

Predicted net efflux of radiocarbon from the ocean and increase in atmospheric radiocarbon content

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Abstract. Prior to changes introduced by man, production of radiocarbon (^{14}C) in the stratosphere nearly balanced the flux of ^{14}C from the atmosphere to the ocean and land biosphere, which in turn nearly balanced radioactive decay in these ^{14}C reservoirs. This balance has been altered by land-use changes, fossil-fuel burning, and atmospheric nuclear detonations. Here, we use a model of the global carbon cycle to quantify these radiocarbon fluxes and make predictions about their magnitude in the future. Atmospheric nuclear detonations increased atmospheric ^{14}C content by about 80% by the mid-1960's. Since that time, the ^{14}C content of the atmosphere has been diminishing as this bomb radiocarbon has been entering the oceans and terrestrial biosphere. However, we predict that atmospheric ^{14}C content will reach a minimum and start to increase within the next few years if fossil-fuel burning continues according to a "business-as-usual" scenario, even though fossil fuels are devoid of ^{14}C . This will happen because fossil-fuel carbon diminishes the net flux of ^{14}C from the atmosphere to the oceans and land biosphere, forcing ^{14}C to accumulate in the atmosphere. Furthermore, the net flux of both bomb and natural ^{14}C into the ocean are predicted to continue to slow and then, in the middle of the next century, to reverse, so that there will be a net flux of ^{14}C from the ocean to the atmosphere. The predicted reversal of net ^{14}C fluxes into the ocean is a further example of human impacts on the global carbon cycle.

Introduction

Radiocarbon is created as neutrons released by stratospheric bombardment with cosmic radiation replace protons in stratospheric nitrogen [Broecker and Peng, 1982]. As this radiocarbon spreads through the atmosphere, land biosphere and oceans, it decays with a half-life of about 5730 yr. The distribution of radiocarbon has been used an important test of global carbon-cycle [e.g., Jain *et al.*, 1996] and ocean models [e.g., Toggweiler *et al.*, 1989a, 1989b; Duffy and Caldeira, 1995], yet there has been little quantitative appreciation of the factors that affect ^{14}C fluxes.

Prior to the advent of widespread deforestation and fossil-fuel burning, the oceans and biosphere are believed to have been nearly in steady-state relative to the atmospheric ^{14}C content, and the net radiocarbon flux into the biosphere and ocean roughly balanced radioactive decay in these two reservoirs. However, this balance has been markedly perturbed by land-use changes, fossil-fuel burning and atmospheric nuclear detonations [Suess, 1955; Keeling, 1973; Keeling *et al.*, 1979]. For example, Suess [1955] discovered a 2 to 3% reduction in atmospheric $^{14}\text{C}/^{12}\text{C}$ from

pre-industrial times to year 1950. This is far less than might be expected from the 10% increase in atmospheric CO_2 (predominately $^{12}\text{CO}_2$) content over this time period. Most of this apparent discrepancy can be explained [Suess, 1955; Keeling, 1973; Keeling *et al.*, 1979] by $^{14}\text{CO}_2$ fluxes from the land biosphere and oceans induced by increasing atmospheric $^{12}\text{CO}_2$ (see also Francey R.J., C.M. Trudinger, and V.A. Levchenko, ^{14}C variations in the atmosphere: A southern perspective. ANARE Research Note, Australian Antarctic Division, ed. M.L. Duldig, submitted) Even though fossil fuels are nearly devoid of ^{14}C , fossil-fuel burning indirectly causes a significant increase in atmospheric ^{14}C content as we will quantify below.

The Model

Here, a model of the global carbon cycle, based on the model of Hesshaimer *et al.* [1994], is used to estimate the impact of fossil-fuel burning, land-use changes, and atmospheric nuclear detonations on atmospheric ^{14}C content and air-sea ^{14}C fluxes, both for the historical past and for the next century. This model consists of a 1-box atmosphere, 3-box land biosphere and a box-diffusion ocean. In this model, the state variables are C, ^{13}C and ^{14}C masses or concentrations. Throughout, fractionation factors for ^{14}C are assumed to be the square of the ^{13}C fractionation factor (which are roughly double the ^{13}C fractionation factors when written in $\delta^{13}\text{C}$ notation), and all fractionation factors are from Tans *et al.* [1993]. The atmosphere is represented by a single, well-mixed reservoir containing 1.773×10^{20} moles.

Our terrestrial biosphere model is identical to the three-box biosphere model of [Hesshaimer *et al.*, 1994], except that we include ^{13}C , allow net-primary-productivity to vary, and permit deforestation fluxes. Deforestation-related CO_2 fluxes to the atmosphere [Houghton *et al.*, 1983; Enting *et al.*, 1994] are assumed to come from the rapid turnover compartment (10%), the medium turnover compartment (80%), and the slow turnover compartment (10%), yielding a weighted mean turnover time scale for deforested material of 59.4 years.

The ocean is represented by a box-diffusion model [Oeschger *et al.*, 1975; Siegenthaler, 1983] with a 75 m thick mixed-layer and a total depth of 3800 m. Ocean carbon chemistry [Stumm and Morgan, 1981] is calculated using a surface temperature of 18 °C, salinity of 35 psu, and alkalinity of 2.23 eq m^{-3} , with constants as specified in Roy *et al.* [1993], Dickson [1990], Millero [1995], and Weiss [1974]. The eddy diffusion and gas-transfer velocity coefficients were chosen such that the change in ocean $^{14}\text{CO}_2$ inventory between 1945 and 1975 matches the estimated 1975 bomb radiocarbon inventory [Broecker *et al.*, 1995] of 305×10^{26} atoms, and the modeled 1975 ocean mean and surface ocean $\Delta^{14}\text{CO}_2$ matches the basin-volume-weighted mean of the natural plus bomb $\Delta^{14}\text{CO}_2$ values measured in the GEOSECS program [Broecker *et al.*, 1985]. $\Delta^{14}\text{C}$ is a normalized and ^{13}C -adjusted $^{14}\text{C}/^{12}\text{C}$ ratio, and $\delta^{13}\text{C}$ is a normalized $^{13}\text{C}/^{12}\text{C}$ ratio

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[Broecker and Peng, 1982]. This tuning yielded a vertical eddy diffusion coefficient is $8,820 \text{ m}^2 \text{ yr}^{-1}$ at the base of the mixed-layer, diminishing with an e-folding length scale of 500 m to a minimum of $2,910 \text{ m}^2 \text{ yr}^{-1}$ at the ocean bottom. The tuned gas transfer velocity is equivalent to $0.0543 \text{ mol m}^{-2} \mu\text{atm}^{-1} \text{ yr}^{-1}$ at 18°C . Similar parameter values were used by other modelers [Oeschger, 1979; Siegenthaler, 1983; Hesshaimer et al., 1994].

We force the model with estimates of fossil-fuel burning [Marland and Boden, 1991; Enting et al., 1994], deforestation [Houghton et al., 1983; Enting et al., 1994] and atmospheric CO_2 content [Nefel et al., 1985; Friedli et al., 1986; Keeling et al., 1989; Enting et al., 1994]. The terrestrial biosphere and ocean models are spun up to steady-state under a 1765 atmosphere; thereafter, cosmogenic ^{14}C production is set to balance the decay of ^{14}C in 1765, and is introduced directly into the atmosphere. Future CO_2 emissions are from the IPCC IS92a "business-as-usual" scenario [Leggett et al., 1992]. For the past, net primary productivity of the terrestrial biosphere is computed as a residual, equal to the C flux from fossil-fuel burning and deforestation minus the net flux of CO_2 into the ocean and atmospheric accumulation. For the future, rather than attempt to guess future biomass changes, we assume that future biomass will remain constant, computing the net primary productivity such that implied CO_2 -fertilization and forest regrowth balances the deforestation specified in the IS92a scenario. This model is schematic, and assumes no variation in cosmogenic ^{14}C production [Stuiver and Quay, 1980; Stuiver et al., 1991], or ocean circulation; hence, model results should be interpreted as indicative of the probable magnitude of the CO_2 -induced $^{14}\text{CO}_2$ fluxes, and not as exact simulations of $^{14}\text{CO}_2$ trends.

Results and Discussion

Because we did not adjust the model on atmospheric results, model results for the atmosphere can be used for model valida-

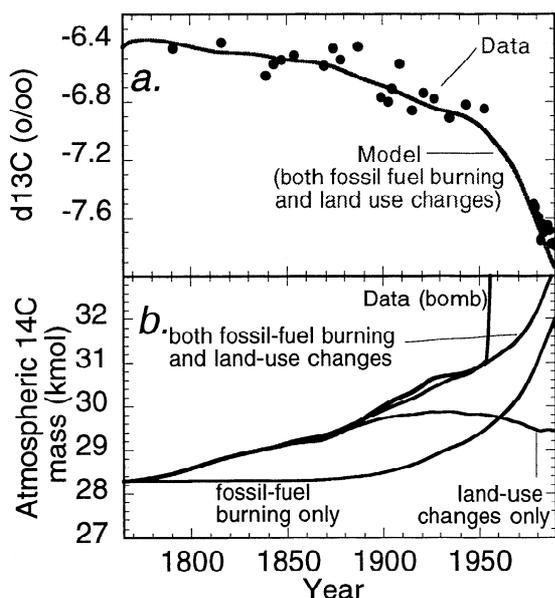


Fig. 1. Comparison of atmospheric (a) $\delta^{13}\text{C}$ data [Friedli et al., 1986; Keeling et al., 1989] and (b) ^{14}C estimates with model results for the period 1765 to 1990. The close correspondence between observations and model results (in the absence of tuning on atmospheric concentrations) indicates that the model has good predictive ability for carbon isotopes.

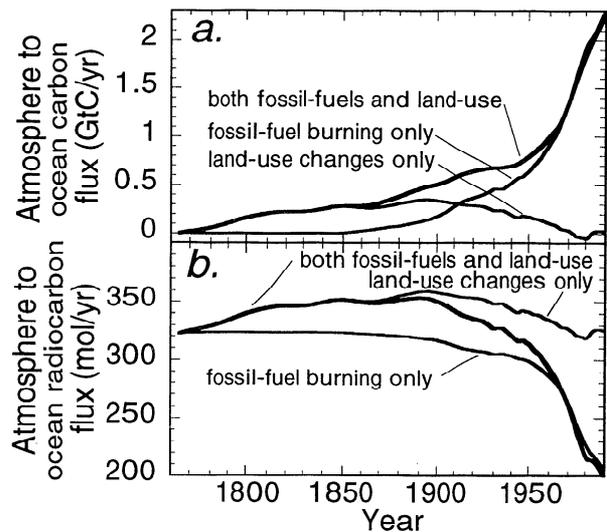


Fig. 2. Net fluxes of (a) C and (b) ^{14}C into the ocean for the period 1765 to 1990 as calculated for the simulations "fossil-fuel only", "land-use only" and "both", using the scenarios and model described in the text. Note that land-use changes have generally produced fluxes of both C and ^{14}C into the ocean, whereas fossil-fuel burning induces a C flux into the ocean but tends to diminish the ^{14}C flux into the ocean.

tion. The model shows good agreement with observed [Friedli et al., 1986; Keeling et al., 1989] atmospheric CO_2 $\delta^{13}\text{C}$ for the period 1765 to 1990 (Fig. 1a), and $^{14}\text{CO}_2$ for the period of 1765 to 1945 (Fig. 1b). The simulated atmospheric $^{14}\text{CO}_2$ mass shown in Fig. 1b has a root-mean-square deviation from observations (calculated from Enting et al. [1994], Friedli et al. [1986], and Keeling et al. [1989]) of 0.26% between 1765 and 1950. This close correspondence between model predictions and atmospheric $\delta^{13}\text{C}$ observations for 1765 to 1990, and $^{14}\text{CO}_2$ concentrations from 1765 to 1950 gives confidence in predicted $^{14}\text{CO}_2$ concentrations for 1950 to 2100.

We present results from four model simulations. In the simulation labeled "both", we consider both fossil-fuel burning and land-use changes, but not changes associated with nuclear weapons tests. The "land-use only" simulation is the same as the "both" simulation, but fossil fuel fluxes are set to zero. The "fossil fuel only" simulation is the same as the "both" simulation, but deforestation and forest regrowth fluxes are set to zero. The "data/bomb" simulation runs the land-biosphere and ocean models under the observed atmosphere until year 1990, thereafter, the model is run as in the "both" case. This last simulation serves as a model test for the historical period, and as a prediction of future ^{14}C fluxes, and is distinct from the "both" simulation in that it also considers bomb ^{14}C . Fluxes associated with atmospheric nuclear detonations are estimated by subtracting the results of the "both" simulation from the results of the "data/bomb" simulation. Whereas the carbon cycle contains non-linear interactions, atmospheric CO_2 changes relative to 1765 in the "both" simulation are within 1.4% of the sum of the changes relative to 1765 in the "land-use only" and "fossil-fuel only" cases. Thus, in the cases considered here, these non-linear interactions are small.

Fig. 2a and 2b show model results for net C and ^{14}C fluxes, respectively, from the atmosphere to the ocean. The model indicates that prior to about 1910, most of the C flux into the ocean was induced by deforestation; after this date, this flux was dominated by the effects of fossil-fuel burning. Partial destruction of

the land biosphere without regrowth directly increases atmospheric ^{14}C content, because land plants and soils contain ^{14}C . Fossil fuel, on the other hand, is nearly devoid of ^{14}C , hence atmospheric CO_2 derived from this source has no direct impact on global ^{14}C budgets. However, the addition of significant quantities of CO_2 to the atmosphere via deforestation and fossil fuel burning has substantial indirect impacts on $^{14}\text{CO}_2$ fluxes [Suess, 1955; Keeling, 1973; Keeling et al., 1979]. For example, injecting ^{12}C -rich CO_2 into the atmosphere lowers the atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio. Because land plant uptake of $^{14}\text{CO}_2$ is roughly proportional to the product of CO_2 uptake times the atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio, a lower atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio diminishes $^{14}\text{CO}_2$ uptake per unit net-primary-productivity. This reduction in $^{14}\text{CO}_2$ uptake may be further exacerbated by increased biotic selectivity for $^{12}\text{CO}_2$ uptake at elevated CO_2 concentrations [Farquhar et al., 1989]. The net effect of the diminished uptake of atmospheric $^{14}\text{CO}_2$ by the land biosphere, without a marked lessening of the respiratory flux of $^{14}\text{CO}_2$ to the atmosphere, is to diminish or reverse the net flux of $^{14}\text{CO}_2$ from the atmosphere to the land biosphere. Indeed, our model predicts that the land biosphere is already returning a net flux of $^{14}\text{CO}_2$ to the atmosphere, although modeling the exact start of this circumstance depends on relatively uncertain land-biosphere time constants.

The ocean-atmosphere $^{14}\text{CO}_2$ flux also responds to the preceding mass and isotopic perturbations in an indirect but profound way. The increase in atmospheric CO_2 content caused by deforestation and especially fossil-fuel burning forces net CO_2 uptake by the ocean. Under constant alkalinity, this net CO_2 uptake reduces the pH of the surface ocean, requiring [Stumm and Morgan, 1981] a greater fraction of the total dissolved inorganic carbon (ΣCO_2) to be in the form of molecular CO_2 ($\text{CO}_2(\text{aq})$). This pH lowering in turn also affects the $\text{CO}_2(\text{aq})$ partitioning of $\Sigma^{14}\text{CO}_2$ (and $\Sigma^{13}\text{CO}_2$) [Mook et al., 1974]. Thus, because a greater fraction of the surface ocean $\Sigma^{14}\text{CO}_2$ occurs as $^{14}\text{CO}_2(\text{aq})$, the resulting increase in ocean $^{14}\text{CO}_2$ fugacity forces a $^{14}\text{CO}_2$ flux to the atmosphere. According to our model, by about year 1940, the tendency for fossil-fuel burning to drive ^{14}C out of the ocean overwhelmed the tendency for deforestation to drive ^{14}C into the ocean, and the net ^{14}C flux into the ocean fell below the value needed to balance ^{14}C decay in the ocean. This a situation persisted until the advent of widespread atmospheric nuclear weapons testing in the mid-1950's.

Tropospheric ^{14}C content was approximately 80% greater in year 1965 than in year 1945 due mainly to atmospheric nuclear weapons tests. Based on the model calculations made here, direct and indirect effects of land use changes and fossil-fuel burning would have produced only a 1.8% increase in tropospheric ^{14}C content during this period. This relatively small impact of the "Suess" effect on the bomb radiocarbon budget has led some [e.g., Toggweiler et al., 1995b; Duffy and Caldeira, 1995] to model the bomb radiocarbon using a "perturbation approach", in which ^{14}C fluxes are considered to be independent of total C fluxes. However, ^{14}C fluxes induced by land-use changes and fossil-fuel burning have become non-negligible. Our model results indicate that about 30% of the increase in atmospheric $^{14}\text{CO}_2$ between 1945 and 1995 was a consequence of land-use changes and fossil-fuel burning, with the remaining 70% associated with atmospheric nuclear detonations (Fig. 3a).

To consider what may happen in the future, we use the IPCC IS92a "business-as-usual" scenario [Leggett et al., 1992]. Model results indicate that atmospheric ^{14}C content should actually start increasing in year 1998, reversing a decreasing trend that was initiated in the mid-1960's. This prediction will soon be testable

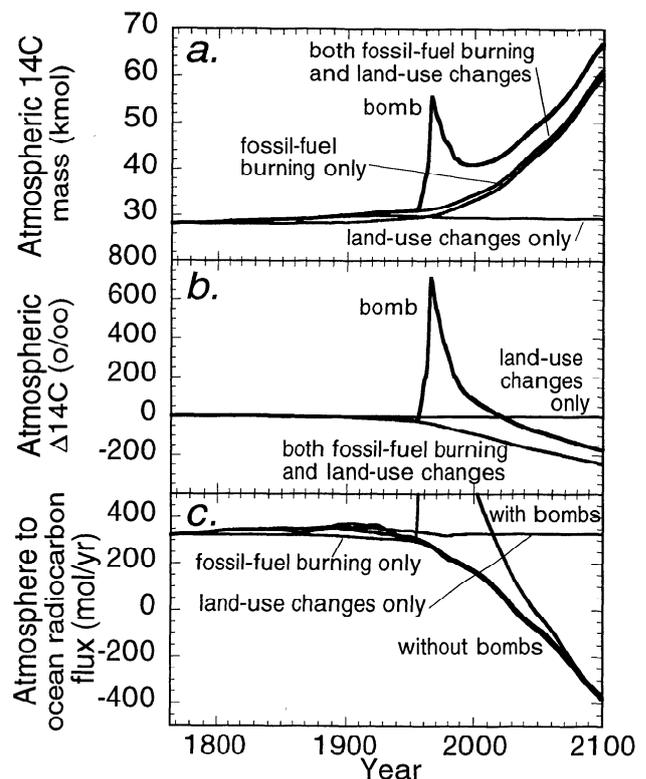


Fig. 3. (a) Atmospheric ^{14}C mass, (b) atmospheric $\Delta^{14}\text{C}$, and (c) net fluxes of ^{14}C from the atmosphere to the ocean predicted by the model for the period 1765 to 2100 as calculated for the simulations "fossil-fuel only", "land-use only", "both", and "data/bomb" using the scenarios and model described in the text. The model estimates a natural ^{14}C flux into the ocean of about 320 mol yr^{-1} . The large increase in atmospheric ^{14}C mass is primarily the result of ^{14}C fluxes induced by fossil-fuel burning. Note that after the late 1990's, atmospheric $^{14}\text{CO}_2$ is predicted to increase, even though atmospheric $\Delta^{14}\text{C}$ is predicted to decrease. The model predicts that the ocean should start losing ^{14}C to the atmosphere sometime in the middle of the next century.

through observations of atmospheric pCO_2 , $\delta^{13}\text{C}$, and $\Delta^{14}\text{C}$, and calculation of atmospheric ^{14}C mass from those values. Fig. 3a shows that most of the increase in atmospheric ^{14}C content in the next century (absent a renewal of atmospheric nuclear detonation) will probably be a consequence of fossil-fuel burning, while land-use changes will probably have a relatively minor impact. Note (Fig. 3b) that this increase in ^{14}C content will be accompanied by a decline in atmospheric $\Delta^{14}\text{C}$ values, due to the disproportionately larger increase in atmospheric $^{12}\text{CO}_2$ content. If fossil-fuel burning continues according to a "business-as-usual" scenario, the fossil-fuel induced ^{14}C flux out of the ocean (Fig 3c) will exceed the bomb ^{14}C flux into the ocean by about year 2015, and the oceanic ^{14}C mass will begin to diminish. The model predicts that the fossil-fuel induced ^{14}C fluxes out of the ocean will exceed the natural ^{14}C flux into the ocean by about year 2030, and will exceed the natural plus bomb ^{14}C flux into the ocean by near year 2050. Hence, by the middle of the next century the oceans should become a net source, rather than a sink, of ^{14}C to the atmosphere. The model predicts that bomb ^{14}C in the atmosphere (as calculated by subtracting the results of the "both" simulation from the "data/bomb" simulation) will reach a minimum near year 2050, and start to increase slightly thereafter. This is because, as discussed above, the changes in ocean pH , resulting

from absorption of anthropogenic CO₂, would affect ocean chemistry sufficiently to cause previously absorbed bomb radiocarbon to degas back to the atmosphere.

Conclusions

In summary, in addition to nuclear weapons testing, anthropogenic perturbations to the carbon cycle, principally the burning of fossil fuels, is markedly affecting the ¹⁴C cycle. We conclude that the atmosphere is now near a local minimum in atmospheric ¹⁴C content, which should start to increase in the next few years as stratospheric ¹⁴C production exceeds net bomb plus natural ¹⁴C uptake by the land biosphere and ocean. The prediction of the timing of this radiocarbon minimum may be an important test of global carbon cycle models, in that the exact timing of the minimum is sensitive to the turnover time of ¹⁴C in the various model reservoirs, and total radiocarbon, unlike bomb radiocarbon, is directly calculable from measurable quantities.

Our model predicts the oceans should become a net source of ¹⁴C to the atmosphere sometime in the middle of the next century. Such a reversal of the ¹⁴C flux into the ocean is not known to have occurred in the past, but could have occurred naturally if, for example, changes in ocean circulation resulted in rapid increases in atmospheric CO₂ content, or if there was natural catastrophic degassing of methane clathrates [Dickens *et al.*, 1997] or other ¹⁴C-depleted carbon reservoir. The predicted reversal of net ¹⁴C fluxes into the ocean is a further example of the degree to which human activity is impacting the global carbon cycle.

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