EC/TC)_c$ standard errors reported in Table 2. The calculation of F_c amplifies the uncertainties in $(EC/TC)_f$ and $(EC/TC)_c$, resulting in errors of 11 to 24 percentage points, depending on the season and F_c. The contour intervals used in Figure 12 are 0.15 or approximately 1 standard error. Consequently, differences of 1 contour level or less are not considered to be significant.

[61] As shown, F_c was 60% or less of the total carbon at the 13 urban sites for both the winter and summer seasons, which is consistent with the radiocarbon measurements in
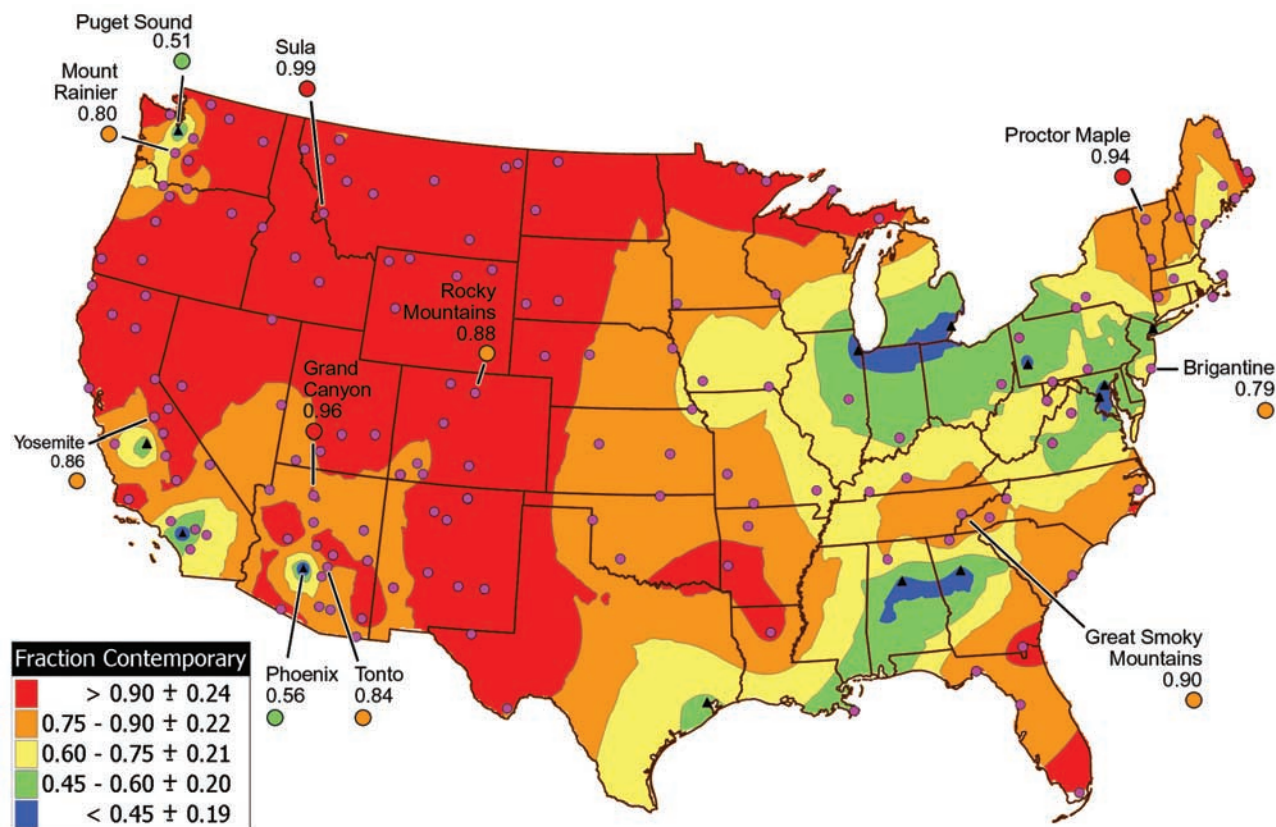
Figure 12. Average contemporary fraction of PM$_{2.5}$ carbon for the summer and winter (next page) estimated from the December 2004 to February 2006 IMPROVE carbon data. The circles are rural IMPROVE sites and triangles urban IMPROVE sites. The measured contemporary fraction of PM$_{2.5}$ carbon at the 12 sites used in this study is also indicated on the maps. The data are spatially interpolated using a Kriging algorithm to help visualize spatial patterns in the data.

the Phoenix and Puget Sound urban sites. In the rural West, over 90% of the carbon was contemporary during the summer, except in the Southwest where F_c was 75–90% and in southern California where F_c was about 60% or less. In the rural northeastern and southeastern United States, 75–90% of the carbon was contemporary during the summer. However, there is a large region from Illinois to the eastern seaboard where only 45–60% of the carbon was contemporary. This is a region with a high population density and high industrial and farming activities. These F_c values are consistent with those measured at the near-urban sites (Figure 3).

[62] During the winter, the F_c generally decreases in most of the West to 45–90%. However, in much of the northwestern United States, contemporary carbon still constituted over 90% of the carbon. In the eastern United States, the winter F_c was 60–90% in the rural areas. With the exception of the southwestern United States, the differences between the winter and summer F_c are generally less than 1 standard error in the analysis and not significant. Consequently, the seasonal differences are smaller than the uncertainty in this analysis. This is consistent with the data from the nine sites with both summer and winter radiocarbon measurements where the differences between the summer and winter F_c were 15 percentage points or less

(Figure 3). *Bench et al.* [2007] also examined the winter and summer differences in these radiocarbon concentrations. They found that while there were significant differences in the concentrations of the contemporary carbon at most sites, most sites did not have significant differences in the contemporary carbon fractions.

4.4.1. Estimation of the Average SOC Contribution to Fossil and Contemporary Carbon

[63] If it is assumed that all EC is primary and the average primary EC carbon fraction, $(EC/TC)_P$, from the contributing sources' emissions to the air shed, is relatively constant and known, then the secondary organic carbon fraction (SOC/TC) can be written as

$$SOC/TC = \left[1 - (EC/TC)/(EC/TC)_P\right] \qquad (3)$$

where $(EC/TC) \leq (OC/EC)_P$.

[64] This is known as the EC tracer method, and has been used in a number of studies to investigate and estimate the contribution of SOC to TC [*Turpin and Huntzicker*, 1991; *Lee and Huang*, 1993; *Castro et al.*, 1999; *Lemire et al.*, 2002; *Lim and Turpin*, 2002; *Cabada et al.*, 2004; *Lewis et al.*, 2004; *Yu et al.*, 2004]. In addition, *Lewis and Stiles* [2006] use the EC tracer method to qualitatively examine the contributions of SOC to contemporary carbon.
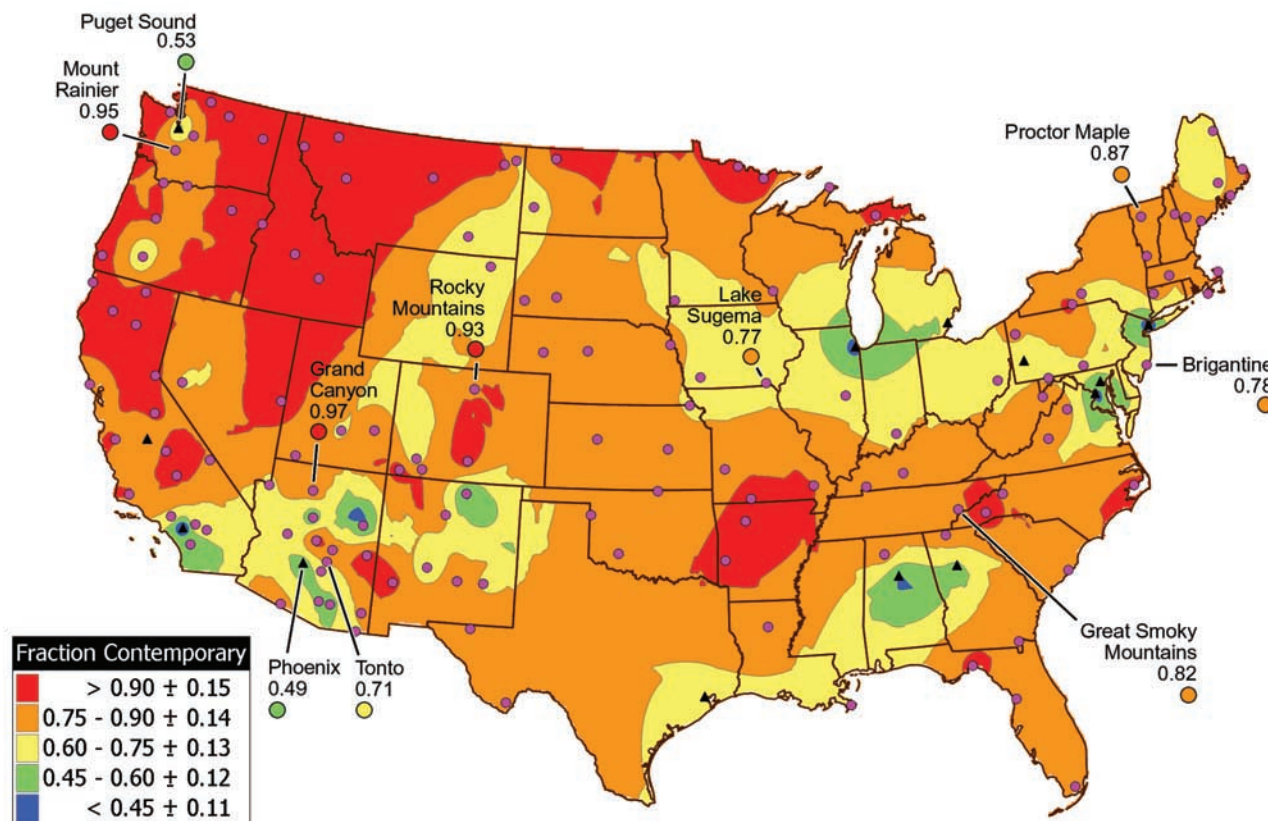
Figure 12. (continued)

[65] Provided the primary EC carbon fractions for fossil and contemporary carbon are known, the EC tracer method can be used to estimate the contribution of SOC to fossil and contemporary carbon for known $(EC/TC)_f$ and $(EC/TC)_c$ ratios. Characteristic $(EC/TC)_f$ and $(EC/TC)_c$ ratios were derived for the winter and summer seasons (see Table 2). As discussed, the winter ratios are interpreted as representative of primary particulate carbon emissions, but the summer ratios have contributions from both primary and secondary particulate carbon. Therefore assuming that the winter EC/TC ratios are representative of the primary carbon emission during the summer, one can estimate the average fossil and contemporary SOCs by setting the (EC/TC) and $(EC/TC)_p$ in equation (3) to the corresponding summer and winter ratios, respectively (see Table 2).

[66] The results of this analysis are presented in Table 6. As shown, the SOC accounted for $41 \pm 7.3\%$ of the contemporary OC and $36 \pm 15\%$ of the fossil OC. Since fossil carbon has a larger EC fraction, the difference in the SOC contribution increases compared to the TC, with SOC accounting for $36 \pm 6.4\%$ of the total contemporary carbon and $23 \pm 10\%$ of the total fossil carbon.

[67] These results indicate that a large and similar fraction of both fossil and contemporary OC during the summer months is SOC. However, these are average results based on a limited data set and limiting assumptions. The primary EC/TC ratios were derived from winter data, assuming no SOC. There is likely some SOC during the winter, particularly in the southern sites such as Phoenix, Arizona, and Tonto, Arizona. This will cause an underestimation of the

summer SOC. In addition, winter and summer seasons are likely to have different mixtures of fossil and biogenic sources of carbon with different EC/TC ratios. For example, contributions from wildfires and pollen occur more often in the summer than winter. It is not known how the errors in the assumptions would affect the results. Last, these results do not account for any geographical variation, but emissions of fossil and biogenic SOC precursors and the formation rates of SOC vary widely [*Lack et al.*, 2004]. For example, *Lemire et al.* [2002] showed that a large fraction of the contemporary carbon in and near Houston, Texas, during August was likely SOC, but in a study of the formation of water soluble organic carbon (WSOC) in urban plumes in the northeastern United States, *Sullivan et al.* [2006] found evidence of contributions of fossil sources to secondary WSOC but no direct evidence of the secondary formation of

Table 6. Estimate of the Contribution of Secondary Organic Carbon to the Particulate Fossil and Contemporary Fractions[a]

	Primary, %	Secondary, %
SOC/TC		
Contemporary	64 ± 6.4	36 ± 6.4
Fossil	77 ± 10	23 ± 10
SOC/OC		
Contemporary	59 ± 7.3	41 ± 7.3
Fossil	64 ± 15	36 ± 15

[a]Errors were estimated by propagating the characteristic EC/TC standard errors reported in Table 2.

WSOC from biogenic sources. Owing to these limiting assumptions, the SOC estimates should be considered semiquantitative and not representative of any single geographical area.

5. Conclusions

[68] In this study we further analyzed fossil and contemporary carbon concentrations estimated from radiocarbon data collected in two different field studies [*Bench and Herckes*, 2004; *Bench et al.*, 2007]. The combined data were from 12 sites in urban, near-urban, and remote areas, and data were collected at most sites during both a winter and summer season. About half of the fine particulate carbon at the two urban areas was composed of contemporary carbon. At the near-urban sites, the fraction of contemporary carbon was 70–97%, depending on the monitoring site location and season, and ~80% on average. The highest fractions of contemporary carbon were at the remote sites, with seasonal averages (F_c) between 82% and 100%. These high levels of contemporary carbon across all sites are consistent with previous radiocarbon studies as well as current emissions inventories and receptor- and source-oriented modeling studies.

[69] Phoenix, Arizona, and Seattle, Washington, each had a monitoring site within the urban area and another rural monitor site within ~90 km at similar elevations. These urban/rural pairs were used to examine the urban excess, that is, a measure of the total contribution from urban sources and possibly enhanced SOC formation rates of the background organic gases. The results indicate that most of the urban fossil carbon during the summer and winter was locally produced. During the summer months, there was a small urban contemporary carbon excess of 11% at Seattle, indicating that the contemporary carbon concentrations and sources were regionally distributed and the urban area added little to these concentrations. The small urban excess also implies that enhanced formation of biogenic SOC in the urban area is at most a small contributor to the summer urban carbon concentrations. Phoenix also had a small summer contemporary carbon excess, but the interpretation of these results was complicated by varying contributions from local wildfires. During the winter months, the urban contemporary carbon excess was over 50% at Seattle and over 80% at Phoenix. The contemporary carbon was also about half of the measured fine particulate carbon. Consequently, anthropogenic sources of contemporary carbon are likely a significant contributor to the winter carbon concentrations in these two urban centers.

[70] Estimates of the OC and EC from TOR analysis were also available at each site. It was found that when the data were aggregated over each season, the fractions of fossil carbon were proportional to the EC/TC ratios across the sites. These results were used to derive characteristic EC/TC ratios for fossil and contemporary carbon. The winter and summer EC/TC ratios for fossil carbon were 0.35 ± 0.039 and 0.46 ± 0.028, respectively, and for contemporary carbon were 0.12 ± 0.011 and 0.19 ± 0.0095, respectively. The fossil EC/TC ratios are consistent with estimates from measured source profiles and empirically derived EC/TC ratios from rural and urban carbon measurements. However, the winter contemporary carbon EC/TC ratio was higher compared to the other estimates and the comparison of the summer contemporary carbon EC/TC ratio was confounded by varying contributions of SOC to the different methods.

[71] A semiquantitative and likely lower bound estimate of the average contribution to the summer fossil and contemporary carbon concentrations was made by assuming that the winter EC/TC ratios were representative of primary emissions and the decreased summer ratios were due to increased TC from the formation of SOC. The results indicate that the SOC accounts for more than a third of the fossil and contemporary carbon.

[72] These characteristic fossil and contemporary EC/TC ratios were also used to estimate the average fraction of fossil (F_f) and contemporary (F_c) carbon from the IM-PROVE fine particulate carbon concentrations to develop a national picture of the F_f and F_c at mostly rural locations in the conterminous United States. The results were consistent with the radiocarbon results for the urban, near-urban, and rural sites. At the rural sites, the high F_c occurred in the Northwest, generally greater than 0.90. In the eastern United States, there was a region of low F_c from Illinois to the Atlantic seaboard with F_c generally less than 0.75 and $F_c > 0.75$ in the surrounding area. The differences in the winter and summer F_c were generally not significant, except in the southwestern United States, where $F_c > 0.75$ in the summer but between 0.45 and 0.75 in the winter.

[73] The estimations of the F_c at the IMPROVE monitoring sites and the fossil and contemporary SOC are based on a number of assumptions, most importantly, valid and stable estimates of the fossil and contemporary EC/TC ratios. As more data becomes available, these ratios can be refined and it may be possible to derive geographically varying ratios. A recommendation for future work is to directly measure the fossil and contemporary carbon in the EC and OC fractions of the sampled particulate carbon. To be consistent with this work, the method for separating the EC and OC carbon for analysis would need to be equivalent to the IMPROVE TOR carbon analysis technique.

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