

## RADIOCARBON MEASUREMENTS OF PAPER: A FORENSIC CASE STUDY TO DETERMINE THE ABSOLUTE AGE OF PAPER IN DOCUMENTS AND WORKS OF ART

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**ABSTRACT.** In a case study to assess the possibilities and limitations of determining the exact age of paper, we measured radiocarbon (<sup>14</sup>C) concentrations in bulk-paper cellulose and starch extracts from 20 known-age paper samples of the last 65 yr. As expected, <sup>14</sup>C concentrations in single-seasonal grown starch extracts are in reasonably good agreement with post-bomb atmospheric <sup>14</sup>C. In contrast, <sup>14</sup>C concentrations in bulk-paper cellulose indicate apparent admixtures of tree-ring fibers spanning up to >50 yr. In a forensic investigation, combining <sup>14</sup>C results from single-seasonal components like starch with those from long-lived fibers, could potentially enhance the precision of paper production-date estimates for samples made after 1955.

**KEYWORDS:** paper cellulose, paper starch extract, post-bomb atmospheric <sup>14</sup>C, radiocarbon AMS dating.

### INTRODUCTION

Usually, paper is a cheap mass product. However, as a medium for historic or important documents and works of art, paper can be of high value. Hence, paper objects are more and more subject to art forgeries and fraud (Bredenkamp et al. 2014). In most cases, the detection of forgeries cannot be done solely on the basis of expert textual, calligraphic, or art-historical analyses. Therefore, scientific analytical methods also have to be employed to determine the real age and even the provenance of a paper (Pigorsch et al. 2015).

Paper as we know it today is a composite, consisting of several organic and inorganic components. For example, until the end of the 19th century the main components of paper were rag fibers (linen or wool fibers), which were then replaced by wood-based cellulose fibers (e.g. Beneke 1999). In addition to fibrous material, paper also contains fillers, pigments, and sizing agents (organic and inorganic), whose introduction and use can be assigned to certain date ranges (e.g. Clapp 1972). However, the detection of chemical components with a known date of invention will only give a terminus post quem date for the production of the paper.

A significant change in paper and cardboard production occurred in the mid-1960s by adjusting the pH from an acid to a neutral pH (~6.8–7.5) environment. This resulted in numerous changes also in material composition of paper and cardboard material, such as the use of synthetic sizing agents in exchange of rosin-sizing, the use of calcite as a filler, and further changes of used additives. An important production change with respect to radiocarbon (<sup>14</sup>C) was the increased application of starch to the paper pulp and surface coating of paper (Gullichson and Paulapuro 1998; Götsching et al. 1999). The starch sources are annual grown plants like potatoes and cereals, with an assumed short time lag between harvesting and final use as binder.

<sup>14</sup>C measurements on short-lived plant tissues formed after 1955, i.e. during the so-called bomb-pulse, will allow a comparatively precise age estimate within a few years due to the large changes in atmospheric <sup>14</sup>C concentrations (e.g. Harkness and Walton 1969, 1972; Stenhouse et al. 1977; Geyh 2001; Canosa et al 2013; Al-Bashaireh et al 2015). As the source of the cellulose fibers in modern paper are trees with a complex chronological signature, thus limiting the usefulness of radiocarbon measurements of paper cellulose, our proposition is to use starch for <sup>14</sup>C measurements.

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In this case study, we performed  $^{14}\text{C}$  measurements on post-bomb known-age paper and paper-like samples on bulk-paper, i.e. cellulose fibers, and starch extracts to assess the possibilities and limitations for estimating paper production dates.

## MATERIALS AND METHODS

### Materials

For this study, 20 paper and cardboard samples from a collection of the Papiertechnische Stiftung (PTS), Germany, have been selected (Table 1). The majority of the samples originate from the so-called *Weissenborner Musterzimmer*, archived in the German National Library in Leipzig, Germany, which contained the whole collection of the Weissenborn paper factory. From around 1930 until the mid 1990s, this paper factory (now belonging to Schoeller Technocell™) collected annual archetypes of current paper productions. Additional paper samples, partially printed, came from private collections and the Zentrum für Bucherhaltung in Leipzig, Germany (ZfB; a center for book preservation). For the latter samples, the production year was approximated from the year of publication (see Table 1).

All paper samples are in principle so-called technical paper, i.e. writing and printing paper (with and without printing), cardboard for drawings, packaging-paper, and packaging-cardboard. All were produced using cut wood-fibers over Fourdrinier wire and cylinder mold paper machines, respectively. Overall, the selected samples are assumed to mirror a representative spectra of manufactured paper over the last 65 years within Central Europe.

Spectroscopic analysis (FTIR, Raman) of the paper samples were performed at PTS and used to identify paper samples containing starch (Table 1; not quantitative). Aside from cellulose, other ingredients such as kaolinite, gypsum, barite, styrene-binder, and resin-glue were detected (for a detailed overview see Pensold and Pigorsch 2015).

Sampling for subsequent sample preparation occurred outside printed areas along the paper edges. Eight paper samples were analyzed on bulk-paper material and extracted starch, nine samples on bulk-paper material alone, due to limited starch content, and two samples only on their starch extracts in a preliminary phase of this study.

### Sample Preparation and AMS-Measurements

#### *Bulk Paper Samples*

To remove hydrophobic components such as resin or styrene binder as indicated by material analysis, bulk-paper samples (~20–60 mg original sample material, cut in mm-sized stripes) were subjected to a soxhlet-type serial extraction. In sequence, samples were extracted several times each with boiling tetrahydrofurane (THF), chloroform, petroleum-ether, acetone and methanol and then rinsed with deionized water (Bruhn et al. 2001). Subsequently, samples were extracted with 1% HCl at 85°C, washed in deionized water and finally dried at 60°C.

#### *Starch Samples*

Three grams of the starch-containing paper samples were crushed in a grinding mill and left to soak 12 hr in 50 mL of distilled water. The resulting pulp was beaten in a mixer and left 30 min in an autoclave at 137°C. The final suspension was centrifuged to separate the fibers completely from the aqueous phase. Calcium carbonate was precipitated by adjusting the pH value to about 8 and by adding 1M disodium carbonate solution. The solution was again centrifuged and the calcium carbonate discarded. Finally, starch was precipitated by adding drops of

ethanol to the aqueous solution. After decanting the liquid, the precipitate was dried, leaving between 2 and 30 mg of starch for <sup>14</sup>C measurements. Due to the high vapor pressure, ethanol is assumed to be removed quantitatively. The final extraction product was qualitatively inspected by Raman spectroscopy to verify that its main component was starch.

### *AMS Measurements*

For AMS-measurement, an aliquot of prepared sample material (cellulose, starch extract) estimated to contain 2–3 mg carbon was converted to CO<sub>2</sub> by sealed quartz-tube combustion with preconditioned copper(II) oxide and silver wool at 900°C. Sample CO<sub>2</sub>, equivalent to 1 mg carbon, was graphitized by the Bosch reaction with an iron catalyst (Vogel et al. 1984; Nadeau et al. 1998). The resulting mixture of graphite and iron powder was pressed into aluminium target holders for AMS <sup>14</sup>C measurements with a 3 MV HVEE Tandem AMS system at the Leibniz Laboratory in Kiel, Germany. Sample <sup>14</sup>C measurements are normalized to modern oxalic acid II standard (NBS SRM 4990C) and corrected for isotopic fractionation and background effects (Nadeau et al. 1998, 2013). Final <sup>14</sup>C concentrations, expressed in percent modern carbon (pMC; Stuiver and Pollach 1977), are shown in Table 1.

With a few exceptions (see Table 1), multiple <sup>14</sup>C measurements of selected paper fractions were performed and a weighted mean calculated. For quality assurance, measurements were controlled by parallel measurements of IAEA C3, -C5, and IAEA C6 standards.

For comparison to measured paper cellulose and starch <sup>14</sup>C concentrations, we used the NH\_zone1 (Hua et al. 2013) and Levin datasets (Levin et al. 2013).

## **RESULTS AND DISCUSSION**

Table 1 and Figure 1 give the results for the <sup>14</sup>C measurements on paper cellulose and starch samples. Measured <sup>14</sup>C concentrations are plotted versus paper production year.

With the exception of sample 2010\_FK (year 2010; multilayer, leveled folding boxboard), all paper starch extracts gave <sup>14</sup>C concentrations close to or slightly above contemporaneous atmospheric <sup>14</sup>C concentrations. Visually fitting apparent measured starch-<sup>14</sup>C concentrations to equivalent atmospheric <sup>14</sup>C values indicates a lag time up to 5 yr between harvesting of the source material (mostly potatoes) and its use as a paper additive.

The starch <sup>14</sup>C concentration in sample 2010\_FK is significantly lower than atmospheric <sup>14</sup>C concentrations in 2010, by about 4 pMC, and may indicate contamination during the starch extraction process. Further studies are needed to evaluate the applied starch extraction method with respect to efficiency, purity of the starch extract, and possible contamination problems. For example, the basic pH 8 step during the starch extraction process may pose a risk of atmospheric carbon contamination, emphasizing the need for improving the extraction protocol. Nevertheless, the close agreement of the other measured starch extracts with the expected atmospheric radiocarbon concentration at their production time shows that other, unidentified organic substances still abundant in starch extracts (not quantifiable during Raman inspection), or atmospheric carbon (which may have been introduced during the basic phase of the starch extraction process), seem not to have had a significant influence on measured <sup>14</sup>C concentration.

In contrast to the short-lived starch extracts, paper cellulose <sup>14</sup>C concentration give a poorer fit with the atmospheric <sup>14</sup>C data, obviously caused by the complex multi-seasonal cellulose mixture.

Table 1 Samples for <sup>14</sup>C analysis and results. Numbers given in parenthesis give measurement amounts of specific fractions.

Sample	Source**	Lab ID	Description and detected additives	Material	Year	Atmospheric <sup>14</sup> C (pMC)*	Cellulose <sup>14</sup> C conc. (pMC)	Starch <sup>14</sup> C conc. (pMC)
1956_01_SP	A	KIA50254	Writing paper, no printing	Cellulose	1956	102.52	96.67 ± 0.17(2)	
1959_01-1_DP	B	KIA50255	Printing paper, printed	Cellulose	1959	123.40	99.38 ± 0.15 (3)	
1965_01_SO	C	KIA50256	Printing paper, printed	Cellulose	1965	176.15	100.75 ± 0.21 (2)	
1969_04_VP	A	KIA50257	Printing paper, no printing	Cellulose	1969	155.54	115.53 ± 0.18 (2)	
1975_01_SO	C	KIA50258	Writing paper, printed	Cellulose	1975	141.47	113.01 ± 0.19 (2)	
1982_01_SP	A	KIA50259	Printing paper, no printing	Cellulose	1982	124.36	118.21 ± 0.32 (1)	
1982_04_AQ	A	KIA50639	Cardboard for drawings,	Cellulose	1982	124.36	122.66 ± 0.19 (2)	
	A	KIA50648	no printing	Starch				124.55 ± 0.3 (1)
1989_03_VP	A	KIA50260	Printing paper, no printing	Cellulose	1989	116.77	123.14 ± 0.2 (2)	
1989_01_SO	A	KIA50640	Writing paper, no printing	Cellulose	1989	116.77	120.58 ± 0.17 (2)	
		KIA50649		Starch				118.96 ± 0.2 (2)
1989_02_DP	A	KIA50641	Printing paper, no printing	Cellulose	1989	116.77	120.33 ± 0.2 (2)	
		KIA50650		Starch				116.59 ± 0.32 (1)
1990_02_SP	A	KIA50261	Writing paper, no printing	Cellulose	1990	115.62	125.47 ± 0.21 (2)	
		KIA50262		Starch				117.3 ± 0.38 (1)
1990_06_SP	A	KIA50642	Writing paper, no printing	Cellulose	1990	115.62	124.72 ± 0.21(2)	
		KIA50651		Starch				119.14 ± 0.44 (1)
1990_11_DP	A	KIA50643	Printing paper, no printing	Cellulose	1990	115.62	125.61 ± 0.22 (2)	
1990_13_SP	A	KIA50644	Writing paper, no printing	Cellulose	1990	115.62	123.71 ± 0.2 (2)	
1990_14_AQ	A	KIA50645	Cardboard for drawings,	Cellulose	1990	115.62	122.36 ± 0.17 (3)	
			no printing					
1998_02	D	KIA49924	Packaging paper	Starch	1998	110.36		114.71 ± 0.62 (1)
1998_03	D	KIA49925	Packaging paper	Starch	1998	110.36		110.95 ± 0.28 (2)
2000_SC	D	KIA50646	Printing paper, no printing	Cellulose	2000	109.33	119.89 ± 0.2 (2)	
		KIA50655		Starch				110.54 ± 0.24 (2)
2010_FK	D	KIA50647	Multilayer, leveled folding	Cellulose	2010	~104.7 <sup>†</sup>	107.25 ± 0.18 (2)	
		KIA50656	boxboard, no printing	Starch				100.2 ± 0.19 (2)
2013_01	D	KIA50253	Printing paper, no printing	Cellulose	2013	~103.0 <sup>†</sup>	106.95 ± 0.16 (2)	
		KIA49927		Starch				103.43 ± 0.14 (4)

\*Average NH1 <sup>14</sup>C concentration (Hua et al. 2013) at the time of production; <sup>†</sup>extrapolated average NH1 <sup>14</sup>C concentration; \*\*source of paper samples (A: “Weissenborner Musterzimmer,” archive of German National Library; B: private collection of art historian Georg Dietz (www.papierstruktur.de); C: ZfB; D: paper prototype collection PTS).

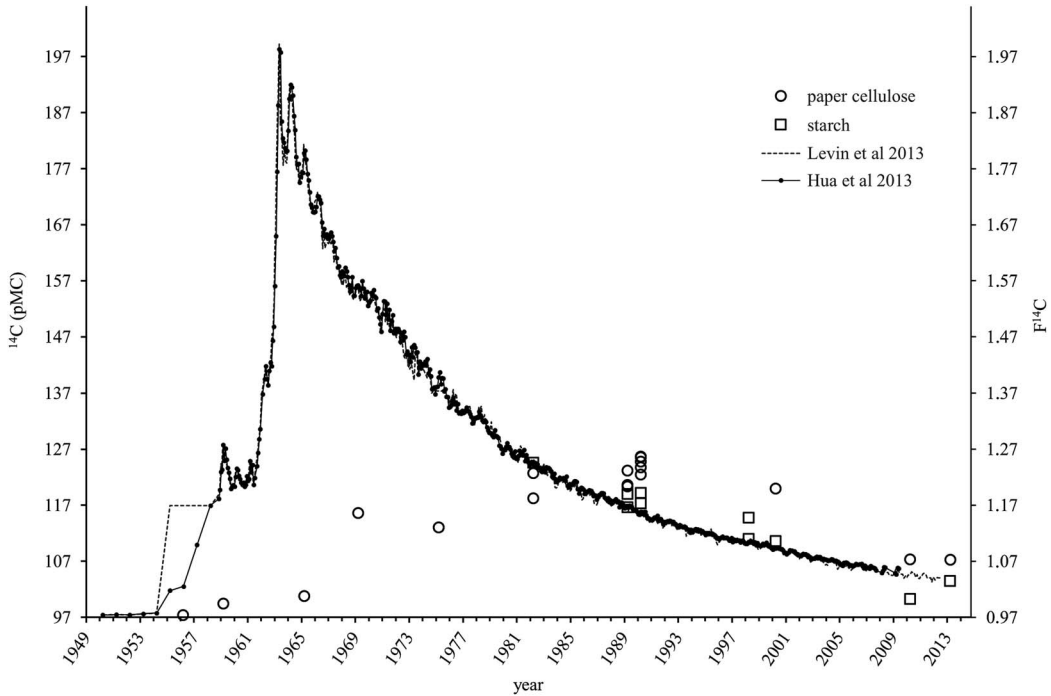


Figure 1 <sup>14</sup>C concentrations measured in starch (rectangles) and solvent-cleaned paper cellulose (circles) with respect to paper production year and compared to Northern Hemisphere NH1 dataset (Hua et al. 2013) and western European atmospheric <sup>14</sup>C concentration (Levin et al. 2013) concentration.

In similar studies with radiocarbon measurements on paper cellulose of known-age paper material, Zavattaro et al. (2007) and Fedi et al. (2013) estimated apparent tree-ring cellulose admixtures of a few decades.

Adopting the approach of Zavattaro et al. (2007), we modeled hypothetical paper cellulose <sup>14</sup>C concentrations with tree-ring admixtures of 10, 25, and 50 years using

$$^{14}C_{paper\_year} = \frac{1}{N^2} \sum_{n=1}^{n=N} ((2n - 1) * ^{14}C_{cellulose\ growth\ year\ n}) \tag{1}$$

with <sup>14</sup>C<sub>paper\_year</sub> being the apparent <sup>14</sup>C concentration of bulk cellulose at the time of paper production, *N* = maximum number of tree-rings (e.g. 10, 25, and 50) and <sup>14</sup>C<sub>cellulose growth year n</sub> being the atmospheric <sup>14</sup>C concentration of the tree-ring growth at year *n*, approximated by calculating mean annual <sup>14</sup>C concentration using the NH1 data set (Hua et al. 2013). The term *n* – 1 refers to the assumption that there is a minimum time-gap of 1 yr between felling of trees and utilization of tree-ring fibers for the paper.

Figure 2 shows the measured bulk paper <sup>14</sup>C concentrations in comparison to atmospheric and modeled <sup>14</sup>C concentrations. With respect to the samples discussed here, paper produced before 1982 seem to contain fibers with tree-ring mixtures spanning >50 yr. For later produced paper samples, however, no clear distinction can be made between short or long-lived tree-ring mixtures.

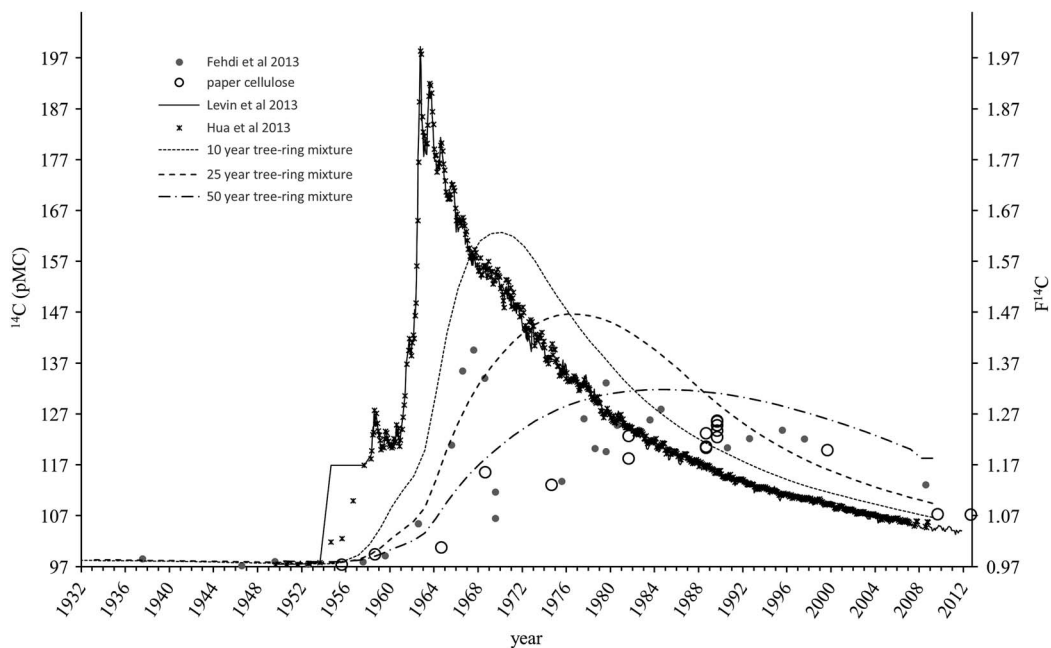


Figure 2 Measured paper cellulose  $^{14}\text{C}$  concentration in comparison to atmospheric  $^{14}\text{C}$  data and modeled  $^{14}\text{C}$  for paper-pulp containing tree-ring mixtures of 10–50 yr.

Fedi et al. (2013) inferred tree-ring cellulose mixtures in paper fibers spanning 10–25 yr for newspaper material before 1970. Later produced newspaper material seemed to indicate longer-lived tree-ring admixtures, comparably to our results. An obvious explanation could be changing production procedures and source materials of paper manufacturers. The use of recycled paper material, either in part or completely, would resemble the utilization of longer-lived tree-ring cellulose mixtures.

Clearly,  $^{14}\text{C}$  dating of multi-yearly paper cellulose will allow an only vague estimate of paper production year in contrast to a more precise estimate by radiocarbon measurement of short-lived organic substances such as starch. However, even then one has to accept uncertainties in production-year estimates, which results from the form of the bomb-pulse, that is one solution lying on the increasing and one on the later decreasing part.

Using two or more sample fractions with different residence times may allow further discrimination. Provided that paper fibers consist of multi-yearly tree-ring cellulose mixtures, a positive  $^{14}\text{C}$  difference may be expected between short-lived organics and paper fibers during the early and increasing phase of the bomb-pulse. Depending on the date range of mixed tree rings, negative  $^{14}\text{C}$  differences could be expected on the decreasing side of the bomb-pulse.

The timing of this cross-over point, i.e. the change from positive to negative  $^{14}\text{C}$  differences between contemporaneous starch (assuming a minimum 1-yr time lag between harvesting and utilization during paper manufacturing) and a certain cellulose mixture, is illustrated in Figure 3. A short, 10-yr paper cellulose mixture will give negative  $^{14}\text{C}$  differences for paper manufactured after 1969, for a larger cellulose mixture, e.g. 50 yr, this transition occurs after 1979.

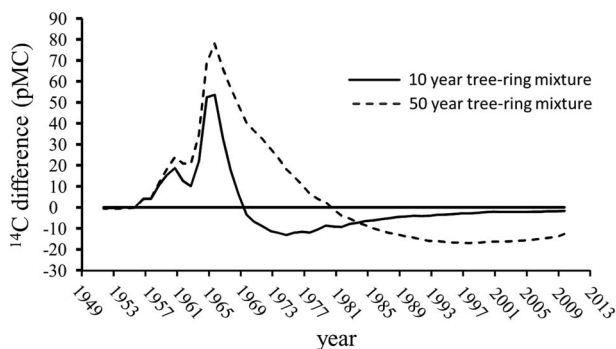


Figure 3 Modeled <sup>14</sup>C difference between short and long-lived organic paper components (starch–paper cellulose).

The combination of radiocarbon measurements of short-lived and long-lived paper fractions therefore could increase the precision for dating paper materials from the post-bomb period, particularly in the near future when atmospheric <sup>14</sup>C concentration will fall below the reference value in 1950 of 100 pMC (Graven et al. 2015).

### CONCLUSIONS

By <sup>14</sup>C analysis of 20 paper samples from the post bomb-period on paper cellulose material, containing long-lived fibers, and short-lived starch extracts, the possibilities and limitations of absolute dating of paper has been investigated.

Measured <sup>14</sup>C concentrations of paper cellulose show an only poor fit with atmospheric <sup>14</sup>C concentrations of the past 65 yr. In comparison with modeled <sup>14</sup>C concentrations of hypothetical 10–50-yr tree-ring cellulose admixtures, measured <sup>14</sup>C concentrations seem to indicate mean apparent mixing periods of >50 yr. Cellulose in recycled paper material will therefore also represent a large temporal cellulose mixture. In a forensic investigation, <sup>14</sup>C measurements on bulk paper cellulose would inevitably allow an only imprecise age estimate before or after 1955.

In contrast, <sup>14</sup>C-AMS measurements on short-lived starch extracts generally are in reasonably good agreement with atmospheric <sup>14</sup>C concentrations and indicate an only small time-lag up to 5 yr between growth and harvesting of source material and subsequent utilization during paper manufacture.

With respect to <sup>14</sup>C dating of post-bomb paper material, combining <sup>14</sup>C measurements from single- and multi-seasonal grown material could potentially increase the precision of production-year estimates by helping to differentiate between periods in the early or later phase of the bomb-spike.

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