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Editors

Isoscapes

Understanding Movement, Pattern, and
Process on Earth Through Isotope Mapping

 Springer

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Cover illustration: Top right: A monarch butterfly. *Top center:* A Boreal landscape in northeastern Alberta, Canada. Oxbow lakes surrounding the Winifred River channel situated 4 km east of the Christina River confluence, looking north. Photo provided courtesy of Alberta Research Council (photo taken 13 September 2007). *Bottom center:* A leaf water isoscape provided courtesy of Jason West (see Chapter 8, this volume).

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Chapter 19

The Carbon Isotope Composition of Plants and Soils as Biomarkers of Pollution

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19.1 Introduction

Urban environments have been compared to the global environment predicted at the end of the twenty-first century, in that urban areas are currently experiencing elevated atmospheric CO₂ concentrations, warmer temperatures, increased nitrogen loads, and elevated concentrations of pollutants (Grimm et al. 2000). It is extremely difficult to predict ecosystem responses to multiple atmospheric and climatic perturbations (Norby and Luo 2004), yet such predictions are critical, both for understanding global change as well as for quantifying critical ecosystem processes in urban areas in which large numbers of people live and work. Plants and soils in urban areas provide important ecosystem services for urban residents which may be adversely impacted by multiple pollutants in the urban environment. There is a great need for methodology to understand the effects of multiple pollutants on plants, soils, and ecosystem services, as well as for mapping ecosystem pollutant exposure and the distribution of pollutants at municipal, regional, and continental scales.

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Stable isotopes in organic matter are affected by exposure to many environmental pollutants and disturbances. Plants that utilize pollution-derived nitrogen (N) have been shown to have distinct nitrogen isotope ratios ($\delta^{15}\text{N}$) from plants using natural N sources (Ammann et al. 1999; Saurer et al. 2004; Stewart et al. 2002). Plant exposure to elevated CO_2 and oxidant pollutants such as ozone and sulfur dioxide have been shown to affect stable carbon isotope ratios ($\delta^{13}\text{C}$) (Boeckx et al. 2006; Dongarrà and Varrica 2002; Grams et al. 2007; J drysek et al. 2003; Lichtfouse et al. 2003; Norra et al. 2005; Novak et al. 2007; Saurer et al. 2003; Savard et al. 2002). However, both the magnitude and direction of reported isotope effects (both enrichments and depletions) have been reported in different experiments and regions, such that it can be difficult to extract general trends.

A somewhat newer application is the use of radiocarbon (^{14}C) to quantify uptake of fossil fuel-derived CO_2 by plants and to track plumes of fossil fuel CO_2 in surface air. Here we review the basis for the use of radiocarbon as a pollution tracer, recent studies that quantified spatial and temporal distributions of radiocarbon in plant "biomarkers," and the relationships between radiocarbon and other isotope tracers in polluted environments.

19.2 Radiocarbon Methodology and Notation

Radiocarbon is most widely known as a method of dating due to its half life of 5700 ± 30 years. Another common application utilizes anthropogenic levels of radiocarbon that were introduced into the atmosphere by aboveground atomic weapons testing in the 1950s and 1960s. Detonations of hydrogen bombs in the late 1950s and early 1960s introduced a "spike" in atmospheric $^{14}\text{CO}_2$ that abruptly declined following the 1963 Test Ban Treaty, primarily due to dilution by gross ocean-atmosphere and biosphere-atmosphere carbon exchange (Levin and Heshaimer 2000; Randerson et al. 2002). Because organic material created in the last several decades contains detectable, elevated levels of ^{14}C relative to the pre-atomic testing period, the ^{14}C "bomb spike" has become a very useful tracer of the age of organic matter in ecosystems and the turnover time of carbon in soils (Trumbore, 1996, 2000; Wang and Hsieh 2002).

In urban areas, atmospheric CO_2 is elevated in concentration due to combustion of fossil fuel (Idso et al. 1998, 2001; Koerner and Klopatek 2002; Pataki et al. 2003a, 2005a, b, 2007). Because fossil fuels are much older than the half life of ^{14}C , the application of radiocarbon methods for mapping fossil fuel exposure is somewhat different than its application as a tracer of carbon age and turnover time. Fossil fuels are old enough to contain virtually no ^{14}C , as all of the ^{14}C present in the original organic matter has decayed to ^{14}N . This creates a very distinct tracer of fossil-fuel derived CO_2 . To fully describe this tracer, we must review the notation of radiocarbon isotope ratios, which differs from the notation for stable isotopes.

The radiocarbon fraction modern (F) compares the $^{14}\text{C}/^{12}\text{C}$ ratio of the sample to $^{14}\text{C}/^{12}\text{C}$ of the standard NIST Oxalic Acid I:

$$F = \frac{\frac{^{14}\text{C}}{^{12}\text{C}}_{\text{sample}[-25]}}{0.95 \frac{^{14}\text{C}}{^{12}\text{C}}_{\text{oxalic}[-19]}} \quad (19.1)$$

The $^{14}\text{C}/^{12}\text{C}$ ratio of the oxalic acid standard is multiplied by 0.95 to correct for radioactive decay between the pre-industrial atmosphere of 1895 and 1950, which is considered “modern” by definition (Stuiver and Polach 1977; Trumbore 1996). The notation $[-25]$ and $[-19]$ refer to corrections for mass dependent fractionation. Because radiocarbon is principally used for dating and for geochemical applications in which mass dependent fractionation is not the process of interest, $^{14}\text{C}/^{12}\text{C}$ ratios are corrected for mass dependent fractionation based on stable carbon isotope ratios, with the assumption that mass dependent fractionation of ^{14}C in relation to ^{12}C is twice as large as fractionation of ^{13}C relative to ^{12}C . The Oxalic Acid standard has a stable carbon isotope ratio of -19‰ in conventional δ notation relative to V-PDB, while all other samples are corrected to an average, C_3 $\delta^{13}\text{C}$ of -25‰ by convention:

$$\frac{^{14}\text{C}}{^{12}\text{C}}_{\text{sample}[-25]} = \frac{^{14}\text{C}}{^{12}\text{C}}_{\text{sample}[\delta]} \left[1 - \frac{2(25 + \delta)}{1000} \right] \quad (19.2)$$

where δ is the measured $\delta^{13}\text{C}$ of the sample relative to V-PDB. Based on measurements of the specific activity of the oxalic acid standard, its $^{14}\text{C}/^{12}\text{C}$ is 1.231×10^{-12} (1950 value), or 1.245×10^{-12} after correction to a $\delta^{13}\text{C}$ of -19‰ (Karlén et al. 1964; Roberts and Southon 2007). Direct determination of $^{14}\text{C}/^{12}\text{C}$ of the standard by accelerator mass spectrometry has yielded slightly different values and the discrepancy is still under investigation (Roberts and Southon 2007).

Mass fractionation-corrected F can be used to calculate the radiocarbon isotope ratio ($\Delta^{14}\text{C}$):

$$\Delta^{14}\text{C} = [F * e^{\lambda(y-1950)} - 1] * 1000 \quad (19.3)$$

where λ is $1/8267$ based on the ^{14}C half life and y is the measurement year. This expression corrects for the decay of the oxalic acid standard since 1950 (Stuiver and Polach 1977).

Using this notation, fossil fuels containing no radiocarbon have a $\Delta^{14}\text{C}$ of $-1,000\text{‰}$. In contrast, CO_2 in the modern atmosphere has a $\Delta^{14}\text{C}$ of $\sim 50\text{‰}$ as of 2007 (Levin et al. 2008), with distinct latitudinal gradients that include a maximum in the tropics and minima in mid-latitudes of the northern hemisphere and over the Southern Ocean (Krakauer et al. 2006). Even with contemporary latitudinal gradients, the difference in $\Delta^{14}\text{C}$ between remote atmospheric sites and fossil emissions provides a very large range of end members for tracing the dispersal of CO_2 from urban sources. In contrast, the end members for CO_2 source apportionment using stable carbon isotopes are approximately -24 to 60‰ for fossil fuel, depending on the fuel type, versus $\sim -8\text{‰}$ for CO_2 in the background atmosphere (Andres et al. 2000; Pataki et al. 2003a, 2005a; Tans 1981).

19.3 Isotope Ratios of Vegetation in Polluted Air

Several studies have noted isotopic depletion in organic matter near fossil fuel combustion sources using $\delta^{13}\text{C}$. Lichtfouse et al. (2003) reported depleted $\delta^{13}\text{C}$ in grasses growing near highways in Paris in comparison to grasses growing in rural areas. They also noted a trend toward greater depletion with decreasing distance to the highway in samples collected from 0–50 m from the road. Dongarrà and Varrica (2002) reported a depletion of 3.6‰ in tree rings sampled in Palermo, Italy representing the period 1880–1998, which they attributed to CO_2 concentrations elevated above the global background in the urban area. Boeckx et al. (2006) showed depletion of $\delta^{13}\text{C}$ of urban soils in Belgium, although a wide range of values were reported across soil and land use types.

In addition to the effects of uptake of isotopically depleted, fossil-fuel derived CO_2 , $\delta^{13}\text{C}$ of organic matter is also strongly influenced by physiological processes in C_3 plants, particularly the ratio of intercellular to ambient CO_2 concentrations, which is determined by the relationship between stomatal conductance and photosynthesis (Farquhar et al. 1989). Therefore, it can be difficult to distinguish uptake of isotopically depleted CO_2 in polluted air from plant physiological responses to pollution and other related environmental factors. Jędrysek et al. (2003) and Šantrůčková et al. (2007) reported enrichment rather than depletion in $\delta^{13}\text{C}$ of tree rings in trees exposed to urban and industrial pollution, which they attributed to the effects of acid deposition and sulfur emissions on plant gas exchange. This is consistent with Savard et al. (2002), who reported an enrichment of 3.5‰ in tree rings following the construction of a copper smelter which emitted SO_2 in a boreal forest in Canada. One potential cause of pollution-derived isotopic enrichment is an increase in the importance of PEP carboxylase, which has a much smaller fractionation factor than Rubisco, and has been found to increase in activity under elevated ozone concentrations (Saurer et al. 1995). Norra et al. (2005) showed enrichment of $\delta^{13}\text{C}$ of soils downwind versus upwind of pollution sources in Germany, which they related to the physiological effects of pollution on local vegetation. Many other environmental factors such as climate variability, soil moisture, and nutrient availability may also influence $\delta^{13}\text{C}$, such that stable carbon isotopes of C_3 plants alone cannot provide a definitive tracer of atmospheric pollution.

The stable carbon isotope ratio of C_4 plants is less affected by physiology than C_3 plants; in regions with C_4 vegetation these species can be used to trace the isotope ratio and in turn the concentrations of anthropogenic CO_2 . Marino and McElroy (1991) showed that $\delta^{13}\text{C}$ of cellulose nitrate in *Zea mays* was a reliable indicator of $\delta^{13}\text{C}$ of the atmosphere in samples dating back to 1948. This method has subsequently been used to estimate the contribution of fumigation CO_2 to the canopies of elevated CO_2 experiments (Pataki et al. 2003b) such as a Swiss experiment in a mature forest (Pepin and Körner 2002). In addition, $\delta^{13}\text{C}$ of C_4 plants was used to identify and map areas of high anthropogenic CO_2 concentrations in the city of Cotonou, Benin (Kélomé et al. 2006).

Radiocarbon can also be used to detect the amount of anthropogenic carbon in plants, which should be directly analogous to the isotopic composition of the

atmosphere during periods of photosynthesis. Because mass-dependent, photosynthetic fractionation is accounted for in $\Delta^{14}\text{C}$, variations in plant $\Delta^{14}\text{C}$ directly correspond to the radiocarbon content of atmospheric CO_2 at the time of fixation, and therefore can be more straightforward to interpret than measurements of plant $\delta^{13}\text{C}$ in polluted areas. In addition, $\Delta^{14}\text{C}$ is very sensitive to small variations in CO_2 caused by fossil fuel emissions, given the large isotopic difference between CO_2 derived from fossil-fuel combustion and CO_2 in the modern atmosphere. This difference is so great that an increase in mixing ratio of fossil fuel-derived CO_2 of only 1 ppm at contemporary atmospheric levels (-8‰ , 380 ppm) results in a depletion of $\Delta^{14}\text{C}$ by 2.8‰. Hence, Alessio et al. (2002) detected a significant depletion of oak leaves, i.e. an elevated level of CO_2 exposure, within 300 m of a major roadway in Rome using radiocarbon, despite the fact that $\delta^{13}\text{C}$ changed by less than 1‰ on average and showed a high degree of variability.

As another illustration, Fig. 19.1 shows both leaf stable carbon and radiocarbon isotope ratios measured across a well-studied pollution gradient in the San Bernardino Mountains of southern California. Arbaugh et al. (2003) described the San Bernardino Mountains Air Pollution Gradient network, which has been measured for ozone concentrations, nitrogen deposition, and their effects on mixed conifer ecosystems since the 1960s. The western portion of this gradient is adjacent to the Los Angeles Basin and experiences high concentrations of photochemical oxidant pollution as well as elevated nitrogen inputs which decline in the eastern portion of the gradient (Arbaugh et al. 2003; Fenn and Bytnerowicz 1997; Lee et al. 2003). Based on diurnal leaf gas exchange measurements, in 1995 early morning CO_2 concentrations averaged 500–600 ppm at polluted sites, compared to mid morning to early afternoon concentrations of 325–350 ppm (N.E. Grulke, unpublished data).

We sampled needles of four conifer species at three sites across the pollution gradient in the winter and spring of 2005. Current year shoots of *Pinus ponderosa*, *Abies concolor*, *Calocedrus decurrens*, and *Pinus lambertiana* were sampled from the mid-canopy of mature trees at highly polluted Camp Paivika ($34^\circ 14.021'' \text{ N}$, $117^\circ 19.338'' \text{ W}$, 1,800 m.a.s.l.), moderately polluted Strawberry Peak ($34^\circ 14.058'' \text{ N}$, $117^\circ 13.955'' \text{ W}$, 2,240 m.a.s.l.) and relatively unpolluted Miller Canyon ($34^\circ 16.116'' \text{ N}$, $117^\circ 17.060'' \text{ W}$, 1,178 m.a.s.l.). Needles were dried at 70° for at least 48 h and ground to a fine powder. Nitrogen isotope ratio ($\delta^{15}\text{N}$) and $\delta^{13}\text{C}$ were measured with an elemental analyzer coupled to an Isotope Ratio Mass Spectrometer (Delta Plus IRMS, Thermofinnigan, San Jose, CA). To measure $\Delta^{14}\text{C}$, ground samples were converted to graphite according to Santos et al. (2004) and analyzed by Accelerator Mass Spectrometry (AMS) at the W.M. Keck Carbon Cycle AMS Facility at the University of California, Irvine. This facility has been described in detail by Southon et al. (2004).

While there were species differences in $\delta^{13}\text{C}$ of leaves measured across the San Bernardino Gradient, there were no significant site differences (Fig. 19.1, ANOVA, $p > 0.05$). This is in contrast to Grulke and Balduman (1999) who found significant differences in $\delta^{13}\text{C}$ of leaf cellulose between the more polluted sites Strawberry Peak and Camp Paivika and an atmospherically cleaner site at Lassen National Forest at the eastern end of the San Bernardino Mountains. In contrast, there were

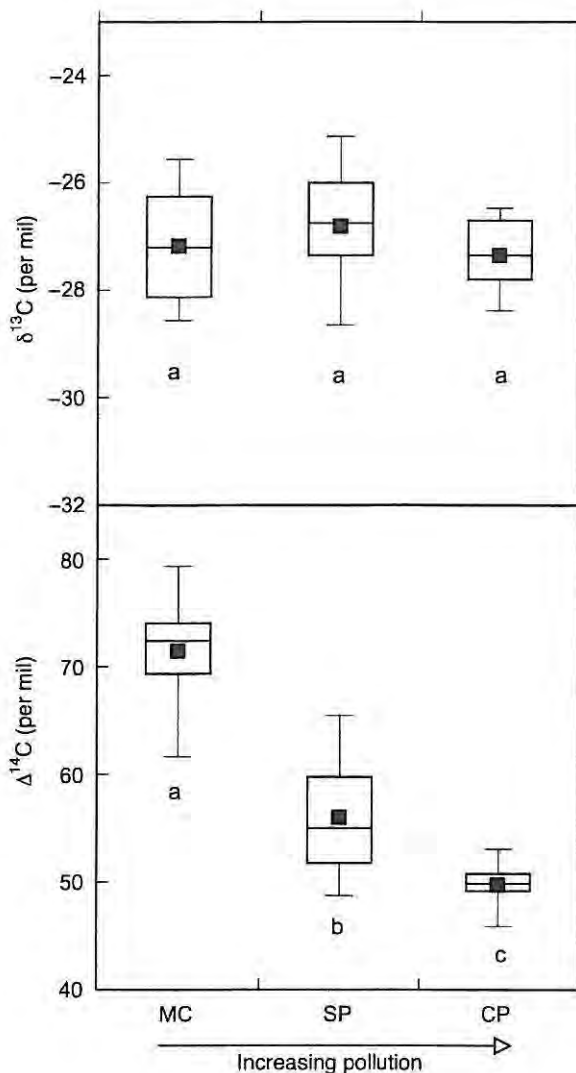


Fig. 19.1 Box plots of leaf stable carbon isotope ratio ($\delta^{13}\text{C}$) and radiocarbon isotope ratio ($\Delta^{14}\text{C}$) in conifer trees sampled across a known ozone and nitrogen deposition gradient in the San Bernardino Mountains in California, USA. MC refers to Miller Canyon, SP is Strawberry Peak, and CP is Camp Paivika. The *square* shows the mean value, the *lower line* of the box shows the bottom quartile of the data, the *middle line* shows the median, the *upper line* shows the top quartile, and the *bars* show the 10th and 90th percentile. *Letters* show significant differences among sites with an LSD post-doc test of an ANOVA, $p < 0.05$

no significant species differences in $\Delta^{14}\text{C}$ (ANOVA, $p > 0.05$) in the current study. However, there was a significant decline in leaf $\Delta^{14}\text{C}$ from the control site at Miller Canyon to the most polluted site at Camp Paivika (Fig. 19.1, ANOVA, $p < 0.05$).

Hence, atmospheric CO_2 concentrations appear to vary across the gradient along with ozone and nitrogen concentrations. To quantify this effect, we can calculate the proportion of fossil fuel-derived CO_2 in plants (f_F), which should correspond to the average, photosynthate-weighted proportion of fossil fuel versus background CO_2 in the atmosphere:

$$f_F = \frac{(\Delta^{14}\text{C}_p - \Delta^{14}\text{C}_B)}{(\Delta^{14}\text{C}_F - \Delta^{14}\text{C}_B)} \quad (19.4)$$

where $\Delta^{14}\text{C}_p$ is the radiocarbon content of the leaf expressed in Δ notation, $\Delta^{14}\text{C}_B$ is the radiocarbon content of the background atmosphere, and $\Delta^{14}\text{C}_F$ is the radiocarbon content of fossil fuel-derived CO_2 , which was specified as -998‰ . According to measurements at Pt. Barrow, AK by X. Xu et al. (unpublished data), $\Delta^{14}\text{C}_B$ was $65.1 \pm 2.4\text{‰}$ in 2004, where the error refers to the standard deviation of bi-monthly measurements. The concentration of atmospheric CO_2 at Pt. Barrow during this period was 378 ppm (Conway et al. 2007). The station at Pt. Barrow is located 8 km from Barrow, AK and has a prevailing east-northeast wind with a largely marine influence (<http://www.esrl.noaa.gov/gmd/obop/brw/index.html>). Hence, air samples from this station are often used as indicators of the composition of unpolluted air (e.g. Keeling et al. 2005). Assuming that background and fossil fuel combustion were the only major sources of CO_2 at the San Bernardino sites, leaves at Miller Canyon contained no anthropogenic CO_2 , whereas leaves at Camp Paivika contained 1.2% of locally-added fossil fuel CO_2 , equivalent to a photosynthate-weighted average CO_2 mixing ratio of 383 ppm. This is similar to direct measurements of atmospheric CO_2 concentrations at this site (N.E. Grulke, unpublished data).

19.4 The Spatial Distribution of $\Delta^{14}\text{C}$ Plant Biomarkers

The distribution of leaf $\Delta^{14}\text{C}$ at Miller Canyon shows some values that were higher than the estimated background value for atmospheric CO_2 of 65.1‰ (Fig. 19.1). While this may be due to measurement errors and variability in $\Delta^{14}\text{C}$ of the background atmosphere and local sources, it is also very possible that the organic matter present in current year leaf tissue contained carbon fixed in a previous year when the atmosphere contained more ^{14}C , as $\Delta^{14}\text{C}$ of atmospheric CO_2 has been declining since the 1960s. Retention of older carbon may be particularly prevalent at more arid sites where leaves are long-lived (Grulke and Balduman 1999). This illustrates a potential complication of using perennial plants as indicators of current atmospheric pollution. For this reason, several studies that have used plants to map spatial variations in $\Delta^{14}\text{C}$ and locally-added fossil fuel CO_2 have used annual plants, whose period of carbon fixation is more constrained. Hsueh et al. (2007) collected samples of corn plants (*Zea mays*) from throughout the United States in the summer of 2004 and measured their radiocarbon composition. They sent packets to residents at varying locations and instructed them to collect corn samples with the following

protocol: samples were collected more than 1.6 km away from highways, more than 45 m from paved roads, and more than 20 m away from buildings that may emit CO_2 from combustion furnaces. Potential point sources of pollution such as power plants were avoided to utilize the radiocarbon content of the samples as integrators of transport of fossil fuel CO_2 over large areas in the well-mixed boundary layer.

Figure 19.2 shows the data from this study plotted as a $\Delta^{14}\text{C}$ anomaly, or the difference between the background $\Delta^{14}\text{C}$ of CO_2 estimated from Pt. Barrow, AK air samples in 2004 and measured values in *Zea mays*, rather than the absolute values. This will allow comparison with data collected in other years when the background atmosphere has a different $\Delta^{14}\text{C}$ value. The results show two regions of depleted plant $\Delta^{14}\text{C}$ that correspond to elevated atmospheric CO_2 concentrations. In the northeastern U.S., plant $\Delta^{14}\text{C}$ was depleted by as much 13‰ relative to atmospheric CO_2 at Pt. Barrow, while in California, plant $\Delta^{14}\text{C}$ was depleted by as much as 28‰. To confirm that this depletion was due primarily to the addition of fossil fuel-derived CO_2 to the atmosphere, Hsueh et al. (2007) used the Model of Atmospheric Transport and Chemistry (MATCH) to independently estimate atmospheric CO_2 derived from fossil fuel releases and the Carnegie-Ames-Stanford Approach (CASA) biogeochemical model to simulate the influence of terrestrial biosphere and marine CO_2 fluxes on atmospheric CO_2 and $\Delta^{14}\text{C}$. The modeling results

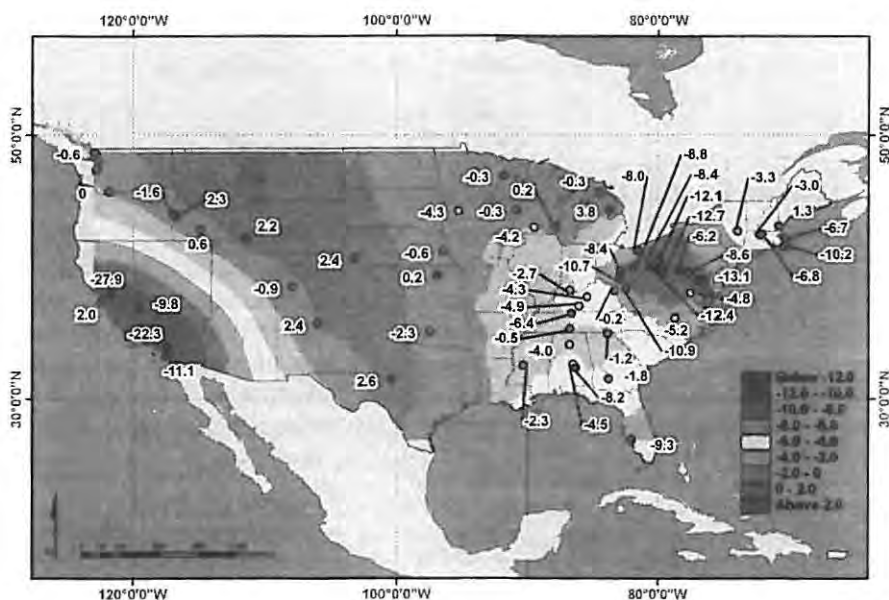


Fig. 19.2 The difference between $\Delta^{14}\text{C}$ of CO_2 in clear air measured in Pt. Barrow, Alaska, and in leaves of corn plants sampled throughout the United States in 2004. Units are per mil (‰) relative to the Oxalic Acid standard (Modified from Hsueh et al. 2007). Fig. 19.2, see Appendix 1, Color Section

confirmed that fossil fuel emissions were the dominant influence on $\Delta^{14}\text{C}$ variability across North America, although biogenic respiration of ^{14}C -enriched CO_2 partially offset the depletion in atmospheric $\Delta^{14}\text{C}$, particularly in the eastern U.S. Overall, the model predicted a mean difference of 8.5‰ between $\Delta^{14}\text{C}$ of background CO_2 and actual CO_2 over the northeast, which was similar to the $7.5 \pm 2.9\text{‰}$ difference observed in the *Zea mays* samples.

As a follow-up to this study, Riley et al. (2008) measured $\Delta^{14}\text{C}$ of annual grasses throughout California in 2005. Unlike *Zea mays*, which grows during the summer months in North America, the grasses sampled in the California study were winter annuals with a growing season around February, March, and April. The sampling protocol in this study focused on samples collected more than 3.2 km from highways, more than 45 m from roads, and more than 20 m from buildings in rural areas. Because this study focused more intensively on urban areas than in the national study, samples were collected on residential streets, neighborhood parks, or abandoned parking lots when it was not possible to collect urban samples in the absence of buildings and roads. At this higher spatial resolution, the anomalies from background $\Delta^{14}\text{C}$ of CO_2 were larger than in the national study, and showed a depletion of up to 62‰ in the Los Angeles Basin and 31‰ in the San Francisco Bay Area (Fig. 19.3). This study also compared observations and modeled estimates of atmospheric $\Delta^{14}\text{C}$ of CO_2 by modeling transport of fossil fuel CO_2 with the MM5 meteorological model integrated with the LSM1 land-surface model. The $\Delta^{14}\text{C}$ of heterotrophic respiration was estimated with functions derived from the CASA model. The modeled and measured $\Delta^{14}\text{C}$ of grasses agreed within 1‰ in the North Coast and Los Angeles regions, and within 5‰ in the Central Valley and San Francisco regions.

Given the agreement between measured and modeled values, Riley et al. (2008) further applied this approach to model the transport of fossil fuel CO_2 across and out of California to trace its fate and dispersion into the larger atmospheric volume. This analysis indicated that 21%, 39%, and 35% of fossil fuel CO_2 left the region to the north, east, and south of California, respectively. This is a particularly useful application of biomarkers and atmospheric models as atmospheric monitoring of CO_2 emissions has become increasingly important both in carbon cycle science and in the implementation of policy to regulate greenhouse gas emissions. In addition, because other pollutants associated with combustion are likely transported along with fossil fuel-derived CO_2 , these results have important ramifications for tracking dispersion of other pollutants of interest for human health (e.g. carbon monoxide, ozone, NO_x , and aerosols) across state and national borders.

A detailed evaluation of the data from the Los Angeles Basin using data reported in Riley et al. (2008) and also Wang and Pataki (2009) provides information at an even finer spatial resolution. In this analysis, the $\Delta^{14}\text{C}$ anomaly (deviation from background) of winter annual plants collected in the 2004 and 2005 growing seasons were mapped in region in and surrounding the Los Angeles metropolitan area. This dataset showed the greatest influence of fossil fuel-derived CO_2 relative to the $\Delta^{14}\text{C}$ of atmospheric CO_2 at Pt. Barrow, with depletion of more than 100‰ in a sample collected near downtown Los Angeles (Fig. 19.4).

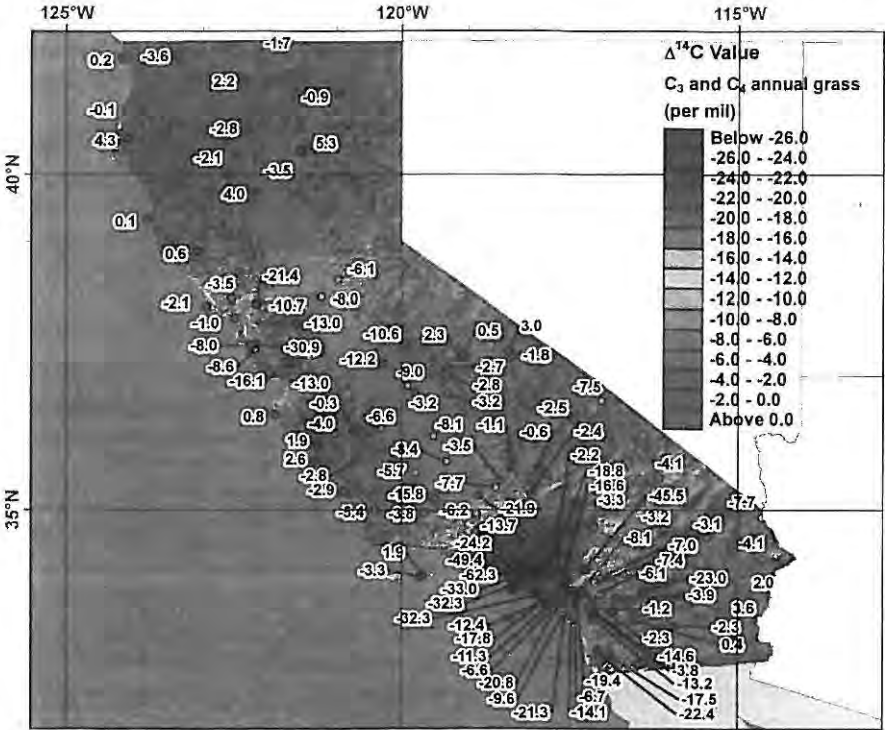


Fig. 19.3 The difference between $\Delta^{14}\text{C}$ of CO_2 in clear air measured in Pt. Barrow, Alaska, and in leaves of winter annual plants sampled throughout California in 2005. Units are per mil (‰) relative to the Oxalic Acid standard (Modified from Riley et al. 2008). Fig. 19.3, see Appendix 1, Color Section

This corresponds to a photosynthate-weighted, average CO_2 concentration of 437 ppm. Moving westward away from the densely populated urban area, plant samples showed increasingly less depletion with several samples within 5‰ of the $\Delta^{14}\text{C}$ at Pt. Barrow in rural areas of Orange and Riverside Counties. When the spatial distribution of plant $\Delta^{14}\text{C}$ was evaluated in relation to population density, geography, meteorological variables, and criteria air pollutants in a multiple regression model, $\Delta^{14}\text{C}$ was found to be significantly related to population density, distance to major roads, atmospheric carbon monoxide concentrations, and in particular to atmospheric ozone concentrations as measured by the local air quality monitoring agency. These four variables explained 53% of the spatial variability in leaf $\Delta^{14}\text{C}$, further supporting the application of $\Delta^{14}\text{C}$ as an integrator of atmospheric pollution that may complement and enhance traditional air quality monitoring networks.

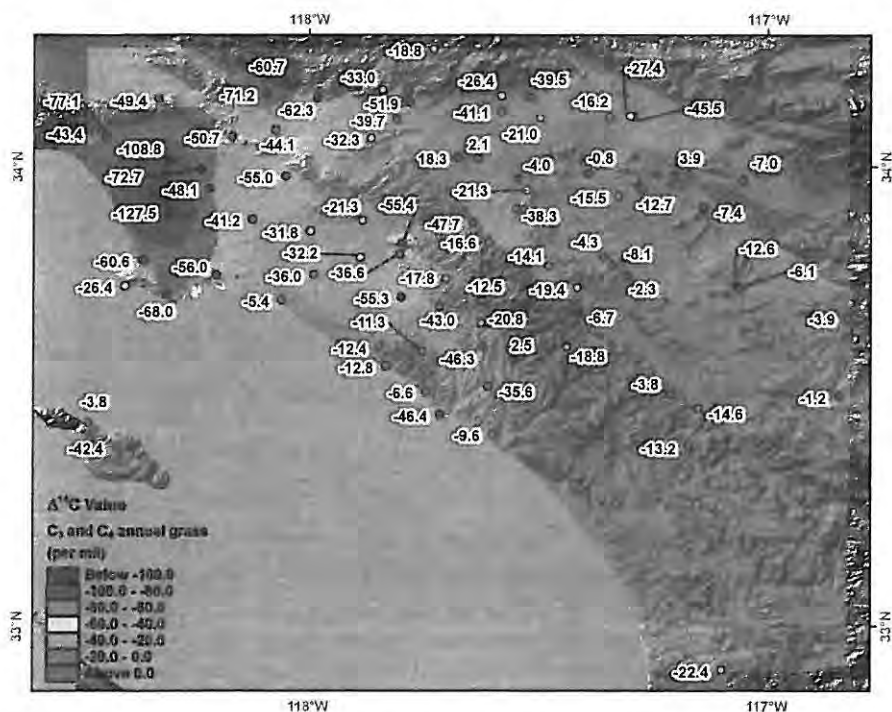


Fig. 19.4 The difference between $\Delta^{14}\text{C}$ of CO_2 in clear air measured in Pt. Barrow, Alaska, and in leaves of winter annual plants sampled throughout the Los Angeles Basin in 2004 and 2005. Units are per mil (‰) relative to the Oxalic Acid standard (Modified from Wang and Pataki 2009). Fig. 19.4, see Appendix I, Color Section

19.5 The Temporal Distribution of $\Delta^{14}\text{C}$ Biomarkers

Because there is a good record of the $\Delta^{14}\text{C}$ of remote atmospheric CO_2 during the industrial period (Levin and Hesshaimer 2000), $\Delta^{14}\text{C}$ of archived organic samples from polluted areas can provide a record of changes in local $\Delta^{14}\text{C}$ and concentrations of CO_2 over time. Rakowski et al. (2004, 2005) showed depletion in $\Delta^{14}\text{C}$ of tree rings in Nagoya, Japan and Krakow, Poland over several decades relative to $\Delta^{14}\text{C}$ of CO_2 in clean air samples from Germany. This corresponded to CO_2 mixing ratios that were elevated above background levels by 5.6–12.6 ppm in Nagoya and 5.9–6.5 ppm in Krakow. In a novel application of organic matter archives as biomarkers of fossil fuel CO_2 , Shibata and Kawano (1994) and Shibata et al. (2005) measured $\Delta^{14}\text{C}$ of rice grains harvested throughout Japan over a 17 year period. They found significant correlations between $\Delta^{14}\text{C}$ and population density as a proxy for local emissions. $\Delta^{14}\text{C}$ varied by more than 40‰ in rural areas versus large cities. With a long enough record, it may be possible to determine whether the slope of

this relationship is changing over time, which may provide very useful information about changes in CO₂ emissions and concentrations per capita. It is likely that this information will be increasingly needed for monitoring compliance with CO₂ emissions reductions programs and regulations in the future.

Long-term records of CO₂ mixing ratios during the industrial period have many applications and are an important new application of measurements of $\Delta^{14}\text{C}$. There is increasing interest in resolving high resolution CO₂ emissions inventories and in linking emissions more quantitatively to urban ecosystem processes in order to understand the mechanistic drivers of emissions, which are both socioeconomic and biophysical (Pataki et al. 2006). There is great potential to better link isoscapes near CO₂ emissions sources with interdisciplinary studies of urban expansion, demography, changes in infrastructure, and other factors that may improve our understanding of the human carbon cycle and improve future CO₂ emissions scenarios.

19.6 Combining Carbon and Nitrogen Tracers

While $\delta^{13}\text{C}$ is one of the most commonly used tracers in natural ecosystems due to the well-described relationship between plant gas exchange and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ has been shown to be a very useful tracer in polluted environments. There are many factors that influence fractionation of nitrogen isotopes in plants and soils, including enzymatic fractionation in soil microbial processes, fractionation in volatilization of gaseous N, mycorrhizal transfers, and nitrogen transformations within plants (Evans 2001; Högberg 1997; Robinson 2001). This complexity can make the interpretation of variations in $\delta^{15}\text{N}$ of organic matter difficult. However, there are now many studies that show consistent differences between $\delta^{15}\text{N}$ of organic matter in more versus less human-impacted environments. Ammann et al. (1999) showed $\delta^{15}\text{N}$ enrichment of spruce needles near a highway in Switzerland which they attributed to uptake of NO₂ pollution-derived dry deposition. Stewart et al. (2002) reported $\delta^{15}\text{N}$ depletion of plants growing near industrial pollution sources in Brazil where the pollution source was dominated by isotopically depleted NH₃ and NH₄⁺. Norra et al. (2005) mapped $\delta^{15}\text{N}$ of both vegetation and soil in an urban area in Germany and found that $\delta^{15}\text{N}$ of both types of organic matter was more strongly correlated with land use than with soil parent material or meteorology. These results were supported by a subsequent study in Belgium which showed that the spatial distribution of plant and soil $\delta^{15}\text{N}$ was also most strongly influenced by land use, with depleted values in unfertilized urban soils containing N-fixing species and enriched values in fertilized agricultural areas and wetlands associated with large gaseous losses (Boeckx et al. 2006).

In the study in the San Bernardino Mountains in California, leaf $\delta^{13}\text{C}$ did not show any trends across the pollution gradient (Fig. 19.1); however, there were significant trends in $\delta^{15}\text{N}$ (Fig. 19.5) and C:N (Fig. 19.6). Both site and species significantly influenced leaf $\delta^{15}\text{N}$ (two-way ANOVA, $p < 0.05$), with most species showing depleted values of $\delta^{15}\text{N}$ at the more polluted sites, although the trend

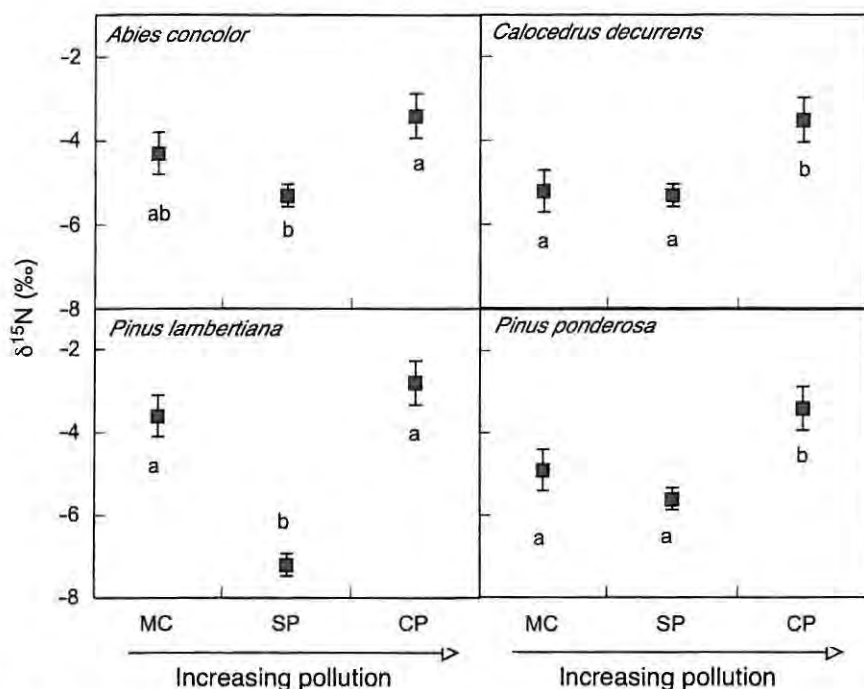


Fig. 19.5 Leaf nitrogen isotope ratio ($\delta^{15}\text{N}$) in four species of conifer trees sampled across a known ozone and nitrogen deposition gradient in the San Bernardino Mountains in California, USA. Letters show significant differences among sites with an LSD post-doc test of an ANOVA, $p < 0.05$

was complex in some species and showed the most depleted values at the intermediate site (Fig. 19.5). Leaf C:N was lowest at the most polluted site in three of the four species (Fig. 19.6), supporting increased plant uptake of pollution-derived N at sites of high anthropogenic N deposition. These results suggest that $\Delta^{14}\text{C}$, $\delta^{15}\text{N}$, and C:N are very promising tracers of anthropogenic tracers that show strong gradients in urbanized regions. To date, natural abundance ^{14}C and ^{15}N tracers have been applied in a relatively small number of urban ecological studies, but there is great potential to evaluate trends and mechanisms of isotope distribution in a wide variety of urban areas.

19.7 Conclusions

While $\delta^{13}\text{C}$ of organic matter can be difficult to interpret in polluted areas due to opposing effects of fossil fuel $^{13}\text{CO}_2$ dilution and the effects of secondary combustion products on physiology, radiocarbon can be used to distinguish between these

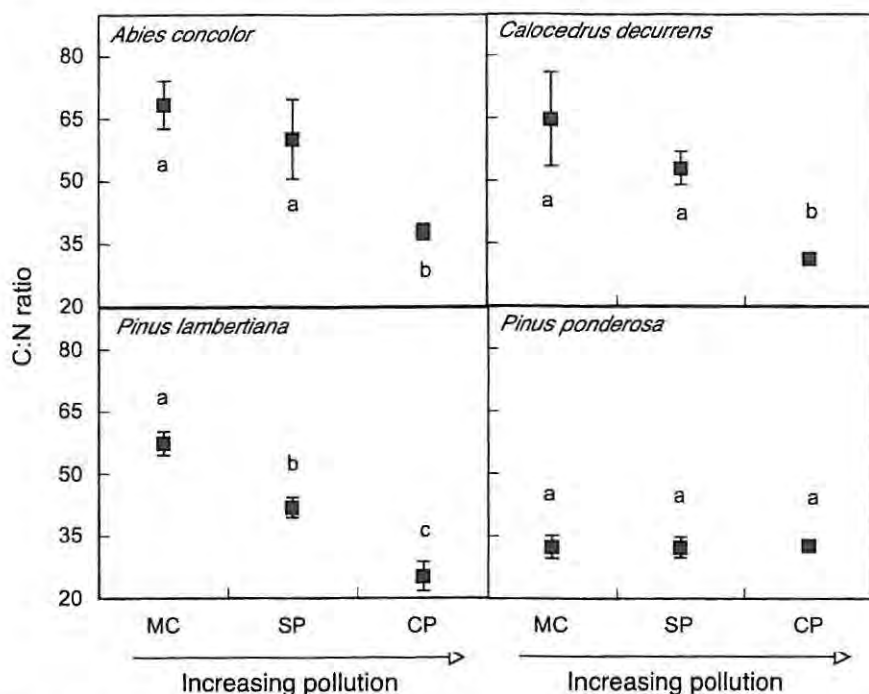


Fig. 19.6 Leaf carbon:nitrogen (C:N) in four species of conifer trees sampled across a known ozone and nitrogen deposition gradient in the San Bernardino Mountains in California, USA. Letters show significant differences among sites with an LSD post-hoc test of an ANOVA, $p < 0.05$

effects. Plant $\Delta^{14}\text{C}$ is solely influenced by $\Delta^{14}\text{C}$ of atmospheric CO_2 at the time of fixation, and therefore can be used to infer atmospheric CO_2 mixing ratios in areas where locally-added fossil fuel-derived CO_2 contributes to elevated CO_2 . Studies at many different spatial scales, from transects a few hundred meters from roadways to mapping studies at regional and national scales, have demonstrated that $\Delta^{14}\text{C}$ is a robust measure of anthropogenic CO_2 . Statistical correlations between isotope ratios and environmental variables can help resolve the complexity of the effects of multiple disturbances in urban environments on plant physiology. These studies can be further informed by detailed studies of mechanistic relationships between altered urban environments and physiological responses, and by comparative studies across varying regions, which are currently at an early stage. Recent interest in developing new applications of isoscapes at varying spatial and temporal scales can greatly contribute to improving our understanding of plant-soil-environment interactions and associated ecosystem services in highly human-dominated and disturbed environments, which are a rapidly increasing proportion of the landscape.

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