

Isotopic composition of carbon dioxide from a boreal forest fire: Inferring carbon loss from measurements and modeling

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[1] Fire is an important pathway for carbon (C) loss from boreal forest ecosystems and has a strong effect on ecosystem C balance. Fires can range widely in severity, defined as the amount of vegetation and forest floor consumed by fire, depending on local fuel and climatic conditions. Here we explore a novel method for estimating fire severity and loss of C from fire using the atmosphere to integrate ecosystem heterogeneity at the watershed scale. We measured the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopic values of CO_2 emitted from an experimental forest fire at the Caribou-Poker Creek Research Watershed (CPCRW), near Fairbanks, Alaska. We used inverse modeling combined with dual isotope measurements of C contained in aboveground black spruce biomass and soil organic horizons to estimate the amount of C released by this fire. The experimental burn was a medium to severe intensity fire that released, on average, about 2.5 kg C m^{-2} , more than half of the C contained in vegetation and soil organic horizon pools. For vegetation, the model predicted that approximately 70–75% of pools such as needles, fine branches, and bark were consumed by fire, whereas only 20–30% of pools such as coarse branches and cones were consumed. The fire was predicted to have almost completely consumed surface soil organic horizons and burned about half of the deepest humic horizon. The ability to estimate the amount of biomass combusted and C emission from fires at the watershed scale provides an extensive approach that can complement more limited intensive ground-based measurements. **INDEX TERMS:** 1615 Global Change: Biogeochemical processes (4805); **KEYWORDS:** boreal forest, fire, carbon isotope, global carbon cycling, radiocarbon, disturbance

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1. Introduction

[2] Boreal forests have been identified as regions of recent net uptake of anthropogenic CO_2 by inverse modeling studies of atmospheric CO_2 and $^{13}\text{CO}_2$ concentrations [Tans *et al.*, 1990; Ciais *et al.*, 1995; Keeling *et al.*, 1996]. However, the status of the boreal forest as a global source or sink of carbon (C) in the future hinges upon the response of ecosystem C cycling to changes in both climate and disturbance regimes. While climate warming

is expected to have a direct effect on boreal C cycling via changes in net primary productivity and decomposition rates [Van Cleve *et al.*, 1990; Shaver and Kummerow, 1992; Bonan, 1993; Goulden *et al.*, 1998], recent attention has been focused on the interaction between warming and fire frequency. High-latitude warming predicted by global climate models [Houghton *et al.*, 1996] has been supported by observational evidence over the last 25 years [Serreze *et al.*, 2000], and has led to decreased moisture availability during summer [Barber *et al.*, 1998]. In combination with more human ignition sources, the warmer, drier climate is associated with documented increases in fires in boreal forests worldwide [Dixon and Krankina, 1993; Kasischke *et al.*, 1995a; Conard and Ivanova, 1997; Kurz and Apps, 1993; Zimov *et al.*, 1999]. Because fires release C directly to the atmosphere

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and have a strong effect on rates of C exchange following fire, changes in fire frequency can have a larger and more rapid effect on C storage in this biome compared to the direct effect of elevated temperatures alone.

[3] As part of the natural disturbance regime in boreal forest, fires affect C storage by (1) direct combustion loss, and (2) by altering the annual balance between net primary productivity and decomposition following fire. Fires release CO₂ directly through combustion of biomass and soil organic matter (SOM) [Seiler and Crutzen, 1980]. Fires also indirectly affect ecosystem C storage by initially decreasing primary productivity, altering the pools of SOM available for decomposition, and changing the physical and chemical environment in which soil processes take place [Dyrness et al., 1986; Kasischke et al., 1995a]. Over the entire fire cycle, fire creates a mosaic landscape of deciduous and evergreen forest stands, with the vegetation-type dependent on fire severity, stand history, and time since last fire [Van Cleve and Viereck, 1981; Bonan and Shugart, 1989; Rapalee et al., 1998; Mann and Plug, 1999]. These deciduous and evergreen stands remove and store C from the atmosphere as the growth of vegetation and forest floor exceeds decomposition of detritus and SOM [Odum, 1969; Schulze et al., 2000]. Changes in the fire return interval affect both the amount of C lost via combustion and the proportion of land area in each particular successional stage.

[4] This paper focuses on direct losses of CO₂ to the atmosphere from combustion as a critical point for C exchange when considering the entire fire cycle. Landscape-scale calculations have demonstrated that even if mature black spruce forests continued their current rate of C assimilation, C uptake by 99% of the land area would be offset by C release by fire on only 1% of the land area [Rapalee et al., 1998]. There have been recent attempts to quantify the spatial extent of fires and fire frequency in boreal forest from satellite imagery [Kasischke and French, 1995; Kasischke et al., 1995b; Amiro et al., 2001]. In order to predict total C loss, these areal estimates are combined with estimates of the fraction of biomass consumed by fire [Sieler and Crutzen, 1980; French et al., 2000]. These estimates of fraction biomass consumed are based on intensive ground-based measurements that are limited in their spatial extent and conducted in relatively few places. However, single fire can burn hundreds to thousands of hectares, and fire severity, defined as the amount of vegetation and forest floor organic material consumed during the fire, can vary widely due to local fuel and climatic conditions.

[5] Here we present a novel approach to quantify C loss from fire at the watershed scale by using the atmosphere to integrate the ecosystem heterogeneity that makes ground-based measurements difficult. We measured CO₂ concentrations, and $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotope values of CO₂ emitted during an experimental forest fire as an integrated measurement of all vegetation and soil pools that were consumed by fire. Measurements of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ in CO₂ indicate the substrates that burned within the ecosystem, while $\Delta^{14}\text{C}$ additionally reflects their age. To predict the fraction biomass consumed, we combined measurements of the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopic signatures of those ecosystem C pools with an inverse model. This numerical model calculated the

contribution of C from different ecosystem C pools (with its corresponding isotopic signature) that could combine to produce the isotopic signature of CO₂ emitted from the fire. Using this model, we predicted the fraction biomass consumed in each of the vegetation and soil source pools and total C release at the watershed scale.

2. Methods

2.1. Site Description

[6] Measurements were made before and during an experimental forest fire in the Caribou-Poker Creek Research Watershed (CPCRW) located near Fairbanks, Alaska at 65°10'N latitude and 147°30'W longitude. This experimental fire was conducted as part of the Frostfire experiment at the Bonanza Creek Long Term Ecological Research Program (BNZ-LTER). The stand-killing fire was initiated on 9 July 1999 in an 838 ha watershed, with the area that burned dominated by closed canopy black spruce (*Picea mariana*) forest (E. Alverado, unpublished manuscript, 2001) up to 75 years old [Fastie, 2000] with feathermoss understory (predominantly *Pleurozium schreberi* and *Hylocomium splendens*, M. C. Mack, unpublished manuscript, 2001).

2.2. CO₂ Sampling

[7] Air samples were collected at ground level on the ridgeline of the watershed at the perimeter of the burn over a 4-hour period during the middle of the day. Smoke and CO₂ from the fire was carried by the prevailing winds out of the watershed up over the ridgeline sampling point. Air from the fire was passed through a magnesium perchlorate water trap and collected into evacuated, 6-L electropolished stainless steel canisters at 45 min intervals over the course of the burn. Samples were taken to UC Irvine where CO₂ concentrations were measured with a Shimadzu thermal conductivity detector gas chromatograph prior to cryogenic purification. Stable isotope ratios ($^{13}\text{C}/^{12}\text{C}$) were measured on subsamples of purified CO₂ using a Finnigan 252 dual inlet isotope ratio mass spectrometer (IRMS). Isotopic values for $\delta^{13}\text{C}$ are reported as deviation in per mil (‰) relative to the isotopic ratio of Pee Dee belemnite, and the analytical precision is 0.1‰. Other subsamples of purified CO₂ were reduced to graphite using a modified reduction method with titanium hydride, zinc, and cobalt catalyst [Vogel, 1992] and sent to Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry (CAMS) for radiocarbon analysis. Isotopic values for $\Delta^{14}\text{C}$ are reported as the deviation in per mil from the $^{14}\text{C}/^{12}\text{C}$ ratio of the oxalic acid standard decay corrected to 1950, and the analytical precision is 5‰. The $\Delta^{14}\text{C}$ value for each sample was also corrected using its $\delta^{13}\text{C}$ value to account for mass-dependent fractionation [Stuiver and Polach, 1977]. For $\Delta^{14}\text{C}$, positive values signify radiocarbon from aboveground nuclear weapons testing that took place in the 1950s and 1960s [Levin and Hesshaimer, 2000] (Figure 1). Changing atmospheric values during this time period provides a record with which to determine the residence time of C in vegetation and soils. Negative $\Delta^{14}\text{C}$ values reflect significant amounts of radioactive decay

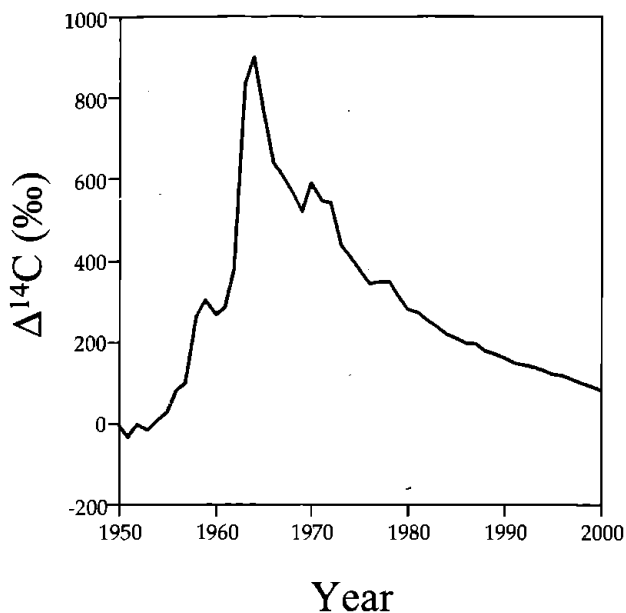


Figure 1. Recent observations of $\Delta^{14}\text{C}$ in atmospheric CO_2 from remote stations in the Northern Hemisphere, adapted from *Levin and Hesshaimer [2000]*. Nuclear weapons testing almost doubled the amount of $\Delta^{14}\text{C}$ in the atmosphere compared to the preindustrial level, defined as zero on the $\Delta^{14}\text{C}$ scale [*Stuiver and Polach, 1977*].

and are used to determine the residence time of C over longer time scales (^{14}C half-life = 5730 years).

2.3. Mixing Model

[8] The air samples represent a mixture of CO_2 from the ambient atmosphere and CO_2 released by combustion. To determine the isotopic signature of CO_2 released from the burn alone, we relied on the difference between the isotopic signatures of CO_2 from the atmosphere and from the fire, and on flask measurements that contained different mixtures of those two sources and thus differed in CO_2 concentration [*Keeling, 1958*]. By plotting the isotopic values from the flask measurements against the inverse of the CO_2 concentration, the y intercept of a linear regression represents the isotopic signature of the combustion source alone. This mixing model approach makes the assumption that all the sources within the ecosystem are well mixed before the combustion- CO_2 reached the flask sampling point. This assumption was supported by the tight correlation between the CO_2 concentration and the isotope value for ^{13}C , and by a separate calculation that treated each sample independently as if the isotope sources were not well mixed. The calculated combustion isotopic signature by this second method differed from that predicted by the mixing model by an amount smaller than the analytical precision of the mass spectrometer.

2.4. Ecosystem Components

[9] Carbon contained aboveground in black spruce biomass was estimated using standard forest inventory and regression techniques. Tree diameters at breast height (dbh) were measured for all black spruce trees in four, $12 \times 12 \text{ m}^2$ plots. These measurements were converted to aboveground

biomass on an area basis using allometric equations derived for black spruce trees at this site (Mack, personal communication, 2001). Briefly, nine trees that varied in dbh were randomly selected, harvested from the site, and separated into components: bole wood, bole bark, needles, fine branches, coarse branches, and cones. All components were dried and weighed in the laboratory. $(\text{Dbh})^2$ as a predictor variable accounted for 99% of the variation in total aboveground tree biomass and >90% of the variation for each individual component.

[10] Percent C, and $\delta^{13}\text{C}$ were measured on ground, randomly selected subsamples of tree biomass components ($n = 5$ per component) from trees that covered the range of sizes with a Europa ANCA 20/20 continuous flow IRMS with a C/N analyzer attachment. Another subsample ($n = 2$ per component) was combusted at 900°C with cupric oxide wire in an evacuated quartz tube. Evolved CO_2 was then cryogenically purified on a vacuum line, reduced to graphite and analyzed for $\Delta^{14}\text{C}$ as described previously. Aboveground biomass was multiplied by percent C as an estimate of C mass per unit area. Soil organic horizons (including roots) were volumetrically sampled from $20 \times 20 \text{ cm}^2$ soil pits randomly distributed at the site, dried, ground, and analyzed for $\delta^{13}\text{C}$ ($n = 4$ per horizon), and $\Delta^{14}\text{C}$ ($n = 2$ per horizon) in the laboratory as described above. The total thickness of the organic soil horizons (surface moss, dead moss, fibric, humic) was approximately 20 cm at this site. Carbon density per unit area was estimated from bulk density and percent C by horizon for the soil pits ($n = 4$).

[11] We used the $\Delta^{14}\text{C}$ values to estimate the average age of vegetation and soil pools following methods described in detail by *Trumbore [2000]*. For the wood, coarse branches, and bark components we assumed constant accumulation of biomass with no turnover. For needles, fine branches, and cones that stay on the tree for a short time relative to the life span of the tree, we used a steady-state model of plant tissue turnover assuming that tissue loss was described by a negative exponential decay function. For soil organic horizons that accumulate on top of the mineral soil, we used a similar approach to estimate the time since each layer accumulated [*Trumbore and Harden, 1997*]. SOM age represents the time since C was assimilated into the ecosystem and thus is the sum of time spent as living plant tissue and as dead organic matter.

[12] Analysis of variance and post hoc Fisher tests were used to distinguish differences in isotope values among ecosystem components [*SYSTAT, 1992*]. Due to the low number of replicates for $\Delta^{14}\text{C}$ ($n = 2$), all pairwise comparisons between ecosystem components for $\Delta^{14}\text{C}$ use $\alpha = 0.1$ as the significance level. All other analyses use $\alpha = 0.05$ as the significance level.

2.5. Model Description

[13] We used an inverse modeling approach with $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ isotope ratios of CO_2 emitted from the forest fire to constrain the relative contribution of different ecosystem components. The basic model framework described 10 C pools representing the major ecosystem components in aboveground biomass (bole wood, bole bark, needles, fine branches, coarse branches, and cones) and forest floor

organic soil horizons (surface moss, dead moss, fibric, and humic). In the model, each ecosystem component contributed C to CO₂ emissions that reflected its δ¹³C and Δ¹⁴C isotopic signatures. Laboratory studies have shown that there is no carbon isotopic fractionation for CO₂ released from combustion of C₃ vegetation [Turekian *et al.*, 1998]. The isotope value of each ecosystem component was weighted by the total C mass of that component and the fraction of that pool that burned during the fire

$$\delta^{13}\text{CO}_2 = \frac{\sum_{i=1}^n \delta^{13}\text{C}_i M_i F}{\sum_{i=1}^n M_i F} \quad (1)$$

$$\Delta^{14}\text{CO}_2 = \frac{\sum_{i=1}^n \Delta^{14}\text{C}_i M_i F}{\sum_{i=1}^n M_i F} \quad (2)$$

where

- δ¹³C, Δ¹⁴C isotope signature of ecosystem component, ‰;
 M mass of ecosystem component, g m⁻²;
 i individual ecosystem component;
 n 10 ecosystem components;
 F fraction burned, %.

[14] The isotope values and the C mass for each ecosystem component were constants parameterized by the field measurements, while the fraction of the pool consumed during fire was allowed to have eight different values ranging from 0 to 100% (12.5% increments). Model predictions were not dependent on number of fractions used. All pools were allowed to vary simultaneously in the fraction of the pool consumed by fire producing approximately one billion permutations.

[15] Model generated results were filtered by two methods. First, model permutations were saved when the sum of weighted δ¹³C and Δ¹⁴C from the combustion of different fractions of ecosystem C pools matched the isotope values ±SE of CO₂ emitted from the forest fire. Next, simple "rules" for combustion were applied to constrain how the different ecosystem components in the forest could burn in relation to one another. Our approach was to apply the minimum number of rules derived from ground-based observations [Stocks, 1980; Stocks and Kaufmann, 1997; Kasischke *et al.*, 2000]. These rules were: (1) Soil horizons near surface had greater fraction combusted than deeper soil horizons. (2) Bole bark fraction combusted was greater than bole wood fraction combusted. (3) Needles and fine branch fraction combusted were greater than coarse branch, bole wood, and cones fraction combusted. (4) Live moss and dead moss fraction combusted were greater than bole wood and coarse branch fraction combusted. (5) Bole wood fraction combusted was less than or equal to 25%.

[16] These rules were based on spatial constraints (rules 1 and 2) and on having fine fuels burn more readily than coarse fuels (rules 3 and 4). Rule 5 is the only rule that specifically limits the combustion of any pool and is based on field observations demonstrating that bole wood combustion is limited [Kasischke *et al.*, 2000]. Valid model solutions that matched both the smoke-CO₂ isotopic signature and these rules of combustion were used to estimate the total amount of CO₂-C transferred from the ecosystem to

the atmosphere during combustion by summing the product of the fraction consumed and the mass of each component. The standard deviations (SD) of the model estimates are based on the variation represented by all solutions that fit these criteria. While other C-containing products of combustion were not quantified by this study, isotopes of carbon monoxide, by far the second most abundant C-containing product of combustion after CO₂, are not fractionated by combustion [Conny, 1998]. If there is little or no isotopic fractionation among products of combustion or the mass of those products is small, then the identity (and total quantity combusted) of the source pools can be determined by measuring the isotopes of carbon dioxide alone. Lastly, because there is no analytical solution to this 10 pool mixing problem and because these error estimates were based only on the error estimate of the flask observations, we tested the sensitivity of model predictions by allowing the isotopic signature and mass of the source pools to vary by their standard errors in separate model runs [Phillips and Gregg, 2001].

[17] In order to predict the CO₂ isotopic signatures that would be emitted from fires of varying severity, the model was reparameterized to control the total amount of combustion of various ecosystem components. A less severe fire was not allowed to burn coarse fuels (bole wood, coarse branches) or the deep soil horizons (fibric, humic). Additionally, no more than 50% combustion of needles, fine branches and bark was allowed. In contrast, a very severe fire was parameterized to burn at least 75% of the deepest humic horizon, needles, fine branches, 25% of the bole wood, and at least 50% of the cones. These model parameters were chosen to represent endpoints in fire severity; the very severe fire released more than four times the C than the less severe fire. This range of C emission corresponds with estimates from over 10,000 fires in boreal Canada [Amiro *et al.*, 2001], and thus defines the range of CO₂ isotopic signatures that are predicted to be emitted by fire. In these forward model runs, the CO₂ isotopic signature was not used as a constant in the model but instead was determined as model output.

3. Results

3.1. Combustion CO₂

[18] Carbon dioxide concentrations in the flasks ranged from 374 to over 570 ppm due to the addition of combustion CO₂ to atmospheric background levels. In turn, the isotopes of CO₂ were influenced by the addition of the combustion source. In the absence of fire, CO₂ concentration above the canopy varies less than 5 ppm during the middle of the day, thus the effect of other CO₂ sources on our flask measurements is negligible. Considering the isotopic signature of combustion alone, the intercept (±SE) for δ¹³C was -26.97 ± 0.88‰ (Figure 2a), reflecting the combustion of C in vegetation and forest floor that was fixed by the C₃ photosynthetic pathway. The Δ¹⁴C intercept was +210 ± 27‰ (Figure 2b) indicating the combustion of vegetation and soil components that had fixed atmospheric CO₂ during the past several decades. Atmospheric Δ¹⁴C due to weapons testing reached its peak

[30] In soils, $\delta^{13}\text{C}$ values of SOM have been observed globally to increase with depth [Nadelhoffer and Fry, 1988; Garten et al., 2000]. This pattern is related to differences in the age of organic matter with depth, and thus the amount of decomposition. Changes in atmospheric $\delta^{13}\text{C}$ deplete younger (surface) SOM in the same manner as younger vegetation components. These shifts, compared with the atmosphere in 1999, ranging from 0.18‰ for surface moss to 0.53‰ for the humic horizon, explain only 7% of the shift in $\delta^{13}\text{C}$ in the soil horizons at this site. More importantly, older (deeper) SOM is thought to be enriched in $\delta^{13}\text{C}$ by heterotrophic fractionation during decomposition through preferential release of ^{12}C [e.g., Nadelhoffer and Fry, 1988; Ehleringer et al., 2000].

[31] In summary, we have demonstrated a method to predict C emission from fires at the watershed scale based on inverse modeling and a dual isotope approach. Using both $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ provides effective separation of ecosystem components with unique isotopic signatures. These systematic differences in vegetation and soils observed in ecosystems globally provide a signal for severe fires that consume more wood and SOM deeper in the soil. The ability to estimate C release from fires at this scale provides a more extensive approach that can complement more limited intensive ground-based measurements. Better and more frequent measurements of consumption from individual fires will provide empirical estimates of ecosystem to regional scale C emissions due to biomass burning.

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