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

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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 δ13C and Δ14C isotopic values of CO2 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 of CO2, 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


1. Introduction

Boreal forests have been identified as regions of recent net uptake of anthropogenic CO2 by inverse modeling studies of atmospheric CO2 and 13CO2 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 lead 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...
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 [Dyrrness 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 [Seiler 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 δ13C and Δ14C 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 δ13C and Δ14C in CO2 indicate the substrates that burned within the ecosystem, while Δ14C additionally reflects their age. To predict the fraction biomass consumed, we combined measurements of the δ13C and Δ14C 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 (13C/12C) were measured on subsamples of purified CO2 using a Finnigan 252 dual inlet isotope mass spectrometer (IRMS). Isotopic values for δ13C 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 Δ14C are reported as the deviation in per mil from the 13C/12C ratio of the oxalic acid standard decay corrected to 1950, and the analytical precision is 5‰. The Δ14C value for each sample was also corrected using its δ13C value to account for mass-dependent fractionation [Stuiver and Polach, 1977]. For Δ14C, 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 Δ14C values reflect significant amounts of radioactive decay
were measured for all black spruce trees in four regression techniques. Tree diameters at breast height (dbh) was estimated using standard forest inventory and approach makes the assumption that all the sources within the signature of the combustion source alone. This mixing model the $y$-intercept of a linear regression represents the isotopic signature of the combustion source alone. This mixing model supports 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 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.

Figure 1. Recent observations of $\Delta^{14}$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 $\Delta^{14}$C in the atmosphere compared to the preindustrial level, defined as zero on the $\Delta^{14}$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

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

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, $12 \times 12$ 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. (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.

Percent C, and $\delta^{13}$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 in an evacuated quartz tube. Evolved CO$_2$ was then cryogenically purified on a vacuum line, reduced to graphite and analyzed for $\Delta^{14}$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 $20 \times 20$ cm$^2$ soil pits randomly distributed at the site, dried, ground, and analyzed for $\delta^{13}$C ($n = 4$ per horizon), and $\Delta^{14}$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 ($n = 4$).

We used the $\Delta^{14}$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.

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 $\Delta^{14}$C ($n = 2$), all pairwise comparisons between ecosystem components for $\Delta^{14}$C use $\alpha = 0.1$ as the significance level. All other analyses use $\alpha = 0.05$ as the significance level.

2.5. Model Description

We used an inverse modeling approach with $^{13}$C/$^{12}$C and $^{14}$C/$^{12}$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 Δ²⁰⁰₁₄C 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.

\[ \delta^{13}CO_2 = \frac{\sum_i \delta^{13}C_i M_i F_i}{\sum_i M_i F_i} \]

\[ \Delta^{14}CO_2 = \frac{\sum_i \Delta^{14}C_i M_i F_i}{\sum_i M_i F_i} \]

where
- \( \delta^{13}C \), \( \Delta^{14}C \) isotope signature of ecosystem component, %;
- \( M \) mass of ecosystem component, g m⁻²;
- \( F \) fraction burned, %;
- \( \Delta^{14}C \) from the combustion of different ecosystem components 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%.

6. 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 \(-26.97 ± 0.88\)%o (Figure 2a), reflecting the combustion of C in vegetation and forest floor that was fixed by the C₃ photosynthetic pathway. The Δ²⁰⁰₁₄C intercept was \(+210 ± 27\)%o (Figure 2b) indicating the combustion of vegetation and soil components that had fixed atmospheric CO₂ during the past several decades. Atmospheric Δ²⁰⁰₁₄C due to weapons testing reached its peak...
close to +900% in 1964 before declining to levels of about +95% in 1999 (Figure 1).

3.2. Ecosystem Components

[19] Total C pools were of similar magnitude in aboveground vegetation and in organic soil horizons (Table 1). Of vegetation compartments, bole wood was the largest pool containing 43% of the total vegetation C. Other pools were roughly similar in size to one another ranging from 7% of the total C pool contained in cones to 14% in coarse branches. Soil C was equitably distributed in the top three horizons that each contained approximately 20% of the total C pool, while the deepest humic horizon contained the remaining 40%. Soil C contained in mineral horizons does not generally contribute significantly to combustion emissions and was not quantified by this study.

[20] Carbon isotopes in components of vegetation and soil ranged between −25 and −31% for δ13C and between +110 and +350% for Δ14C. Vegetation components differed widely in their δ13C signature (p < 0.01) with needles being the most depleted and wood the most enriched (Figure 3a). All components had unique δ13C isotope values (p < 0.05) except for cones, bark, and coarse branches that could not be distinguished from one another. Measurements of Δ14C largely confirmed this pattern (p = 0.02) with needles and fine branches being significantly less enriched (p < 0.1) than cones, wood, bark, and coarse branches. Cones were the most variable in Δ14C of all components and could not be distinguished from wood or bark, but were significantly different than coarse branches (p < 0.1).

[21] Soil horizons differed significantly in both δ13C (p < 0.01) and Δ14C (p = 0.01) and varied largely by depth (Figure 3b). The surface moss and dead moss horizons had more depleted δ13C and lower Δ14C than either the fibric or the humic horizons deeper in the soil profile. All horizons were significantly different from one another for δ13C (p < 0.05) and Δ14C (p < 0.1) except for the surface moss and dead moss layers that were marginally different in δ13C (p = 0.08) and not different in Δ14C.

[22] In summary, needles, fine branches, surface moss, and dead moss all had significantly different isotope values and were relatively depleted in both δ13C and Δ14C. These components all differed from cones, bark, coarse branches, and the fibric horizon, which had intermediate δ13C and Δ14C values and could not be distinguished from one another. Finally, both wood and the humic horizon were

**Figure 2.** The concentration and isotope value of carbon dioxide from air samples collected downwind from a boreal forest experimental burn for (a) δ13C, and for (b) Δ14C. The data are presented as the isotope value as a function of the inverse of concentration, thus the y intercept represents the isotopic signature of carbon dioxide emitted from combustion alone.

**Table 1.** Carbon Contained in Aboveground Biomass and Soil Organic Horizons, and the Average Age Estimated from Δ14C Isotopic Signatures

<table>
<thead>
<tr>
<th>Ecosystem Component</th>
<th>C mass, g m⁻² (±SE)</th>
<th>Average Age, yr (±SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P. mariana Biomass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Needles</td>
<td>273.0 (32.3)</td>
<td>5 (1)</td>
</tr>
<tr>
<td>Fine branches</td>
<td>207.5 (24.6)</td>
<td>5 (1)</td>
</tr>
<tr>
<td>Cones</td>
<td>125.1 (14.8)</td>
<td>13 (7)</td>
</tr>
<tr>
<td>Coarse branches</td>
<td>306.6 (36.3)</td>
<td>52 (4)</td>
</tr>
<tr>
<td>Bole bark</td>
<td>179.2 (21.3)</td>
<td>56 (1)</td>
</tr>
<tr>
<td>Bole wood</td>
<td>807.9 (95.4)</td>
<td>64 (7)</td>
</tr>
<tr>
<td><strong>Organic Soil Horizons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface moss</td>
<td>439.2 (13.5)</td>
<td>9 (3)</td>
</tr>
<tr>
<td>Dead moss (Oi)</td>
<td>398.0 (109.4)</td>
<td>13 (5)</td>
</tr>
<tr>
<td>Fibric (Oe)</td>
<td>484.5 (12.5)</td>
<td>19 (1)</td>
</tr>
<tr>
<td>Humic (Oa)</td>
<td>892.2 (89.1)</td>
<td>38 (1)</td>
</tr>
</tbody>
</table>
relatively enriched in both $\delta^{13}$C and $\Delta^{14}$C and had distinct isotopic signatures from one another and the rest of the components.

The estimated average age of C contained in trees ranged from 4 years for components such as needles and fine branches, to over 60 years for bole wood (Table 1). Soil organic horizons were estimated to have largely accumulated over approximately the past 40 years (Table 1).

### 3.3. Model Results

The model was run with rules and parameters described above. Less than 0.03% of all possible permutations were both allowed by the rules of combustion and also matched the observed combustion CO$_2$ isotopic signature ($\pm$SE). The mean C ($\pm$SD) emission predicted by the model was 2.47 ± 0.32 kg m$^{-2}$. Of the C originally contained in vegetation and soil organic horizons, the model predicted that 60 ± 8% was consumed by the experimental fire. The model predicted that the fraction of ecosystem C pools consumed by fire ranged from 25–30% for coarse branches and cones, to about 65–75% for bark, needles, and fine branches moss, and fibric soil horizons were largely consumed by fire, which was predicted to have burned down into the deepest humic horizon (Table 2). While bole wood combustion was limited by rule 5, relaxing this assumption had little effect on predictions of total C emissions. Allowing the bole wood to burn without rule 5 increased the C emissions by only 2%. In that case, the fraction of bole wood consumption was 36%, and the fraction of humic layer consumption was 43%. Restricting bole wood combustion increased humic layer combustion and reduced the variability in the predicted combustion of other soil horizons.

Differences in fire severity affected the forward model prediction of C isotope emissions. A low-severity fire, where coarse fuels and deeper soil horizons were not allowed to burn, was predicted to release CO$_2$ with a mean $\delta^{13}$C ($\pm$SD) of $-29.28 \pm 0.30\%$, and a mean $\Delta^{14}$C ($\pm$SD) of 155 ± 7%. Surface soil horizons largely comprised components that burned in the low-severity fire, in addition to some contribution from needles, fine branches, and bark. A very severe fire, where the humic horizon and the fine fuels were required to burn substantially, was predicted to release CO$_2$ with a mean $\delta^{13}$C ($\pm$SD) of $-27.52 \pm 0.07\%$, and a mean $\Delta^{14}$C ($\pm$SD) of 227 ± 4%. Almost all the soil organic horizons, needles, and fine branches were combusted in the severe fire, along with significant amounts of bark and cones. Predicted C emission from the severe fire was more

### Table 2. Model Estimated Combustion of Aboveground Biomass and Soil Organic Horizons in the Frostfire Experimental Forest Fire

<table>
<thead>
<tr>
<th>Ecosystem Component</th>
<th>Percent Combusted ($\pm$SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P. mariana Biomass</strong></td>
<td></td>
</tr>
<tr>
<td>Needles</td>
<td>73.3 (20.8)</td>
</tr>
<tr>
<td>Fine branches</td>
<td>76.0 (20.3)</td>
</tr>
<tr>
<td>Cones</td>
<td>27.4 (21.8)</td>
</tr>
<tr>
<td>Coarse branches</td>
<td>28.6 (21.7)</td>
</tr>
<tr>
<td>Bole bark</td>
<td>67.1 (24.4)</td>
</tr>
<tr>
<td>Bole wood</td>
<td>15.6 (9.8)</td>
</tr>
<tr>
<td><strong>Organic Soil Horizons</strong></td>
<td></td>
</tr>
<tr>
<td>Surface moss</td>
<td>96.8 (8.1)</td>
</tr>
<tr>
<td>Dead moss (Oi)</td>
<td>91.6 (13.5)</td>
</tr>
<tr>
<td>Fibric (Oe)</td>
<td>81.6 (17.9)</td>
</tr>
<tr>
<td>Humic (Oa)</td>
<td>62.7 (18.0)</td>
</tr>
</tbody>
</table>

Figure 3. The $\delta^{13}$C and $\Delta^{14}$C isotopic signature of components of (a) P. mariana biomass and (b) organic soil horizons. Letters denote statistical significance for $\delta^{13}$C and $\Delta^{14}$C. Ecosystem components that share letters in common are not statistically different.
than a factor of 4 times greater than C emitted from the low-severity fire, and was enriched both in $\delta^{13}C$ and $\Delta^{14}C$. Because $\Delta^{14}C$ values are time-dependent (Figure 1), isotopic emissions predicted by the model will change over time as atmospheric $\Delta^{14}C$ continues to decrease.

4. Discussion

[26] Inverse modeling of C isotopes in CO$_2$ emitted from biomass burning can be used to predict the severity of fire and amount of C released from terrestrial ecosystems to the atmosphere. Differences in fire severity could have resulted in more than a fourfold range in C loss from terrestrial ecosystems to the atmosphere in this experimental fire, according to model predictions. The Frostfire experimental burn, which released CO$_2$ with an isotopic value of $-26.97\%$ for $\delta^{13}C$ and $+210\%$ for $\Delta^{14}C$ (Figures 2a and 2b) and consumed 60% of the C contained in vegetation and soil organic horizons, was estimated to be a medium to severe intensity fire based on a comprehensive review of boreal forest fires [Amiro et al., 2001]. The total amount of C release predicted here agreed with several other estimates of C release from Frostfire derived from independent methods such as ecosystem modeling (A. McGuire, personal communication, 2001), and ground-based observations before and after fire (E. Alverado, personal communication, 2001).

[27] Model predictions were controlled primarily by the isotopic signature of combustion in combination with the combustion rules. In order to produce the observed combustion isotopic signature, there needed to be significant contribution from the humic horizon, the bole wood horizon, or both (Figures 3a and 3b). In turn, the combustion of other ecosystem components was strongly constrained by the rules that related those pools to the combustion of the humic and wood components. Sensitivity analyses that allowed the isotopic signature of the source pools to vary had little effect on the variability of the fraction combusted of different aboveground biomass components. In contrast, variation in the isotopic signature of source pools determined the amount of the humic horizon that was required to burn to produce the observed combustion isotopic signature. Including isotopic variability in the source pool signatures increased the variability in the fraction combusted of the humic horizon somewhat, but compensated by decreasing the variability in the fraction combusted of the surface moss and dead moss horizons. This variation did not significantly affect the total amount of C loss predicted by the model, and was similar in magnitude to the sensitivity of C loss to variation in source pool C mass.

[28] Our ability to predict combustion loss of C was dependent on the differences in isotopic signature among ecosystem components [Phillips and Gregg, 2001]. Differences in $\Delta^{14}C$ values among biomass components are related to the lifetime of each component. Components such as leaves and fine twigs that have life spans on scales from 1 to 10 years [Reich et al., 1992] should primarily reflect the $\Delta^{14}C$ of the atmosphere over that same time period (Figure 1). Needle and fine branches in this study were estimated to be, on average, 4 years old, while cones had an average age of 12 years (Table 1). Black spruce cones are semiserotinous and tend to be retained on the tree until fire stimulates seed dispersal [Greene et al., 1999], thus leading to the older age of cones. Components such as large branches and bole wood have longer life spans and have higher $\Delta^{14}C$ values because they retain more of the bomb peak $\Delta^{14}C$ values [Hua et al., 1999]. The age of long-lived components such as bole wood, bole bark, and coarse branches (Table 1) corresponded to independent estimates of stand age. Black spruce recruitment at CPCRW was found to have occurred after 1924 [Fastie, 2000]. Averaging the isotopic composition over the entire tree bole could be somewhat misleading since the bole burns from the outside, and is not isotopically homogenous. However, bole wood is not thought to burn in significant amounts [Kasischke et al., 2000], thus this model assumption has a limited effect on C emissions. Soil radiocarbon values also reflected stand age, although the deepest humic horizon was younger than the spruce tree wood (Table 1). This suggests that establishment of a moss layer and the accumulation of significant amounts of soil organic C did not occur until after black spruce recruitment. This pattern has also been observed in black spruce forests in Canada [Trumbore and Harden, 1997], and is likely due to the requirement for a closed evergreen canopy to precede the spread and dominance of a moss understory [Van Cleve et al., 1991]. Also, deciduous leaf litter that forms the bulk of litterfall in early successional forests has high-decomposition rates thus may not contribute much to the accumulation of soil organic horizons [Van Cleve et al., 1991].

[29] Variation in $\delta^{13}C$ values for vegetation components and soil organic horizons is likely a result of multiple mechanisms. The decline of atmospheric $\delta^{14}C$ over the past 100 years by almost 1.5‰ due to combustion of $\delta^{13}C$-depleted fossil fuel contributed to higher $\delta^{13}C$ in longer lived plant tissues and older SOM [Enting et al., 1995; Trolier et al., 1996; Fung et al., 1997]. Shifts in $\delta^{13}C$ from the atmosphere in 1999, calculated from $\Delta^{14}C$-derived age estimates, range from 0.06‰ for needles and fine branches, 0.18‰ for cones, and 0.67‰ to 0.75‰ for coarse branches, bark and wood, and explained 22% of the range of $\delta^{13}C$ values in vegetation components. The remainder of the variation in $\delta^{13}C$ values can be explained by plant physiological processes. Systematic difference in $\delta^{13}C$ values between foliage and wood have been observed repeatedly in evergreen and deciduous ecosystems worldwide [Deines, 1980]. A comprehensive survey of 33 tropical forest tree species demonstrated that wood was on average 4% more enriched than foliage [Martinelli et al., 1998]. Leavitt and Long [1982] showed that $\delta^{13}C$ values in same-age cellulose differed between foliage and wood due to fractionation during respiration and translocation of photosynthate [Leavitt and Long, 1986; but see Lin and Ehleringer, 1997], or to the timing of wood production [Francey et al., 1985; Pate and Arthur, 1998]. A final contributing factor to differences in wood versus foliage $\delta^{13}C$ is biosynthetic fractionation that causes systematic differences in the isotope ratio of specific carbon compounds. Compounds such as lignin and plant waxes tend to have depleted $\delta^{13}C$ values whereas cellulose tends to be enriched [Park and Epstein, 1961; Benner et al., 1987; Leavitt and Long, 1986; Pate and Arthur, 1998].
[30] In soils, δ13C 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 δ13CO2 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 δ13C in the soil horizons at this site. More importantly, older (deeper) SOM is thought to be enriched in δ13C by heterotrophic fractionation during decomposition through preferential release of 12C [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 δ13C and Δ14C 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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