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Biogeosciences Discussions

Interactive comment on "Comment on: "Possible source of ancient carbon in phytolith concentrates from harvested grasses" by G. M. Santos et al. (2012)" *by* L. A. Sullivan and J. F. Parr

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In their comment Sullivan and Parr (2012) raise several concerns which, to their opinion, weaken the soil-derived phytOC (or phytC) hypothesis of Santos et al. (2012). They believe that their concerns are mostly justified by their own 14C phytC dates from bamboo (leaves harvested alive to decomposed litter) published in the progress report no.AINGRA08061/2008 by Sullivan et al. (2008). This report was publicly displayed on line from 2009 to 2011, and is readily available on request from AINSE (at http://www.ainse.edu.au). In the present reply, we answer those points and show that

our hypothesis is still valid. To facilitate our discussion here, we reproduce the Sullivan et al. (2008) isotopic results (Table 1).

1) Selective use of two of twelve 14C phytC dates reported in the progress report by Sullivan et al. (2008).

In the Santos et al. (2012) publication, we discussed just 2 phytC results from Sullivan et al. (2008) (Table 1): the leaves harvested from the living plants themselves, and the green litter. This is because the only sample in their entire dataset for which the age of the original bamboo leaf tissues is known absolutely and that is unequivocally not contaminated by soil organic matter (SOM) is the sample of leaves picked from the living bamboo, with the recently senesced litter a close second. For all other litter samples, contamination by SOM and effects of bioturbation cannot be completely discounted. The main issue here is that, if the C occluded in the phytoliths is from a 100% photosynthetic source, Δ14C phytC values for at least these 2 undisturbed samples should be "modern" (i.e. these Δ14C values should closely match the atmospheric radiocarbon signatures from the time the bamboo leaves were growing). However, these two pristine leaf samples were the two that showed the grossly anomalous old 14C ages of 1,855 and 3,510 yrs BP.

Furthermore, although we did not discuss their other results, the fact is that the entire Sullivan et al. (2008) 14C phytC dataset failed to reproduce the expected atmospheric 14C concentration of the bomb-pulse (Figure 1); and the authors devoted much of their 2008 report to attempting to explain these anomalies. Note that there can be confusion between percent Modern carbon (with capital M) and the term modern (with small m), which is normally used in the sense of 14C equal to contemporary atmospheric values, as defined in Santos et al. (2012), and as required by the photosynthetic phytC hypothesis. However, the term is sometimes used as shorthand for samples containing bomb 14C, as in table 1 of Sullivan et al. (2008) reproduced here.

Bomb radiocarbon peaked in the Southern Hemisphere atmosphere at $\sim$170pMC, and

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has recently been falling at the rate of about 0.5pMC/year as the excess mixes into other parts of the carbon cycle. Hence litter representing 2008 photosynthate should be ∼105pMC, with values of 105.5pMC for 2007, 106pMC for 2006 and so on. The highest 14C results from the phytC extracted by the authors yielded just 105.4pMC (the decomposed litter layer 3, which was material from the deepest layer in the set, and should have returned a significantly higher 14C value; Table 1). Since these samples were collected during or before 2008, the phytC 14C values associated with them are depleted by ∼5pMC relative to the atmosphere (an offset of ∼400 radiocarbon years), reflecting incorporation of a substantial amount of "old" carbon (Figure 1). Interestingly, this is similar to the initial offset observed in one of our tested phytC samples (Kandara, extracted from a top-soil layer) before we applied more stringent sample preparation techniques (Santos et al. 2010).

As Sullivan et al. (2008) pointed out, their litter 14C results averaged ∼100pMC, significantly below the 105pMC level of 2008, or the higher values expected for the older (deeper litter) from previous years. Figure 1 shows that 100pMC corresponds to ∼1957, which would require that the litter was mixed on a multi-decadal timescale and was overwhelmingly pre-bomb, in violent disagreement with their litterfall measurements. Hence these results also showed that old carbon was present in all of their phytolith concentrate samples. However, since the 10 leaf litter layers were collected after contact with the soil-floor, it is hard to ascertain whether these depleted 14C results are just artifacts (i.e. if the pool of C analyzed was contaminated by old soil OM residues, not properly removed by their phytolith extraction procedure), or if they also support the old phytC hypothesis. Therefore, we refrained from discussing the phytC 14C results from the 10 litter samples in Santos et al. (2012).

2) Inefficiency of phytolith protocols

Although we tested several wet oxidation extraction methods we indeed did not test the microwave digestion process of Parr et al. (2001), which seems useful for minimizing the amount of oxidizers needed as well as the duration of extractions. However, optical

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microscopy pictures published in Parr et al. (2001) and Parr (2002) clearly showed organic remains in the phytolith concentrates obtained using this technique. Moreover, their 14C phytC dataset produced the same massive 14C depletion phenomenon in pristine samples that we observed ourselves (Table 1). Our objective in Santos et al. (2012) was not to deprecate one extraction protocol in favor of another, but was to emphasize that the question of whether phytoliths occlude photosynthetic and/or old soil-derived C will remain unresolved until it can be clearly demonstrated that an extraction method has the ability to remove all external organic material. In our investigations, we found that particle characterization through SEM-EDS, which is more powerful than microscopic evaluation alone, is extremely helpful to scan the phytolith concentrates upon extractions for their purity before samples are to undergo isotope analyses.

3) Fractionation or partitioning?

In their comment Sullivan and Parr (2012) implied that we hypothesized that the anomalous 14C phytC results are somehow related to "a carbon fractionation mechanism" (their page 13775, 2nd paragraph). This is confusing, because if by this phrase they meant "isotopic fractionation", we note that this hypothesis was first raised by the authors in their 2008 progress report, was refuted in Santos et al. (2012) (last paragraph; page 1876), and indeed is explicitly rejected by Sullivan and Parr (2012) themselves later in the text (page 13776 last paragraph). On the other hand, if they used "fractionation" in a more general sense of chemical partitioning, as suggested elsewhere in their comment, we entirely agree that something very unusual is taking place. It has been established that plants do not photosynthesize all carbon found within their tissues: C is taken up from soil both as organic carbon through nitrogen assimilation and as soil dissolved inorganic carbon (DIC) (Santos et al. 2012). Soil-C incorporated into the plant tissue during its lifetime may be unevenly partitioned within the plant material, though whether it is occluded in the biosilica or not is an open question. Nevertheless, the very old phytC 14C ages make it clear that the carbon fraction measured by us and by Sullivan et al (2008) is highly refractory and much older than bulk SOM, regardless

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of whether it comes from the biosilica or from elsewhere in the plant.

4) Sample preparation: contamination removal and biosilica carbon yields.

In Santos et al. 2010, we initially focused on obtaining reproducible 14C results on replicate phytolith concentrates from soils, and used fine silica powder as a blank material to evaluate phytolith chemical extractions. When 14C results of phytoliths from a topsoil sample (Kandara; Santos et al. 2010) were found to be slightly older than expected, the focus of the study shifted to investigate sources of exogenous C contaminant. We used established procedures to remove what we initially assumed was older OM contaminant through sequential acid digestions and low-temperature prebaking, before the final sample processing for 14C-AMS.

After these additional steps of chemical extraction the Kandara phytolith concentrates produced lower C yields, as Sullivan and Parr (2012) noted in their comment (their Table 1). However, it is important to point out that these steps also produced older 14C results that in our view are surprisingly reproducible given the range of treatments and sample sizes (note that single result for treatment #4 has sigma of $\pm$120 years, omitted from Sullivan and Parr (2012) Table 1). This suggests that these samples were probably clean and that the final associated 14C values are from C occluded in the biosilica rather than from an external contaminant. Similarly, Fallon et al. (2010) studied the effects of acid digestions and pre-roasting on C yields and 14C values from siliceous deep sea sponge skeletons and concluded that all external C was removed at >400°C, producing low C yields but consistent 14C results. Nevertheless, since the Kandara samples had been in contact with soil, doubts about soil OM contamination will always remain, just as with the Sullivan et al. (2008) litter samples. Therefore, in order to produce 14C phytC from absolutely known "modern" matrices that are unequivocally not contaminated by exogenous SOM, we chose to shift our investigations to 14C-AMS dating of phytoliths extracted from living plants. When those in turn produced anomalously old 14C ages, we begin to question the fundamental assumption that phytC is 100% photosynthetic.

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Sullivan and Parr (2012) cautioned against “over-vigorous extraction procedures” that could somehow lead to 14C depletion. They refer to Watling et al. (2011) who showed using Raman, FT-IR and X-ray photoelectron spectroscopies that the chemical composition of organic compounds measured in crushed phytolith concentrates extracted from bamboo was dependent on the extraction protocol used. However, independent of the extraction technique used or the chemical fraction selected, 14C depletion without corresponding changes in d13C can only happen if older forms of organic C are present, regardless of whether these are within the biosilica or external to it. Furthermore, the phytolith samples measured in Sullivan et al. (2008) underwent a microwave digestion procedure to extract phytoliths, modified from Parr et al. (2001). Therefore, no “over-vigorous extraction procedures” that according to the authors “can also have important adverse consequences” were applied, yet their procedures, like ours, produced highly anomalous 14C phytC ages on living and recently senesced leaves, that are incompatible with a 100% photosynthetic source.

5) Supporting evidence for old phytC ages.

Surprisingly the authors also dismissed the works of several researchers cited in Santos et al. (2012), concerning the difficulties of matching 14C ages of phytoliths with expected values and/or independent chronologies (Wilding 1967, Kelly et al. 1991, Boaretto 2009). We would like to emphasize that when “odd” phytC 14C results have been found; those were normally not published in peer reviewed papers, though they have been reported in other scientific materials accessible by the public (Prior et al. 2005, Rieser et al. 2007, Sullivan et al. 2008, Mintz et al. 2009). Our objective in citing the Sullivan et al. (2008) 14C phytC results was not to diminish the work of the authors, but rather to highlight that there is substantial neglected information in the phytolith literature that needs to be examined more closely and rigorously. To disregard those reports is simply acting contrary to facts.

6) Summary

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If the results of Sullivan et al. (2008) are not just a product of contamination, they failed to provide any reasonable scientific explanation to the ancient values of the 14C phytC from the living bamboo tissue and green litter. As we show above, they also failed to reproduce the actual bomb-pulse 14C values when extracting phytC from the litter/soil sample mixtures: the fact that most of their 14C results are ∼100pMC does not imply that they are correct. The obvious question then is if this set of 14C phytC results is robust (i.e. is not due to contamination that was not removed), how do they explain the 14C depletions if the C occluded in the phytolith is indeed 100% photosynthetic? To simply look the other way and sweep these anomalous phytolith 14C dates into the abyss of the literature footnotes is perilous to the growth and development of this exciting field of research.

We suggest that the concerns of Sullivan and Parr (2012) are easily answered and that the soil-derived phytC hypothesis is still intact. However, we would like to stress again the importance of developing phytolith extraction protocols proven to be 100% efficient at removing contaminants as a necessary precursor to determining the sources of C within biosilica of higher plants, and its further implications.

7) Acknowledgment

We thank the invitation of Dr. Victor Brovkin to reply Sullivan and Parr comment.

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Table 1: Radiocarbon and $\delta^{13}C$ results from phytC isolated from leaves of a bamboo (Bambusa vulgaris cv. Vittata) and the underlying litter layer (table from Sullivan et al., 2008). Note i) the samples were collected before 2008; ii) "modern" as used in the table refers to samples that contain bomb ^{14}C from atmospheric nuclear weapons testing. It does not mean that the ^{14}C values are necessarily equal to those of the contemporary atmosphere

Layer	Mean soil depth (cm)	ANSTO code	$\delta^{13}C$	pMC	Conventional ^{14}C age (yrs BP)	$\Delta^{14}C$ (‰)
living leaves	n.a.	OZL339	-27.5	64.6	3,510	-354
recently senesced leaves	n.a.	OZL340	-30.1	79.4	1,855	-206
litter layer 1	0.5	OZK756	-30.7	97	250	-30.4
litter layer 2	1.5	OZK757	-30.5	104	modern	40.1
litter layer 3	2.5	OZK758	-29.9	99.1	70	-8.6
litter layer 4	3.5	OZK759	-30.1	102.6	modern	26.6
litter layer 5	4.5	OZK760	-29.8	100.9	modern	8.5
litter layer 6	5.5	OZK761	-30.3	102.3	modern	23.3
litter layer 7	6.5	OZK762	-30.5	99.3	60	-7.4
decomposed layer 1	8	OZK765	-30.8	98.9	85	-10.8
decomposed layer 2	10.5	OZK764	-31.1	104.2	modern	42.3
decomposed litter layer 3	13.5	OZK763	-30.2	105.4	modern	53.5

Fig. 1.

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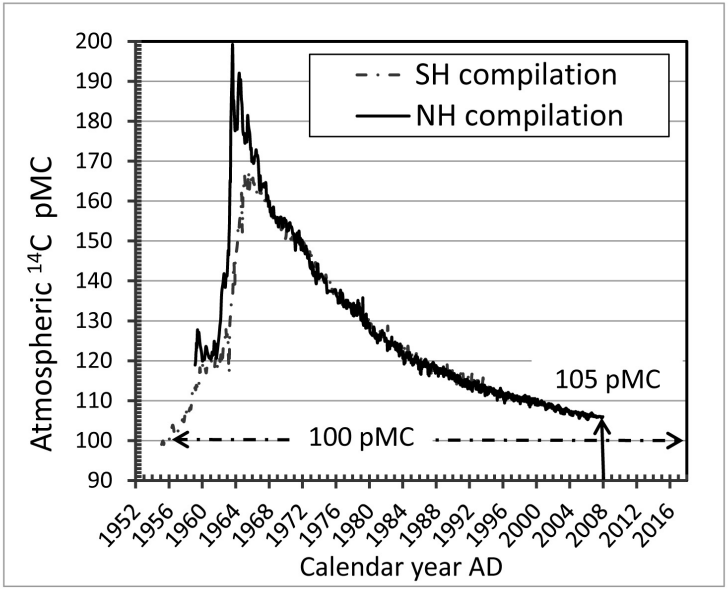

Figure 1: Atmospheric ^{14}C in Southern and Northern Hemispheres for the periods AD 1955–2001 (Hua and Barbetti, 2004) and 1959-2009 (Levin and Kromer 2004, Levin et al. 2008 and Levin pers. comm. - after 2006 AD), respectively. For a 100pMC value in phytC bamboo litter (dashed line), the bomb ^{14}C peak delivers one possible calendar date at ~1957. In all cases the ^{14}C phytC results of Sulivan et al. (2008) dataset were significantly lower than the atmospheric ^{14}C value of the year 2008 (~ 105pMC).

Fig. 2.

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