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## ASSESSING $^{14}\text{C}$ BLANKS IN THE SMALL-SCALE ANALYSIS OF *N*-ALKANE COMPOUND-SPECIFIC-RADIOCARBON-ANALYSIS

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**ABSTRACT.** Compound-specific radiocarbon analysis (CSRA) provides the possibility to date sample material at a molecular level. *N*-alkanes are considered as specific compounds with high potential to CSRA. As these compounds originate from plant waxes, their radiocarbon ( $^{14}\text{C}$ ) analysis can provide valuable information about the age and origin of organic materials. This helps to reconstruct and understand environmental conditions and changes in vegetation in the past. However, CSRA has two main challenges: The small sample size of CSRA samples, making them extremely sensitive to blank effects, and the input of unknown amounts of extraneous carbon during the analytical procedure. According to the previous study from Sun and co-workers, we used different-sized aliquots of leaves *Fagus sylvatica* (*n*C27, *n*C29) and *Festuca rubra agg* (*n*C31, *n*C33) as modern standards and two commercial standards (*n*C26, *n*C28) as fossil standards for blank determination. A third commercial standard (*n*C27) with predetermined radiocarbon content of  $F^{14}\text{C} = 0.71$  ( $^{14}\text{C}$  age of 2700 BP) serves to evaluate the blank correction. We found that the blank assessment of Sun and co-workers is also applicable to *n*-alkanes, with a minimum sample size of 15  $\mu\text{g C}$  for dependable CSRA dates. We determined that the blank introduced during the analytical procedure has a mass of  $(4.1 \pm 0.7) \mu\text{g}$  carrying a radiocarbon content of  $F^{14}\text{C} = 0.25 \pm 0.05$ . Applying the blank correction to a sediment sample from Lake Holzmaar (Germany) shows that all four isolated *n*-alkanes have similar  $^{14}\text{C}$  ages. However, the bulk material of the sediment and branches found in the sediment core are younger than the CSRA dates. We conclude that the disparity between the actual age of analysed organic material and the age inferred from radiocarbon results, which can occur in sediment traps due to delayed deposition, is the reason for the CSRA age.

**KEYWORDS:** blank assessment, compound-specific radiocarbon analysis, *n*-alkanes.

### INTRODUCTION

For the last three decades,  $^{14}\text{C}$  dating of sample material at molecular level (e.g., *n*-alkanes, alkenones, lignin oxidation products, fatty acids methyl esters, phospholipid fatty acids), so-called compound-specific radiocarbon analysis (CSRA), has been increasingly used. In particular, *n*-alkanes (leaf wax molecules) are proven biomarkers to detect vegetation changes in a landscape and the environment, as shown by studies in lake (Gierga et al. 2016) as well as in marine sediments (Pearson and Eglinton 2000), and loess (Haas et al. 2017).

However, CSRA has two main challenges:

- (1) The most significant is the input of unknown amounts of extraneous carbon to a sample with unknown mass and unknown radiocarbon content (here expressed as  $F^{14}\text{C}$ -values as described in Hemingway (2021) during the analytical procedure (Shah and Pearson 2007). This so-called process or procedural blank—if large enough compared to the sample size—alters the sample's radiocarbon age; hence a correction is mandatory. The preparation of a single substance to be dated requires many individual analytical steps, including compound extraction by Soxhlet, purification with solvents, isolation of single compounds by preparative gas chromatography and their concentration, and finally the radiocarbon

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determination by accelerator mass-spectrometry (AMS). Each step could potentially add extraneous carbon to the compound causing an unknown blank contribution. To make matters worse, the individual blanks of each step may not be constant throughout time. They might change with even slight modifications in the sample-processing procedure and instrument configurations. Hence, finding the total blank is challenging (Hanke et al. 2017).

- (2) CSRA samples typically have low amounts of carbon ( $< 100 \mu\text{g C}$ ). That makes  $^{14}\text{C}$  dating at molecular level extremely sensitive to a blank contribution (Mollenhauer and Rethemeyer 2009). The smaller the mass of the sample, the more the blank affects the  $^{14}\text{C}$  date. So, it is important to find a minimum mass carbon sample limit above which CSRA samples can be considered and below which the uncertainty becomes too great. Studies by Pearson et al. (1997), Sarkar et al. (2014), and Shah and Pearson (2007) give a concentration of  $25 \mu\text{g C}$  as the limit. It is technically possible to measure carbon by accelerator mass spectrometry (AMS) in the range from  $2 \mu\text{g}$  to  $10 \mu\text{g C}$  (Santos et al. 2007) when using a gas ion source. However, according to Ziolkowski and Druffel (2009)  $^{14}\text{C}$ -dates of samples with less than  $5 \mu\text{g C}$  are not interpretable.

There are diverse ways to correct the described blank contribution. One of these approaches is the direct determination of the process blank for each analytical step. Here, blank material runs through chemical analyses and preparative gas chromatography in the same way a sample would (Ziolkowski and Druffel 2009). An indirect approach is to find the total blank contribution of the whole analytical procedure independent of the individual procedural steps.

Samples and standards (substances with known  $F^{14}\text{C}$  or known  $^{14}\text{C}$  age) have the same blank contribution provided they have undergone the same analytical procedure. Therefore, standards with different sample sizes and known  $F^{14}\text{C}$  can be used to capture the mass and isotopic signature of the blank (Pearson et al. 1997; McNichol et al. 2000; Hwang and Druffel 2005; Shah and Pearson 2007).

A further standard dilution method to determine the blank mass, combined with a mass balance equation to find the isotopic signature of the blank reduced the uncertainty of the blank assessment (Hwang and Druffel 2005). For samples with low mass Hwang and Druffel (2005) recommended a standard dilution method with a minimum of two different standards, so that the mass balance calculation is no longer necessary.

This kind of blank assessment was later taken up by Sun and co-worker (2020) and developed into a simpler assessment of the total process blank. They devised a standardized blank assessment to determine unknown mass and  $F^{14}\text{C}$  value of the blank contribution. The authors used modern  $^{14}\text{C}$  material (*n*-alkanoic acid and vanillin) extracted from apple peel and woodchips, respectively. As fossil standards Sun et al. (2020) used *n*-alkanoic acids extracted from Messel shale and the commercially available standard material ferulic acid (Sigma-Aldrich, Prod. No.12,870-8, Lot STBB6360).

Correcting the blank contribution uses the mass balance equation that assumes a constant contamination independent of the amount of the sample (Ziolkowski and Druffel 2009). The measured  $F^{14}\text{C}$  of a sample ( $F^{14}\text{C}_{\text{sample}}$ ) consists of the true  $F^{14}\text{C}$  of the unaltered sample ( $F^{14}\text{C}_{\text{true}}$ ) and the  $F^{14}\text{C}$  of the blank ( $F^{14}\text{C}_{\text{blank}}$ ). It can be expressed as:

$$F^{14}\text{C}_{\text{sample}} = F^{14}\text{C}_{\text{true}} * \frac{m_{\text{true}}}{m_{\text{sample}}} + F^{14}\text{C}_{\text{blank}} * \frac{m_{\text{blank}}}{m_{\text{sample}}} \quad (1)$$

where the mass of the sample is the sum of the true sample mass and the mass of the blank  $m_{\text{sample}} = m_{\text{true}} + m_{\text{blank}}$ .

According to Sun et al. (2020) the mass balance equation can be rearranged showing that  $F^{14}\text{C}_{\text{sample}}$  only depends on  $1/m_{\text{sample}}$  if all other terms are constant and  $F^{14}\text{C}_{\text{sample}}$  can be calculated when  $F^{14}\text{C}_{\text{blank}}$  and  $m_{\text{blank}}$  are known:

$$F^{14}\text{C}_{\text{sample}} = (F^{14}\text{C}_{\text{blank}} * m_{\text{blank}} - F^{14}\text{C}_{\text{true}} * m_{\text{blank}}) * \frac{1}{m_{\text{sample}}} + F^{14}\text{C}_{\text{true}} \quad (2)$$

Hence, aliquots of different sized standard (6–151  $\mu\text{g C}$ ) were used and graphically evaluated by plotting the results of  $1/m_{\text{sample}}$  vs.  $F^{14}\text{C}_{\text{sample}}$  to determine  $F^{14}\text{C}_{\text{blank}}$  and  $m_{\text{blank}}$ .

The usage of standard material of different  $F^{14}\text{C}$  value (modern and fossil) results in regression lines for each material that need to intersect each other in one point that defines the mass of the blank and its  $F^{14}\text{C}$ .

Using a Bayesian model that considers the uncertainties of the  $F^{14}\text{C}$  and mass determinations and is based on an inverse linear relationship between the measured  $F^{14}\text{C}$  values, and the mass of the aliquots, Sun and co-workers (2020) were able to determine the total contribution of the process blank and its uncertainty.

The objectives of our study are (1) whether the blank correction recommended by Sun et al. (2020) can also be applied to *n*-alkanes, (2) to find the lower carbon mass limit for dependable CSRA, (3) application of blank correction for the dating of a sediment sample.

## MATERIAL AND METHODS

### Samples

Leaves of *Festuca rubra agg* (red fescue) and *Fagus sylvatica* (common beech) served as modern standard material. The plant material was collected in 2019 in Elfringhausen (Germany) (51°19'29.2"N 7°10'11.9"E). The material was homogenized by crushing in a mortar grinder before biomarker extraction.

Commercial petroleum-based standards (*n*C26, *n*C27 and *n*C28) (Sigma Aldrich, Steinheim, Germany) were used as fossil references. It turned out that the *n*C27 standard is not entirely of fossil origin but carries a  $^{14}\text{C}$  content of  $F^{14}\text{C} = 0.6$  (as determined by standard  $^{14}\text{C}$  analysis using graphite), so it was not included in the data set of fossil standards.

Three mg of sample material (equivalent to 1000  $\mu\text{g C}$ ) of those modern materials and fossil standards were dated by the standard radiocarbon procedure using graphite to determine their true  $F^{14}\text{C}$  value.

In our investigations, we included a sample of a sediment layer of core HM1 from the Holzmaar lake archived in the Eifel Laminar Archive (ELSA) (Sirocko et al. 2013). The Holzmaar is one of the best-studied maar lakes in the Eifel (Germany) (Kienel et al. 2013; Mollidor et al. 2013; Musa Bandowe et al. 2014; Prasad and Baier 2014; Lehnendorff et al. 2015;

Brunck et al. 2016; Sirocko et al. 2016; Birk et al. 2021). Since, CSRA samples require considerable amounts of carbon, enough core material is necessary (typically 15–25 g), so we decided to sample a 10 cm long section of the core (between 3.80 to 3.90 m). To compare our CSRA results with radiocarbon dates of bulk material from the core, we selected the depth in the core where radiocarbon dating above (3.30 m, 3342 BP) and below (4.20 m, 2580 BP) was carried out (Sirocko et al. 2021). The sediment sample was dried at 40°C, sieved < 2 mm and finely ground in an agate mill.

### Laboratory Equipment

All laboratory materials (glass, metal, fiberglass tubes) for analytical procedure as well as quartz sand and boiling pearls, were heated in a muffle furnace at 300°C and at 450°C, respectively. Glass and metal ware were cleaned up with purifier Decon from Decon Laboratories (Sussex, United Kingdom) and Teepol from Bio-Connect (Huissen, Netherlands). Gas chromatography (GC)-ultra-grade solvents were from Carl Roth GmbH + Co. KG (Karlsruhe, Germany). The silica gel (60 Å, 0.063–0.200 mm, 70–230 mesh size; (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) was used for solid phase extraction (SPE). Nitrogen (N<sub>2</sub>) (99.999 %, Messer AG, Münster, Germany) was used for solvent removal from samples.

### Sample Extraction

All samples were treated with the same analytical procedure. Samples were directly weighed into glass-fiber tubes. The sample masses of modern material ranges between 2–14 g. Fossil standards were weighed-in at 2 mL each (1 mg mL<sup>-1</sup>). Soxhlet extraction was performed with *n*-hexane (200 mL) for 36 hours. Each time the extract was transferred, it was rinsed three times with *n*-hexane. Extracts were purified with solid phase extraction (SPE). For this purpose, the extract was reduced via a rotary evaporator (Rotavapor R-3, Büchi Labortechnik GmbH, Essen, Germany), transferred with *n*-hexane into a vial, reduced again under N<sub>2</sub> and redissolved with 10 mL *n*-hexane. SPE columns (30 mL PP, Macherey–Nagel, Düren, Germany) were packed with 5 % deactivated silica gel and preconditioned with 30 mL *n*-hexane. The extract was transferred to the column and *n*-alkanes were eluted with 60 mL *n*-hexane. The solvent was removed via a rotary evaporator, *n*-alkanes were redissolved with *n*-hexane and transferred to a vial, the solvent was reduced again under N<sub>2</sub> and a defined volume of *n*-hexane, depending on the desired mass carbon, was added. Here it has been shown that a volume between 2–5 mL is useful.

### Instrumental Analysis

Identification and quantification of *n*-alkanes was performed by gas chromatography (GC) equipped with a flame ionization detector (GC-FID) (7890B G3440B), Agilent Technologies, Santa Clara, CA, USA). An HP5, 30 m fused silica capillary column, 0.250 mm i.d. and with a film thickness of 0.25 µm (Agilent Technologies, Santa Clara, CA, USA) was used. Helium (99.9999 %) was the carrier gas at a constant flow 30 mL min<sup>-1</sup>. The injection port was at 300°C (pressure front inlet 18 psi), and a sample volume of 1 µL was injected in splitless mode. The oven temperature program was 80°C (1.5 min), ramp ran from 5°C min<sup>-1</sup> to 300°C, hold time was 20 min. The detector temperature was 300°C, and H<sub>2</sub> flow was 30 mL min<sup>-1</sup>.

Individual *n*-alkane homologs (*n*C26, *n*C27, *n*C28, *n*C29, *n*C31, *n*C33) were isolated by preparative capillary gas chromatography (prepGC) (7890B G3440B), Agilent Technologies,

Santa Clara, CA, USA). The prepGC was fitted with a cold injection system (CIS 4, Gerstel, Mühlheim a. d. Ruhr, Germany) and a preparative fraction collector (PFC, Gerstel, Mühlheim a. d. Ruhr, Germany). A megabore column (HP5 30 m  $\times$  0.530 mm  $\times$  2.65  $\mu\text{m}$ ) (Agilent Technologies, Santa Clara, CA, USA) was used with a constant flow (5.5 mL  $\text{min}^{-1}$ ) and helium as carrier gas (99.9999%). The front inlet temperature program was 100°C (start CIS), CIS ramp 12°C  $\text{s}^{-1}$  to 350°C, and hold time 2.11 min. The injection speed was 40,000  $\mu\text{L min}^{-1}$ , injection volume 14  $\mu\text{L}$ , and transfer time (hold time oven) 2 min. The oven temperature was 100°C, with a hold time of 2 min and a ramp of 10°C  $\text{min}^{-1}$  to 300°C, hold time of 33 min.

To reach the highest concentration of *n*-alkanes close to stop flow parameters were used with a vent flow of 90 mL  $\text{min}^{-1}$ , vent time of 0.11 min and vent pressure of 1.10 psi. The transfer line was heated up to 310°C and the switch to 320°C. The switch was equipped with a converted trap heater. In this way, it was possible to use 100  $\mu\text{L}$  traps. The trap heater ran constant at 250°C during harvesting. Subsequently, analytes were washed out with 10 mL *n*-hexane, collected in glass tubes, and completely dried under a gentle flow of  $\text{N}_2$ . Tubes were closed by a cap of aluminum foil and additionally sealed with parafilm to avoid contamination with dust or other larger particles.

Purity and amount of analyte were determined by GC-FID. The mean average recovery of individual *n*-alkanes after prepGC was 62 % (Table S1).

### $^{14}\text{C}$ Analysis

The sealed tubes were transported to the radiocarbon laboratory in Mannheim (Kromer et al. 2013). Within days after arrival, the tubes were prepared for the classic method of closed/sealed-tube combustion to convert the samples to carbon dioxide ( $\text{CO}_2$ ). The sample treatment and CSRA are described in detail in (Hoffmann et al. 2017). The tubes containing the samples were attached to a custom-built vacuum system, the air was removed by vacuum pumping, and pure oxygen gas was added (instead of  $\text{CuO}$  to avoid the introduction of contamination) to the tubes before flame sealing the glass tubes. The tubes were placed into a muffle furnace and the sample material combusted at 900°C overnight. Since the combustion of the *n*-alkanes produces not only  $\text{CO}_2$  but also water, the gaseous samples were cleaned by separating the carbon from other gases and quantifying the gas quantity within the aforementioned vacuum extraction system. A sequence of cold traps operated with acetone dry ice (for trapping the water vapor) and liquid nitrogen (for trapping the  $\text{CO}_2$ ) is used to separate the  $\text{CO}_2$  from all other gases and transfer the clean gas into small glass ampoules. The flame-sealed ampoules were inserted in and measured by the commercially available gas interface system (GIS, IonPlus, Dietikon, Switzerland) of the AMS of the type MICADAS (IonPlus, Dietikon, Switzerland). Determination of the process blank of the combustion and gas-cleaning procedure using empty glass tubes processed identical to samples on the vacuum extraction line showed no measurable carbon contribution. The GIS and MICADAS system was standardized by gas aliquots of pre-combusted oxalic acid II standard material (NIST SRM 4990C) and fossil  $\text{CO}_2$ . Data evaluation was performed with the software BATS (Wacker et al. 2016).

Overall, 24 modern standards (modern plant material) with mass ranges 5–72  $\mu\text{g C}$  and 24 fossil standards (*n*C26, *n*C28) with mass ranges 8–51  $\mu\text{g C}$  were analyzed together with sample material. The sample masses were those determined during gas analysis by the GIS.

### Blank Calculation

The calculation assumes that the blank is constant for a substance during the same analytical procedure. A constant blank is also hypothesized in prior studies before (Hwang and Druffel 2005; Santos et al. 2007). The detailed calculation of the  $F^{14}C_{\text{blank}}$  and  $m_{\text{blank}}$  using a Bayesian model is described by Sun et al. (2020).

Different-sized aliquots of modern ( $F^{14}C \cong 1$ ) and fossil ( $F^{14}C \cong 0$ ) standards are plotted against their inverse masses and regression lines are calculated.  $F^{14}C_{\text{blank}}$  and  $m_{\text{blank}}$  are derived from the intersection points of the modern and fossil regression lines.

The Bayesian model estimates the numerical bivariate distribution of the intersection of modern and fossil regression lines. Uncertainties of the linear fit and measurement uncertainties were considered.

The Bayesian model run with our data set of 24 modern and 24 fossil standards, in 3 Markov chains; the fitting process run with 3,500 iterations taking the uncertainties into account. Those calculated values of  $F^{14}C_{\text{blank}}$  and  $m_{\text{blank}}$  were used in the blank correction of the sample in order to determine the uncontaminated  $F^{14}C_{\text{sample\_blank\_corrected}}$  of the sample as follows:

$$F^{14}C_{\text{sample blank corrected}} = \frac{((F^{14}C_{\text{sample measured}} * m_{\text{sample}}) - (F^{14}C_{\text{blank}} * m_{\text{sample}}))}{m_{\text{sample}} - m_{\text{blank}}} \quad (3)$$

## RESULTS AND DISCUSSION

### Blank Assessment

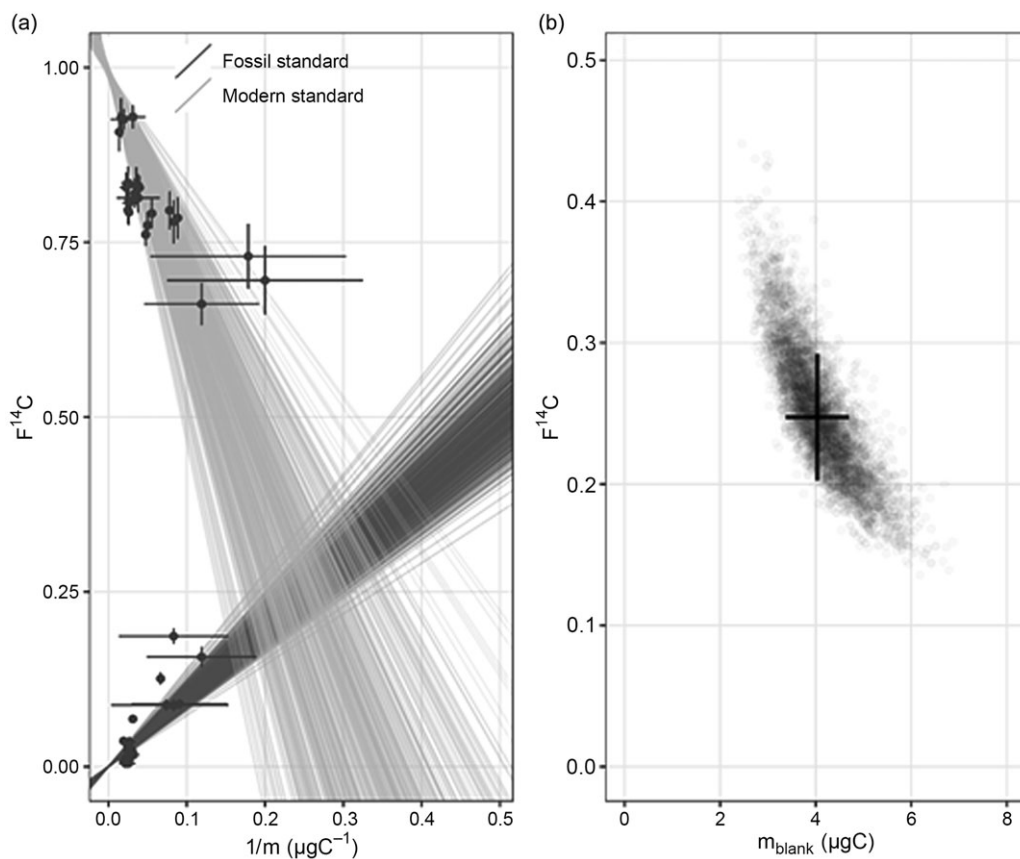
The  $^{14}C$  measured on the large-sized graphite targets resulted in  $F^{14}C = 0.0027 \pm 0.0005$  (average  $\pm$  standard deviation of 2 measurements) for the fossil standards ( $nC26$ ,  $nC28$ ),  $0.71 \pm 0.00003$  (average and standard deviation of 2 measurements) for the  $nC27$ -standard and  $1.00 \pm 0.01$  (average and standard deviation) of the  $F^{14}C$  of the red fescue sample with  $F^{14}C = 0.995 \pm 0.003$  and the common beech sample with  $F^{14}C = 1.009 \pm 0.002$  for the modern plant material. Due to the enormous size of those samples, the material is virtually unaffected by a blank and we assume those numbers to be the “true”  $F^{14}C_{\text{true}}$  values.

The  $nC27$  standard is neither fossil nor modern, so we continuously process this standard with every CSRA batch (Table 1).

Figure 1 shows the result of the blank assessment for  $n$ -alkanes resulting in a calculated blank mass of  $m_{\text{blank}} = 4.1 \pm 0.7 \mu\text{g}$  and  $^{14}C$  value of a  $F^{14}C_{\text{blank}} = 0.25 \pm 0.05$ . The mass of the blank, which is determined by the analytical equipment and sample handling procedure, is similar to the blank of  $n$ -alkanoic acid ( $m_{\text{blank } n\text{-alkanoic acid}} = 4.898 \mu\text{g C}$ ) in the previous blank assessment by Sun and co-workers (Sun et al. 2020). In addition, our blank is close to the blank of  $n$ -alkanes from marine sediments (Druffel et al. 2010). The analytical procedures for CSRA of  $n$ -alkanoic acids, lignin phenols, and  $n$ -alkanes are fundamentally different, so the blank values may differ. However the blank must be calculated for every substance and will change with another analytical protocol (Sun et al. 2020).

Table 1 Uncalibrated bulk and compound-specific radiocarbon dates of the standard *n*C27—the measured  $\text{F}^{14}\text{C}$ , corrected  $\text{F}^{14}\text{C}$ , and corrected  $^{14}\text{C}$  ages.

Sample number	Sample description	Mass ( $\mu\text{g}$ )	$\text{F}^{14}\text{C}$	$\sigma_{\text{F}^{14}\text{C}}$	$^{14}\text{C}$ (BP)	$\text{F}^{14}\text{C}_{\text{blank}}$ corrected	$^{14}\text{C}$ (BP) <sub>blank</sub> corrected	$\sigma_{^{14}\text{C}}$ (BP) <sub>blank</sub> corrected
30	Bulk <sup>1</sup>	3061	0.71	0.00	2706	—	—	—
31	Bulk <sup>1</sup>	3314	0.71	0.00	2706	—	—	—
42	Bulk <sup>1</sup>	3144	0.71	0.00	2729	—	—	—
40	CSRA <sup>2</sup>	15	0.63	0.01	3776	0.77	2141	844
41	CSRA <sup>2</sup>	21	0.62	0.01	3827	0.71	2740	732
86	CSRA <sup>2</sup>	41	0.66	0.01	3338	0.71	2802	513
90	CSRA <sup>2</sup>	23	0.62	0.01	3788	0.71	2807	666
96	CSRA <sup>2</sup>	18	0.63	0.01	3699	0.74	2383	782
97	CSRA <sup>2</sup>	20	0.62	0.01	3840	0.72	2691	782
110	CSRA <sup>2</sup>	50	0.67	0.01	3240	0.71	2803	394

<sup>1</sup>Measured on graphite targets.<sup>2</sup>Measured as gas sample.Figure 1 Blank assessment for *n*-alkanes: (a) Bayesian model ran with 3500 iterations, the visual check depicts 500 regression lines of modern and fossil standard, (b) the posterior distribution of  $\text{F}^{14}\text{C}$  values and masses of the blank.

### Lower Mass Limit for Dependable CSRA

The standard *n*C27 has been repeatedly measured both as a graphite sample (where the blank contribution is negligible due to the large sample mass) and as a small-weight gas sample. Contrary to the information received from the manufacturer of the *n*C27 standard, our dating results show a non-fossil age of  $F^{14}C = 0.71$  or a  $^{14}C$  age of approximately  $2,706 \pm 86$  BP (Table 1). This standard with known  $F^{14}C$  can now be used as a quality control standard that, when applying the blank correction, should lead to the correct value of  $F^{14}C = 0.71$ . This standard offers the possibility to make a self-assessment of the blank assessment and to define a minimum threshold value for the mass of carbon at which a corresponding blank value correction is no longer useful because the proportion of the blank in the sample is too large. If we perform the blank assessment on the *n*C27 standard measured as a gas sample, considering the limit of  $15 \mu\text{g C}$ , we get the radiocarbon age of about approximately  $F^{14}C = 0.63$  ( $2141 \pm 844$  BP) (Table 1). With increasing mass, the blank corrected ages deviate slightly from each other (Table 1). Sun and co-workers found that if the proportion of the blank is 30 % of the sample, the blank correction is not reliable (Sun et al. 2020). Accordingly, with our blank ( $m_{\text{blank}}$  of  $4.107 \mu\text{g}$ ), at least  $18 \mu\text{g C}$  would be necessary for reliable results. The standard *n*C27 ( $18 \mu\text{g C}$ ) had a blank corrected  $F^{14}C$  of  $0.63$  ( $^{14}C$  age of  $2383 \pm 782$  BP). This differs slightly from the known bulk radiocarbon value  $F^{14}C = 0.71$  ( $2706 \pm 86$  BP). Previous studies have already determined that  $25 \mu\text{g C}$  is necessary for a dependable blank assessment (Pearson et al. 1997; von Reden et al. 1998; Shah and Pearson 2007). The blank correction and the additional uncertainty resulting from the correction is strongly dependent on the mass of carbon. A lower relative blank contribution leads to more precise blank-corrected ages (Table 1). Even if it is technically possible to measure extremely low masses ( $< 10 \mu\text{g C}$ ) on the AMS, the appropriate lower limit of at least  $15 \mu\text{g C}$  should be considered.

### Application of Blank Assessment to Sediment Samples

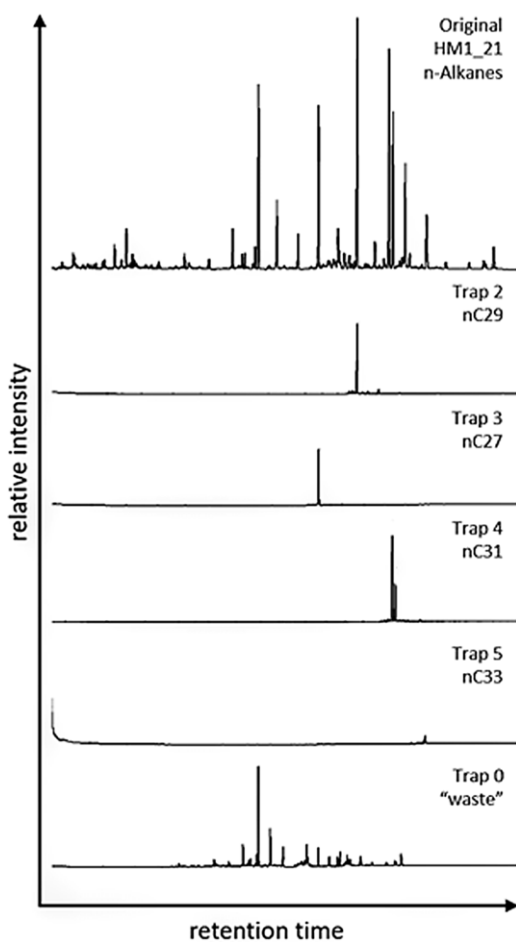
Individual *n*-alkane homologs *n*C27, *n*C29, *n*C31 and *n*C33 were isolated from sediment sample of the Holzmaar using prepGC. The peaks were baseline-separated. The separation of the different carbon chains from the lipid mix was checked with GC-FID. Traps 2 to 5 show the cleanly isolated analytes (Figure 2). Their  $F^{14}C$  and mass was  $0.465 \pm 0.007$  and  $20.9 \mu\text{g}$  (*n*C27),  $0.469 \pm 0.006$  and  $31.5 \mu\text{g}$  (*n*C29),  $0.479 \pm 0.007$  and  $37.9 \mu\text{g}$  (*n*C31),  $0.421 \pm 0.011$  and  $10 \mu\text{g}$  (*n*C33). After the blank correction using the blank values above, ages of the four *n*-alkanes examined differed. Following uncalibrated ages resulted for the *n*-alkanes, homologs were  $5286 \pm 594$  BP (*n*C27,  $F^{14}C = 0.465 \pm 0.007$ );  $5548 \pm 444$  BP (*n*C29,  $F^{14}C = 0.469 \pm 0.006$ );  $5451 \pm 854$  BP (*n*C31,  $F^{14}C = 0.479 \pm 0.007$ );  $4960 \pm 537$  BP (*n*C33,  $F^{14}C = 0.421 \pm 0.011$ ) (Table 2). One of the four dated *n*-alkanes had a mass  $< 15 \mu\text{g C}$  (*n*C33), which was determined to be the limit of excessive uncertainty in CSRA. Therefore, the radiocarbon age of the *n*-alkane *n*C33 is not dependable. In contrast, *n*-alkanes *n*C27, *n*C29 and *n*C31 with a mass  $\geq 20.9 \mu\text{g C}$  are very close in age with a mean value of,  $429 \pm 600$  BP ( $F^{14}C = 0.47 \pm 0.007$ ). However, these CSRA are all older than the corresponding bulk and twigs samples determined by Sirocko and co-workers (Sirocko et al. 2016) (Figure 3).

An age offset is common and has been frequently described in other studies (Kusch et al. 2010; Feng et al. 2013; Douglas et al. 2014; Gierga et al. 2016; Nelson et al. 2018; Makou et al. 2018). Reasons for this may include: (1) Different transport processes of *n*-alkanes require contrasting times to be deposited in the sediment trap. Aeolian transport of *n*-alkanes occurs on a regional scale and can lead to an age offset of one year (Freimuth et al. 2021). During fluvial transport



Table 2 Uncalibrated compound-specific radiocarbon dates of the sediment sample HM1\_21—the measured  $\text{F}^{14}\text{C}$ , corrected  $\text{F}^{14}\text{C}$ , and corrected  $^{14}\text{C}$  ages.

Sample number	<i>n</i> Alkane	Mass ( $\mu\text{g}$ )	$\text{F}^{14}\text{C}$	$\sigma$ $\text{F}^{14}\text{C}$	$^{14}\text{C}$ (BP)	$\text{F}^{14}\text{C}$ blank	$^{14}\text{C}$ (BP) blank	$\sigma$ $^{14}\text{C}$ (BP) blank
						corrected	corrected	corrected
105	nC27	20.9	0.465	0.007	6144	0.52	5286	594
106	nC29	31.5	0.469	0.006	6088	0.5	5548	444
107	nC31	37.9	0.479	0.007	5904	0.51	5451	854
108	nC33	10	0.421	0.011	6951	0.54	4960	537

Figure 2 The top trace shows the initial sample HM1\_21 before prepGC. Trapped *n*-alkanes are isolated by prepGC (no. of runs = 40).

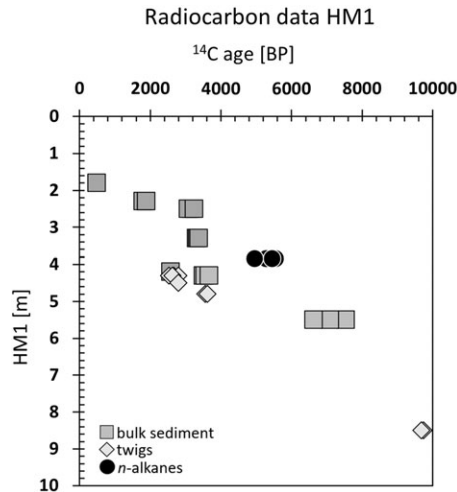


Figure 3 <sup>14</sup>C-data from core HM1 Lake Holzmaar. Bulk sediment and twig uncalibrated radiocarbon data are already published in Sirocko et al. 2021. All radiocarbon dating, including CSRA measurements, were performed at the Curt-Engelhorn Center for Archaeometry in Mannheim, Germany. *N*-Alkanes of the sample HM1\_21 have the following uncalibrated CSRA dates: *n*C27 (5286 ± 594 BP), *n*C29 (5548 ± 444 BP), *n*C31 (5451 ± 854 BP) and *n*C33 (4960 ± 537 BP). Due to the time axis, the error bar for all the data shown here are so small that they are not visible in the figure.

(Kusch et al. 2010; Galy et al. 2011; Ponton et al. 2014; Häggi et al. 2016; Hemingway et al. 2016; Simoneit et al. 2017), *n*-alkanes from sediments of different riparian areas can be mixed and enter the sediment trap (Aichner et al. 2021). The river Sammetbach flows into the Holzmaar. Therefore, a mixture of terrestrial *n*-alkanes, eroded from several riparians, may enter the sediment of the Holzmaar. The *n*-alkanes can be incorporated into the soil in the lake's catchment area via litter (Freimuth et al. 2021). The age mixture of sources of the carbon pool in soils can range between hundreds to thousands of years before soil erosion transports the carbon including *n*-alkanes into the lake sediment (Diefendorf et al. 2017). Eroded soil with age-mixed *n*-alkanes may also result in an age difference in CSRA samples. This could be also a reason for the reverse chronology of bulk samples between 3.30 m (3342 BP) and 4.20 m (2580 BP) in HM1.

Additionally, (2) the hard-water effect can influence the radiocarbon measurements. Dissolved inorganic carbon (DIC) reaches the maar lake via groundwater (Sirocko et al. 2016). Additionally, rising mantle CO<sub>2</sub> cannot be excluded (Dahm et al. 2020). The impact of hard water is not limited to bulk measurements, but also affects CSRA. Mischke and co-workers (2017) determined the hard water effect by dating algae <sup>14</sup>C. Modern algae had an F<sup>14</sup>C of 0.8914, thus a correction of the hard-water effect was necessary, which can cause an age shift of approximately 2000 years in submerged aquatic plants (Gross 1957). The impact of hard water on the radiocarbon dating of bulk sediment is possible, as the heterogeneous bulk sample may

contain a proportion of algae. However, it is unclear if this effect influences the terrestrial CSRA of *n*-alkanes.

(3) Inhomogeneous distribution of *n*-alkanes. The *n*-alkanes are never homogeneously distributed in a lake sediment, as evidenced by various samples within a lake (Sarkar et al. 2014; Kou et al. 2021).

### Intrinsic Blank Assessment

An alternative approach of blank assessment without using fossil and modern standards at all is by dating a single sample multiple times (or using multiple *n*-alkanes as subsamples) with

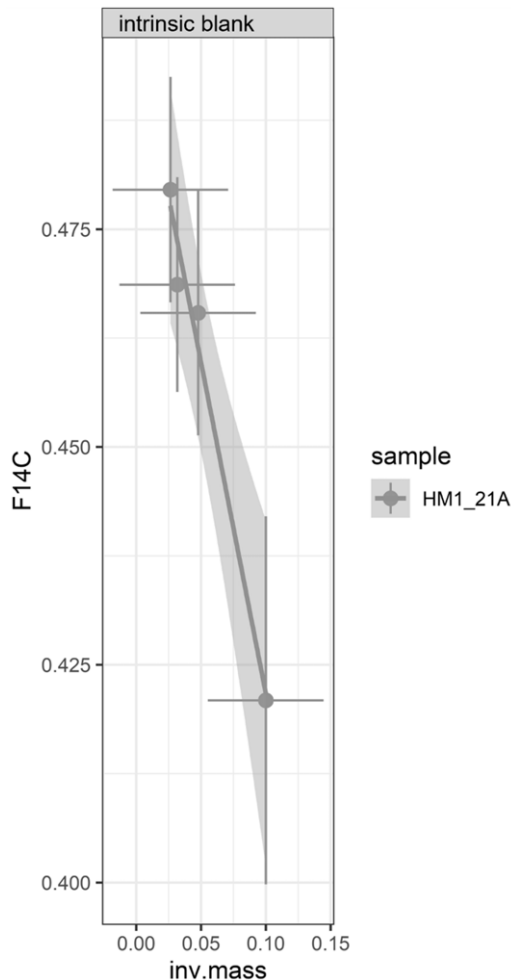


Figure 4 Intrinsic blank assessment for *n*-alkanes: The different masses of the *n*-alkanes are distributed in such a way that it is possible to use linear regression to determine an intersection with the y-axis. The intersection is the  $F^{14}\text{C}$  value of the intrinsic blank. The intersection with modern and fossil samples is not included in the  $m_{\text{blank}}$  assessment.

different masses. The  $F^{14}C$  values of the individual subsamples will obey the aforementioned mass-balance equation. Similar to the data in Figure 1, the individual  $F^{14}C$  values will fall onto one line and define a linear equation with a given slope and intercept. While the mass and  $F^{14}C$  value of the blank cannot be independently determined from the slope of the linear equation, its intercept equals the true  $F^{14}C$  of the whole sample.

Figure 4 shows the results of Holzmaar samples. The  $F^{14}C$  values of the individual *n*-alkanes lie on a straight line determining the intercept of the linear equation. Using this method, the true  $F^{14}C$  of the Holzmaar sample from which the *n*-alkanes were extracted is  $0.5 \pm 0.01$  resulting in a  $^{14}C$  age of  $(4464 \pm 738 \text{ BP})$  which agrees well with the individual resulting blank corrected dates.

However, this approach also presents challenges, such as the amount of sample material available for subsampling and how many samples need to be analyzed. For example, when only a limited amount of sample material is available or a large number of samples need to be analyzed, it can be more efficient to use only a few fossil and modern standards to analyze many samples. In this way, it would require less effort and time to carry out the analysis and it would make sense to use the blank assessment according to (Sun et al. 2020). However, when very few samples are available with sufficient mass of carbon to extract more than one *n*-alkane, as in the Holzmaar sample, an intrinsic blank assessment can be performed.

Despite these challenges, this method offers advantages. For example, it allows more flexibility in the analytic process and could potentially be adapted to diverse types of samples. In addition, the sample itself serves as an intrinsic blank, which can increase the robustness of the method. In addition, this method could allow for different sample preparations without the need to use fossil and modern standards for each.

In summary, while blank assessment without fossil and modern standards by measuring a sample of different masses may have limitations, it has potential advantages that could make it a useful analytical tool.

## CONCLUSION

Using fossil and modern standard material the contribution of the procedural blank to extracted *n*-alkanes could be determined in terms of blank mass and blank  $F^{14}C$ . Thus, biomarker extraction and CRSA is successfully established at the participating laboratories. We conclude that we have a reliable blank assessment for samples with more than  $15 \mu\text{g C}$ , supplemented by the internal control by the commercial standard *nC27*, but have an age offset in the Holzmaar sediment sample.

Three out of four isolated *n*-alkanes from a sediment sample from the Holzmaar have sufficient carbon for a reliable blank assessment. The CSRA ages of these three *n*-alkanes are close, but round about 1000–2000 years older than radiocarbon-dated twigs and bulk samples. We did not consider the age offset being caused by the hard-water effect. Instead, we assume that the input of organic matter with a long residence time in the soil determines the CSRA age of the terrestrial *n*-alkanes in the sediment as the decisive factor for the age offset. In addition, the Sammetbach transports a mix of terrestrial *n*-alkanes into the Holzmaar.

The intrinsic blank assessment using a sample of different masses offers advantages, such as increased flexibility in the analytical procedure and potentially being adaptable to different

sample types, although it has limitations when limited sample material is available. Overall, the methods described in this text are useful for understanding the age and sources of organic matter in sediment samples.

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## SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2024.26>

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