Reading between the lines: Papers report on global change

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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 allow us to estimate CO_2 uptake by land plants and the ocean, and assess plants' response to climate. Here I show that the atmospheric ^{13}C trend is 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, a –1.65±1.00‰ trend between 1880 and 2000, compared with –1.45‰ and –1.57‰ 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 WWII period.

The preferential uptake of $^{12}CO_2$ over $^{13}CO_2$ in plant photosynthesis (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 (Penuelas et al., 2008; Saurer et al, 2004; Waterhouse et al., 2004; Leavitt et al, 2003; Feng, 1999). 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. (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 record exists -- based mostly on air trapped in firn and ice -- for the atmospheric ^{13}C trend over the last 1000 years (e.g. Francey et al., 1999). While extensive, high-precision monitoring of atmospheric ^{13}C only started in 1990s, there have been several attempts to detect fossil fuel signal on century time-scales via the $^{13}C/^{12}C$ ratio in organic material, primarily using tree-rings (e.g. Feng & Epstein, 1995; McCarol & Loader, 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 (Encyclopedia Britannica). 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 (ca 40 years at the time of harvest). This essentially provides large-scale, running mean values of the isotopic composition of the wood. Using paper may also involve several complications. For example, manipulations of paper quality may involve various sources of pulp that can mix wood from various tree species, trees ages and geographical sources. The increasing extent of recycling in recent years can also result in the loss of time-resolved signal in some paper products.

I sampled paper in 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) that have accessible archives spanning at least the past one hundred years. I used samples from publications dated between 1880 and 2000. Samples from the periodicals were obtained from my local campus libraries and from the Boston Globe's archives in Boston, Massachussetts, USA. Preliminarily, attempts to trace the sources of the papers at the 100-year range were generally unsuccessful. For Nature, during the past few decades, the paper used for printing could generally be traced to Finnish pulp. Material for the Boston Globe, as for most daily newspapers, came from regional wood, in this case, from the northeastern US and Canada (personal communications with paper manufacturers). In all cases, 20-by-5 mm non-printed samples were clipped from the bottom of a page of a single, arbitrary selected, volume/issue from each year for which the publication was available. (For the Journal of the Chemical Society, volumes from only every 2-3 years were sampled). About 0.2 mg sub-samples were combusted at 1090˚C in the presence of excess oxygen in an elemental analyzer (Carlo Erba 1108) to quantitatively convert all carbon in the paper to CO_2. The CO_2 was purified by gas chromatography and injected, using helium carrier gas, into an isotope ratio mass spectrometer (IRMS, Optima, Micromass, UK) for determination of the $^{13}C/^{12}C$ ratios (R). Twelve arbitrarily selected sub-samples from one publication (Journal of the Chemical Society), spread over the entire record length, were used for chemical purification of cellulose (see Klein et al., 2005), which was subsequently analyzed for $^{13}C/^{12}C$ ratios, as above. Isotopic ratios were reported in the conventional delta notation, where $\delta^{13}C=R_{sampl}/R_{standard}-1$ 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; c.f. McCarol and Loader, 2004) and tree-rings samples (Feng et al 1995, 1999). The isotopic data for each publication were filtered by de-trending the data and identifying data points that were different by more than one $\pm\sigma$ from the mean. For the Journal of the Chemical Society, samples of paper dated before 1900 were off by about +2‰ from all 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 $\delta^{13}C$ 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 this record (see Table 1).

A decrease in ^{13}C content was observed in the paper records over the 1900s (Fig.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 $\delta^{13}C$ values of cellulose purified from paper samples with the $\delta^{13}C$ values of the original paper showed high correlation, with a slope near 1 and a small offset ($\delta^{13}C_{paper} = \delta^{13}C_{cellulose} + 3.4$; $R^2=0.99$; Fig. 2). This indicated the lack of any significant effect of the isotopic signal associated with the paper production on the environmental signal. On average, the $\delta^{13}C$ values of paper decreased between 1882 and 2000 by 1.65±1.00‰, 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‰, Feng et al., 1995; c.f. McCarol and Loader, 2004; Penuelas et al., 2008). The decrease in the plant-derived material was, on average, larger than the atmospheric trend by 0.20‰ (Table 1), generally consistent with the 0.12‰ greater changes in the tree-ring record. Such differences between the atmospheric and plant-derived records indicate changes in the extent of discrimination in atmospheric CO_2 as compared to organic matter. Mean discrimination between atmospheric CO_2 and wood used for paper production was 16.5‰ in 1882, increasing to 16.7‰ in 2000. It is generally assumed that increased discrimination by plants indicates greater intrinsic water-use efficiency (WUEi: the ratio of CO_2 assimilation rate to leaf conductance; Seibt et al., 2008; Farquhar et al., 1982; Francey and Farquhar, 1982). Increase in plant WUEi is expected in many plants in response to increasing atmospheric CO_2 concentrations (Penuelas et al., 2008; Saurer et al., 2004; Leavitt et al., 2003; McCarol et al., 2009; Klein et al., 2005; see also Waterhouse et al., 2004), and/or an increase in conductance to CO_2 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 or differences 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.

The results provide a proof of concept that, in spite of the complicated production process used in paper for the printing of periodicals, and to a lesser extent for daily newspapers, could provide a “running mean” type record of wood $\delta^{13}C$ values and, in turn, of atmospheric change. If the atmospheric ^{13}C record is independently available, the paper record could provide an indicator of a large-scale mean change in plant discrimination against ^{13}C during photosynthesis, a useful ecophysiological indicator of plant response to climate change. The natural isotopic signal recorded in paper could also provide a means for authentication of old manuscripts.

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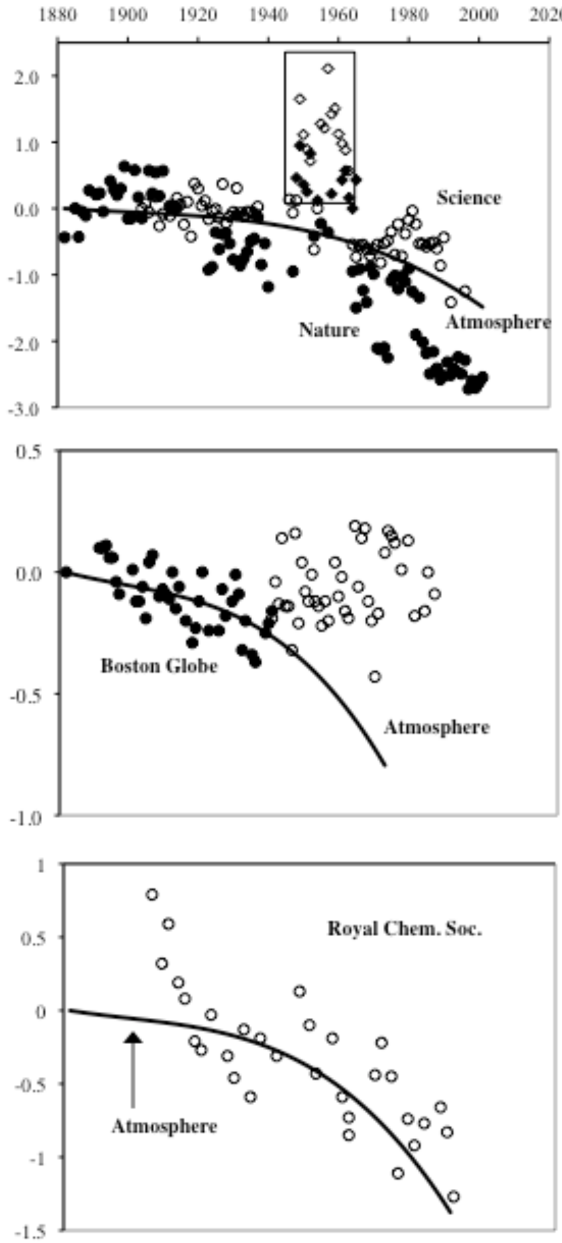

Figure 1. Changes in the ^{13}C content of the paper used in the printing of periodicals and a daily newspaper (names indicated in figure), compared to available record of the ^{13}C changes in atmospheric CO_2, during the 1882 to 2000 period. Paper samples were taken from an arbitrarily selected issue of each year for which the archive was available. The isotopic data were normalized for comparison of the atmospheric and paper records. The normalizing offset and summary of the changes in ^{13}C values are indicated in Table 1. The outliers associated with the period immediately following World War II are indicated.

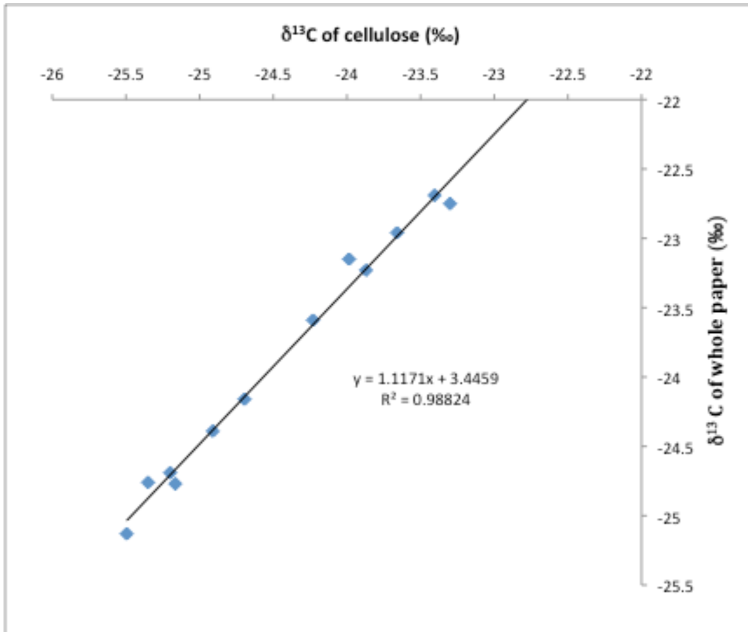

Figure 2. Comparison of the ^{13}C content (expressed as $\delta^{13}C$ values) in a subsample of the paper samples collected from the periodical of the Royal Chemical Society, and the ^{13}C in the purified α-cellulose from those samples. The data indicate that variations in the printing paper are consistent with those of purified cellulose.

Table I. Summary of the atmospheric and paper ^{13}C values associated with in 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 ±SD from the detrended fit line) excluded from the data analysis is also indicated. $^{13}\Delta$ indicates discrimination during photosynthetic CO_2 uptake [$^{13}\Delta=(\delta^{13}C_{air}- \delta^{13}C_{plant})/(1+\delta^{13}C_{air}/1000)$]

Source	Normalizing factor (‰)	1882-2000 change (‰)	Number of samples/outliers
Atmospheric trend			
Francey 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	
$^{13}\Delta$	16.48	+0.20	