The paper trail of the $^{13}$C of atmospheric CO$_2$ since the industrial revolution period

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Abstract

The $^{13}$C concentration in atmospheric CO$_2$ has been declining over the past 150 years as large quantities of $^{13}$C-depleted CO$_2$ from fossil fuel burning are added to the atmosphere. Deforestation and other land use changes have also contributed to the trend. Looking at the $^{13}$C variations in the atmosphere and in annual growth rings of trees allows us to estimate CO$_2$ uptake by land plants and the ocean, and assess the response of plants to climate. Here I show that the effects of the declining $^{13}$C trend in atmospheric CO$_2$ are recorded in the isotopic composition of paper used in the printing industry, which provides a well-organized archive and integrated material derived from trees’ cellulose. $^{13}$C analyses of paper from two European and two American publications showed, on average, $-1.65 \pm 1.00$ permil trend between 1880 and 2000, compared with $-1.45$ and $-1.57$ permil for air and tree-ring analyses, respectively. The greater decrease in plant-derived $^{13}$C in the paper we tested than in the air is consistent with predicted global-scale increases in plant intrinsic water-use efficiency over the 20th century. Distinct deviations from the atmospheric trend were observed in both European and American publications immediately following the World War II period.

Keywords: atmospheric CO$_2$, $^{13}$C, carbon 13, global change, tree rings, wood cellulose

1. Introduction

The preferential uptake of $^{12}$CO$_2$ over $^{13}$CO$_2$ in plant photosynthesis (Francey and Farquhar 1982, Farquhar et al 1982) has two important implications. First, the extent of this biologically dominated discrimination is sensitive to environmental conditions, making $^{13}$C content in wood and other plant materials a useful indicator of climate change and plant response to it (Feng 1999, Leavitt et al 2003, Peñuelas et al 2008). Second, removal of $^{13}$C-depleted CO$_2$ from the atmosphere via land photosynthesis results in $^{13}$C accumulation in the remaining atmospheric CO$_2$, the extent of which reflects the strength of the land sink (Ciais et al 1995, Tans et al 1993), while CO$_2$ exchange with the ocean, in contrast, is dominated by physical processes that have relatively little effect on $^{13}$C. In both cases we must also account for the effects of anthropogenic activities over the industrial period. Fossil fuel emissions and biomass burning involve the combustion of photosynthetically derived material. In all cases, $^{13}$C-depleted CO$_2$ is returned to the atmosphere diluting its $^{13}$C content. Continuous records of the atmospheric $^{13}$C trend over the last 1000 years exist mainly based on air trapped in firn and ice (e.g. Francey et al 1999). While extensive, high-precision monitoring of atmospheric $^{13}$C only started in 1990s (www.esrl.noaa.gov/gmd/ccgg/globalview/co2c13/co2c13_intro.html), there have been several attempts to detect the fossil fuel signal on century time-scales via the $^{13}$C/$^{12}$C ratio in organic material, primarily using tree rings (McCarroll and Loader 2004, Feng and Epstein 1995, Waterhouse et al 2004). Paper used in the printing industry also provides a well-preserved, -organized and -dated archive of partially purified cellulose from plants. The pulping industry made major technological advancements in the early 19th century, and since then, paper is made almost exclusively from cellulose extracted from wood (Britt 2011). The sources of wood for the paper industry in the developed world are...
largely confined to major forestry centers in the northern temperate and boreal forests. Further, pulp production is well tuned to paper consumption, with short time-gaps between wood harvesting and dated publications that use the paper products. Paper integrates materials from many trees and the pulp contains a record of the entire age of the trees (about 40 years at the time of harvest). On the one hand, this may limit the identification of specific tree species and the ability to obtain isotopic records at high spatial and temporal resolution. But on the other hand, it has the advantage of providing large-scale, running mean values of the isotopic composition of the wood, often the ultimate goal even in the high resolution tree-ring studies. Using paper may also involve several complications. For example, manipulations of paper quality may involve various sources of pulp, paper treatment to improve quality may affect it isotopic compositions, and the increasing extent of recycling can also result in the loss of time-resolved signal. The main question addressed here is can we see the temporal signal in atmospheric $^13$C, in spite of the range of the potential pitfalls. The surprisingly optimistic results obtained in our trial could motivate further development of this attractive but neglected tool.

2. Materials and methods

Paper was sampled from one American and two European periodicals (Science magazine, Nature magazine, and the Journal of the Chemical Society of London, respectively), and one daily newspaper (the Boston Globe) for which I had accessible archives spanning at least one hundred years. I used samples from publications dated between 1880 and 2005), which was subsequently analyzed for $^{13}$C delta notation, where $\delta$ as above. Isotopic ratios were reported in the conventional notation, where $\delta^{13}C = R_{\text{sample}}/R_{\text{standard}} - 1$ and the standard is PDB carbonate. Trends of atmospheric $^{13}$C in atmospheric CO$_2$ over the past 120 years were obtained from the literature on air samples (Francey et al 1999) and tree-rings (Feng and Epstein 1995, Feng 1999). The isotopic data for each publication was filtered by detrending the data and excluding data points that were different by more than $2\sigma$ from the mean. For the Journal of the Chemical Society, samples of paper dated before 1900 were off by about $+2\%$ from subsequent samples. These samples may not have been derived from wood—early paper was sometimes made from cloth—and were not included in the data analysis. Because photosynthesis results in plant organic matter depleted by 16–18% relative to the $^{13}$C value of atmospheric CO$_2$ (Farquhar et al 1982), trends in both atmospheric and plant samples were normalized for comparison. The atmospheric trend was normalized by setting the best-fit line to zero in 1882, and all other data sets were normalized to best fit the starting point of this record (see table 1).

3. Results and discussion

A decrease in $^{13}$C content was observed in the paper records over the 1900s (figure 1). This is in spite of such large sources of variability in the bulk records as the age of the trees and their sources, which undoubtedly contributed to relatively large scatter in the data. Comparison of $^{13}$C values of cellulose purified from paper samples with the $^{13}$C values of the original paper showed high correlation, with a slope near 1 and a small offset ($\delta^{13}C_{\text{paper}} = 1.18 \delta^{13}C_{\text{cellulose}} + 3.4; R^2 = 0.99$; figure 2). The high correlation and relatively small deviations from ideal 1:1 relationships clearly indicated the lack of any significant effects associated with the paper production on the isotopic trend (temporal variations) and the environmental signal. Cellulose purification may improve signal/noise ratio but is labor intensive and may not always be justified if the focus of interest is the temporal trend. On average, the $^{13}$C values of paper decreased between 1882 and 2000 by $1.65 \pm 0.90\%$, in good agreement with the atmospheric CO$_2$ record of $-1.45\%$ (Francey et al 1999), as well as with records derived from tree rings $(-1.57\%$,

Table 1. Summary of the atmospheric and paper $^{13}$C values associated with the results presented in figure 1. The starting point values used to adjust all data to zero in 1880 are indicated as the normalizing factor. The number of samples used and the outliers (greater than $\pm$ SD from the detrended fit line) excluded from the data analysis is also indicated. $^{13}\Delta$ indicates discrimination during photosynthetic CO$_2$ uptake $[^{13}\Delta = (\delta^{13}C_{\text{atm}} - \delta^{13}C_{\text{plant}}) / (1 + \delta^{13}C_{\text{plant}}/1000)]$.

| Source                  | Normalizing factor (%o) | 1882–2000 change (%o) | Number of samples/outliers |
|-------------------------|-------------------------|------------------------|-----------------------------|
| Atmospheric trend (Francey et al 1999) | +6.57 | -1.45 | — |
|                           (Feng 1999) | +6.56 | -1.57 | — |
| European paper           |                        |                        |                             |
| Nature                  | +21.85 | -3.05 | 97/19                       |
| Royal Chem. Soc         | +22.64 | -1.71 | 32/11                       |
| American paper          |                        |                        |                             |
| Boston Globe            | +24.24 | -0.91 | 83/18                       |
| Science                 | +23.49 | -0.94 | 68/21                       |
| Mean (paper)            | +23.05 | -1.65 |                             |
| $^{13}\Delta$           | 16.87 | +0.17 |                             |

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Figure 1. Comparing paper and atmospheric records: changes in the $^{13}$C content of the paper used in the printing of periodicals and a daily newspaper (names indicated in figure), compared to the trend line produced from available record of the $^{13}$C changes in atmospheric CO2, during the 1882–2000 period (e.g. Francey et al 1999, note change in scale in different panels). Paper samples were taken from arbitrarily selected issues during the period for which the archive was available. The isotopic data were normalized for comparison of the atmospheric and paper records (see table 1), and the dataset for the Boston Globe was divided into two parts (full symbols up to 1940 empty symbols thereafter) to highlight the possible agreement with the atmospheric record in the earlier part. Distinctive outliers associated with the period immediately following World War II are indicated and were not included in the trend analysis discussed in the text.

Figure 2. Effects of cellulose fortification from printed paper on isotopic signal: comparison of the $\delta^{13}$C content (expressed as $\delta^{13}$C values) in a sub-sample of the paper samples collected from the periodical of the Royal Chemical Society, and the $^{13}$C in the purified $\alpha$-cellulose from those samples. The data indicate that variations in the printing paper are consistent with those of purified cellulose.

Feng and Epstein 1995, Feng 1999; cf McCarroll and Loader 2004, Penuelas et al 2008). The decrease in plant-derived material, 0.17‰, was on average larger than the atmospheric trend, generally consistent with the 0.12‰ greater change in the tree-ring record (table 1). Such differences between the atmospheric and plant-derived records may indicate changes in the extent of discrimination between atmospheric CO2 and organic matter. Mean discrimination between atmospheric CO2 and wood used for paper production was 16.9‰ in 1882, increasing to 17.0‰ in 2000. It is generally assumed that increased discrimination by plants indicates greater intrinsic water-use efficiency (WUEi: the ratio of CO2 assimilation rate to leaf conductance; (Seibt et al 2008, Farquhar et al 1982)). Increase in plant WUEi is expected in many plants in response to increasing atmospheric CO2 concentrations (Leavitt et al 2003, Saurer et al 2004, Penuelas et al 2008, Waterhouse et al 2004, Klein et al 2005, McCarroll et al 2009), and/or an increase in conductance to CO2 from the atmosphere to the site of assimilation in the leaves. The observation of such response in the paper records likely indicates a large-scale response by managed forests in the northern hemisphere to increasing atmospheric CO2 concentrations.

Large-scale effects may also be deduced by comparing European and American publications, assuming they represent local production (see above). In the beginning of the study period, in 1882, European paper was more depleted in $^{13}$C by 1.6‰, compared to the American paper used. But this difference decreased to less than 0.2‰, on average, in 2000. Differences in $\delta^{13}$C values of papers can reflect the use of different tree species, in forest management or industrial technology, in addition to the ecophysiological response of the forests. It is likely, however, that changes associated with technological aspects of paper production would be more abrupt than the relatively smooth changes observed in the Nature magazine records. From the ecophysiological standpoint, the observed changes may reflect more rapid increase in discrimination, and in WUEi, in the European forests, associated with differences in forest management. The data from the Boston Globe seem generally to follow
the atmospheric trend in the early part of the record, but clearly deviate from it in the later part. There is not enough information for reliable interpretation of these observations, but it is possible that the introduction of recycling in the crude paper used for daily newspapers reduced its reliability in tracing atmospheric changes over time. This may also be the case for the large excursion in the paper isotopic signal immediately following World War II period, when contribution from non-wood raw materials also increased.

This study did not attempt to account for all the possible contributing factors to variations in the paper $^{13}\text{C}$ signal (see section 1) that will require future research but, instead, focused on testing the hypothesis that in spite of their existence the atmospheric $^{13}\text{C}$ trend is preserved and remains visible in the record. The results support our hypothesis and provide a ‘proof of concept’ that atmospheric trend in $^{13}\text{C}$ is still clearly visible in the paper used in magazine (but not for daily newspapers) and could provide an accessible but so far neglected ‘running mean’ type record of wood $\delta^{13}\text{C}$ values directly related to atmospheric changes. If the atmospheric $^{13}\text{C}$ record is independently available, the paper record could provide a large-scale indicator of smaller changes in plant discrimination against $^{13}\text{C}$ during photosynthesis, a powerful ecophysiological indicator of plant response to climate change. This approach complement and extend the high resolution tree-ring studies and could also be extended to the evaluation of archeological material and for document authentication.

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