Radiocarbon, Vol 62, Nr 2, 2020, p 349–360 DOI:10.1017/RDC.2020.8
© 2020 by the Arizona Board of Regents on behalf of the University of Arizona

PRETREATMENT OF TERRESTRIAL MACROFOSSILS

Margaret W Norris[1] • Jocelyn C Turnbull[1,2*] • Jamie D Howarth[3] • Marcus J Vandergoes[1]

[1]Rafter Radiocarbon Laboratory, GNS Science, Lower Hutt, New Zealand
[2]CIRES, University of Colorado at Boulder, CO, USA
[3]Victoria University of Wellington, New Zealand

ABSTRACT. Acid-alkali-acid (AAA) pretreatment is widely used to clean terrestrial plant macrofossil samples for radiocarbon (^{14}C) dating. There is wide variation amongst laboratories in the AAA method details and less rigorous AAA pretreatment is often used on fragile or small samples. Yet there is little evidence as to the efficacy of the different methods and whether the use of less rigorous methods is justified. We investigated four variations of AAA pretreatment: acid only (no alkali wash); room temperature AAA; "standard" AAA at 85°C; and "aggressive" AAA at 85°C with alkali washes repeated until no discoloration was detected. We tested six different terrestrial macrofossils from four different locations and ranging in age from mid-Holocene to the Last Glacial Maximum. Our results demonstrate that while acid only is not always sufficient to remove young material, there is no difference in ^{14}C age of samples pretreated by any of the AAA variants. We also observed mass loss of 85–90% in the standard and aggressive AAA pretreatments, and much more modest mass loss in the room temperature AAA pretreatment. Therefore, we conclude that room temperature AAA pretreatment is optimal to remove contaminating material from fragile terrestrial macrofossils while retaining the majority of the authentic sample material.

KEYWORDS: AAA pretreatment, macrofossil pretreatment.

INTRODUCTION

Radiocarbon (^{14}C) dating is widely used to constrain timing of deposition of sediment, peats, swamp material and other terrestrial archives. Applications include paleoclimate reconstructions (Vandergoes et al. 2013b, 2018), past earthquake and tsunami events (Clark et al. 2015; Howarth et al. 2016; Cochran et al. 2017) and archaeology (McWethy et al. 2010; Maxwell et al. 2016).

Terrestrial macrofossils are usually considered the most reliable targets for ^{14}C dating in these terrestrial environments (Olsson 1986; Taylor 1987; Oldfield et al. 1997). Terrestrial macrofossils such as leaves and small twigs take their carbon from the atmosphere and are not subject to any hard-water or other lake reservoir effects. Being fragile, they are unlikely to survive reworking intact. They are often identifiable by species or genus, further ensuring that they are appropriate dating targets for a particular environment. Yet because they are fragile, only small fragments of such macrofossils are usually available, and they are easily damaged during coring, core sampling, and ^{14}C pretreatment.

Improvements in the ability to measure smaller samples at many ^{14}C laboratories have expanded possibilities for dating small, fragile terrestrial macrofossils. Yet measurement of small samples usually requires preparation of additional standards and processing blanks (Santos et al. 2007) and typically results in higher measurement uncertainties and possible biases. Thus, larger samples are generally preferable if possible.

Pretreatment is required to remove contaminating material and isolate the original macrofossil material. Acid-alkali-acid (AAA), sometimes called acid-base-acid (ABA), pretreatment is commonly used to pretreat terrestrial macrofossils. The method was developed in the early days of ^{14}C dating and is widely believed to be sufficient to remove contaminating material (De Vries and Barendsen 1954; Olsson 1976; Taylor 1987). AAA starts with an acid wash intended to remove carbonates as well as acid soluble humic material such as fulvic acids.

*Corresponding author. Email: j.turnbull@gns.cri.nz.

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

This is followed by alkali wash(es) to remove humic acids. The final acid wash is primarily aimed at removing any carbon absorbed into the solution and onto the sample during the alkali washes.

While AAA is very commonly used, there is a wide variation in how AAA pretreatment is applied, and surprisingly little literature documenting why the particular choices have been made. Most laboratories use hydrochloric acid (HCl) at molarities of 0.5–1 M, and sodium hydroxide (NaOH) at molarities of 0.1–0.5 M, although a few use stronger solutions and a potassium hydroxide (KOH) is occasionally used in place of NaOH. Most laboratories heat each solution to 80 or 90°C, although some use room temperature, and the duration of each step also varies widely from 15 min to several hours (Andree et al. 1986; Tornqvist et al. 1992; Bradley and Stafford 1994; Kitigawa et al. 1995; Kretschmer et al. 1997; Hajdas et al. 1998; Brock et al. 2010; Dunbar et al. 2016; Crann et al. 2017; Knowles et al. 2019). Some repeat the alkali wash several times, often using the color of the supernatant liquid to determine how many washes to perform. Many laboratories (including our own) use less rigorous pretreatment for fragile or small macrofossils (< 5 mg), typically using shorter duration washes at lower temperatures, and sometimes omitting the alkali step altogether. Yet these less rigorous pretreatments appear to be applied based on expert opinion and there is little information on whether they are sufficient to remove contamination. One study (Santos and Ormsby 2013) investigated the effect of several different AAA procedures and showed that room temperature or short duration pretreatment may not be sufficient for very old wood samples, whereas another study showed that AAA is most often sufficient to remove contamination even in very old wood samples (Hajdas et al. 2017). However, both of these experiments were limited to testing the effectiveness of AAA on very old wood samples.

This paper aims to determine the rigor of AAA pretreatment required for terrestrial plant macrofossils to ensure removal of contamination, while retaining as much sample material as possible. We aim to understand whether the less rigorous pretreatments commonly applied to small or fragile macrofossils are sufficient to remove contamination and provide reliable ages. We test a series of samples collected from lake sediments and swamps representing the range of environments of interest for ^{14}C dating and spanning Holocene to Last Glacial Maximum in age. In this experiment we focus on the effect of different temperatures and the extent of alkali washes.

METHODS

Sample Selection

The objective was to test a range of pretreatment methods on macrofossil samples that are typically recovered from peat bogs and lake sediments. Ideally for this experiment, we would have tested known age samples, but obtaining known age samples of fragile macrofossils from authentic depositional environments is challenging. An alternative of deliberately contaminating known age fragile macrofossils could be used but is likely to become an experiment in how well a laboratory-created contaminated sample can represent authentic depositional contamination, rather than addressing the problem at hand. Therefore, we chose to use authentic samples recovered from New Zealand locations that were readily available to us, and with approximate ages known from the depositional environment and other information. The chosen environments have high humic loading and varying carbonate content. We expect that they reasonably represent the range of terrestrial macrofossil

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

Table 1 Samples tested in this study.

Sample ID	Macrofossil type	Sample provenance	Expected age
H3B Heath	Heath (Styphelioideae)	Organic-rich silt from alluvial sequence, Howard Valley, New Zealand	Last Glacial Maximum 20,400 – 21,700 BP
MAV Leaf MAV0901-2-1	*Lophozonia menziesii* (Silver beech) leaf	Ombrotrophic peat bog, Mavora Lakes, New Zealand	Mid-Holocene
BST Leaf BST1-1113-T3 0–3 cm	*Phyllocladus trichomanoides* (Celery Pine) Leaf	Lake sediment core, Boundary Stream Tarn, Pukaki, New Zealand	Holocene
BST Twig BST1-1113-T3 16–18 cm	Twig (species unknown)	Lake sediment core, Boundary Stream Tarn, Pukaki, New Zealand	Holocene, older than BST Leaf
OK Twig OK1702 1.5–2.0 m 11–14 cm	Twig (species unknown)	Peat core, Okarito bog, Westland, New Zealand	Late Holocene
OK Wood OK1702 2.0–2.5 m 40–43 cm	*Leptospernum scoparium* (Manuka) wood fragment	Peat core, Okarito bog, Westland, New Zealand	Early Holocene, older than OK Twig

environments that are encountered globally. We selected a total of six samples recovered from a range of depositional environments. In the New Zealand context, most geological and archaeological studies are primarily focused on the Holocene, so we choose a set of test samples expected to be of Holocene age and included one much older (Last Glacial Maximum) sample as any unremoved younger contamination is expected to be more apparent in an older sample. All sites would have been bordered by forest for the duration of the Holocene prior to human occupation (Vandergoes et al. 1997, 2008, 2013b). Grassland/herbfield and low forest probably dominated around the Howard Valley site during the Last Glacial Maximum (Callard et al. 2013). Descriptions of the sites, deposits and expected ages are as follows and summarized in Table 1 and the locations are shown in Figure 1.

At Howard Valley in southeast Nelson (41°46'38"S, 172°39'43"E, 480 m asl, H3B), an alluvial sequence exposed in a river terrace edge contains 10 cm of the Kawakawa/Oruanui tephra (KOT) enclosed above and below by brown organic-rich silt (Callard et al. 2013; Vandergoes et al. 2013a). Well-preserved heath macrofossils (species Styphelioideae), in-situ and flattened during burial by the KOT, were collected from the base of the KOT providing a close pre-eruption age of the KOT. An age for the KOT based on 22 ^{14}C ages from optimal materials directly above, within, or directly below KOT eruptives consistently range between ca. 20,400 and 21,700 ^{14}C yr BP with a previously dated plant macrofossils from below KOT at Howard Valley providing an age of 21,100 ± 110 (Vandergoes et al. 2013a).

At Mavora Lakes bog in Southland (45°19'08"S, 168°10'46"E, 830 m asl, MAV), 3 m of fibrous and compact ombrotrophic peat overlay silt deposits from the last glaciation (Turner et al. 2015) The MAV leaf macrofossil selected from this sequence relates to the expansion and

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

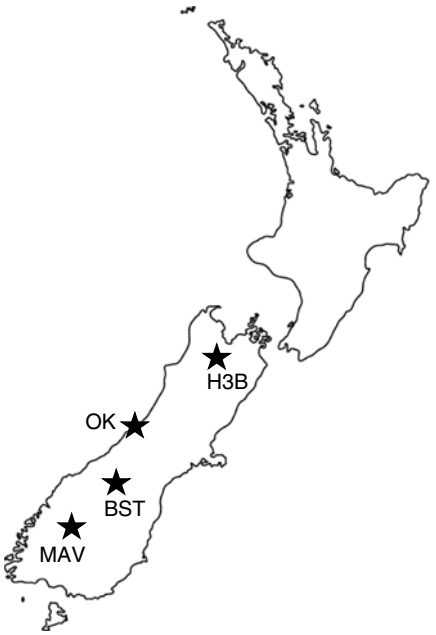


Figure 1 Map of New Zealand showing the sampling locations used in this study.

dominance of Lophozonia menziesii (Silver beech) in this region during the early to mid Holocene and is supported by regional pollen evidence (McGlone and Bathgate 1983).

At Boundary Stream Tarn in inland Canterbury (44°02'S, 170°07'E, 830 m asl, BST), 3 m of organic lake mud overlay inorganic silty lake mud dated to the last glacial transition (Vandergoes et al. 2008). The two samples were selected from the sequence at ~3.15 m and pollen analysis from this sequence identifies that the upper 3 m of mud represent Holocene accumulation since ~11,000 ^{14}C yr BP. The position of leaf macrofossils within these silts compared to the current age model and previously dated material are likely to fall within ~8000–9000 ^{14}C yr BP (Vandergoes et al. 2008). Both BST samples were from the same 1-m core section collected from about 3-m depth. The BST leaf was from the top 3 cm of this core section, and the BST twig is expected to be slightly older as it was from the 16–18 cm section of this core section.

At Okarito bog (43°14'30"S, 170°13'E, 70 m asl, OK), 3 m of fibrous and compact sedge peat overlay silt deposits dated to the last glaciation and glacial transition. These ages and pollen analysis from this sequence identify that these peats represent Holocene peat accumulation since ~11,000 ^{14}C yr BP (Vandergoes et al. 2005). The OK twig is expected to be ~5000 ^{14}C yr BP (Vandergoes et al. 2005) and younger than the OK wood, which was collected from a deeper section of the same core and has an expected age of ~8000 ^{14}C yr BP (Newnham et al. 2007).

Leaf samples of heath, silver beech and celery pine were selected as they are unlikely to survive reworking intact. Therefore, they are likely to have fallen directly into the depositional environment and should not have inherited age. New Zealand species typically hold their

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

Table 2 Chemical pretreatment methods.

Pretreatment method	Acid wash	Alkali wash	Acid wash
Acid only (hot acid wash)	0.5M HCl 15 min 85°C	N/A	N/A
RT AAA (room temperature AAA)	0.5M HCl RT	0.1M NaOH 1 wash only RT	0.5M HCl RT
STD AAA (hot AAA)	0.5M HCl 85°C	0.1M NaOH 85°C Repeat until final solution amber	0.5M HCl 85°C
Aggro AAA (aggressive hot AAA)	0.5M HCl 15 min 85°C	0.1M NaOH 85°C many repeats until supernatant clear	0.5M HCl 85°C

leaves for up to two years before dropping. The other three samples are twigs and a wood fragment. The twigs are small enough that they represent only one or two years of growth, and the wood is likely manuka, which has a lifetime of 25–50 yr. These are less ideal dating targets since they are more robust and thus more likely to be reworked before ending up in sediment. The wood could also have an inherited age. However, their greater robustness means that they are commonly dated from sediment and peat bog samples. Some carbonate may be present in the terrain for some samples, potentially biasing the samples to older ages, although no effervescence was observed during the acid pretreatments, indicating that this kind of contamination was likely minimal in all samples. More significant contamination is likely to come from humic material that can translocate within the depositional environment. This is of particular concern in the peat bog environments where humic loading is high, but also possible in the sediment cores. Humic contamination may be younger or older than the sample itself.

Although wood and twigs are ideally pretreated to extract cellulose (Gaudinski et al. 2005; Southon and Magana 2010), the amount of sample material recovered from sediment cores and its preservation state is commonly insufficient to perform cellulose extraction. Therefore, AAA is usually performed on this type of sample, and in our experiment we treated the wood and twig samples in the same manner as the fragile leaf and heath macrofossil samples.

Physical Pretreatment

All samples were picked or sieved from the host sediment. They were ultra-sonicated to remove residual sediment and non-target macro-organics were removed by picking under microscopic examination. Almost no residual sediment remained on any sample. Samples were then dried at 50ºC. Once dry, each individual macrofossil was sectioned to produce five subsamples with approximately equal masses of material. The fifth subsample was kept in reserve to allow for additional future experiments.

AAA Chemical Pretreatments

Four different variations of the acid alkali acid (AAA) method were trialled (Table 2). All pretreatment methods were performed in 15-mL polypropylene centrifuge tubes. Acid

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

was 0.5 M hydrochloric acid solution, and alkali was 0.1 M sodium hydroxide solution. Where heating was required, the tube was immersed in a water bath to a level that the liquid in the tube was covered. For each wash, the solution was added, the sample immersed in the water bath (except for room temperature) for 15 min. After 15 min the sample was removed from the water bath and the liquid decanted off with a pipette. Following acid and alkali washes, the remaining solid sample was rinsed to neutral with deionized water.

The acid only treatment used only a single acid wash, intended to remove carbonate material and any acid soluble material such as fulvic acids. In this method, there is no serious attempt to remove humic material. The acid solution was heated to 85°C.

The room temperature AAA ("RT AAA") method is a room temperature variant of the commonly used AAA method. The first acid wash is intended to remove carbonate and acid soluble material. It is followed by a single alkali wash intended to remove humic material. Finally, a last acid wash is intended to remove any carbon absorbed during the alkali step. All steps were done at room temperature.

The standard AAA ("STD AAA") method is the version of AAA pretreatment that has most commonly been used in our laboratory, consisting of acid and alkali washes done at 85°C. The solutions are the same as for RT AAA except that (a) the sample and solution are heated to 85°C, and (b) the alkali step is repeated until the supernatant solution is amber in color, pipetting off and replacing the alkali solution between each 15-min 85°C wash. In all cases in this experiment, only one alkali wash needed to be applied to meet the color criteria. In fact, all were pale yellow in color after the single alkali wash, likely in part due to the small mass of these samples relative to the volume of the solution.

The aggressive AAA ("Aggro AAA") method is the same as STD AAA except that the alkali washes are repeated until the supernatant liquid is completely colorless. The alkali solution is pipetted off and replaced between each 15-min 85°C wash. In this experiment, all samples required three or four alkali washes to meet this criteria.

Dried samples were weighed before and after pretreatment to determine the mass loss during the pretreatment process. We arbitrarily estimate the uncertainty in the pretreatment yield as 10% for all samples.

Combustion, Graphitization, and AMS Measurement

The remaining solid sample material after AAA pretreatment was dried in a 50°C oven and weighed to determine the mass loss during pretreatment, then combusted to CO_2 gas by sealed tube combustion (Baisden et al. 2013). Each sample was reduced to graphite using hydrogen reduction (Turnbull et al. 2015). The graphite amount was determined manometrically from the CO_2 pressure in the graphite reactor. Samples were measured by AMS at the Rafter Radiocarbon Laboratory and data reduced to determine the ^{14}C content (Zondervan et al. 2015). Results are reported as conventional ^{14}C age (CRA) (Stuiver and Polach 1977; Donahue et al. 1990). Total ^{14}C measurement precision is typically 25–35 yr BP at 1σ for Holocene samples, and larger for the Late Glacial samples. The fractionation correction is performed using the ^{13}C content measured in the AMS (Zondervan et al. 2015), $\delta^{13}C$ was also measured by IRMS on a split of CO_2 gas from each combusted sample, except for three samples for which insufficient CO_2 was available for this measurement. Nominal IRMS $\delta^{13}C$ precision is 0.3‰.

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

The mass loss during the more aggressive AAA pretreatments meant that a few samples produced less than 0.3 mg carbon (mgC). These < 0.3 mgC samples were treated as small samples and their CRA determined following the protocols of Santos et al. (2007). In this protocol modern known age materials and blank materials spanning the size range of the small samples are measured concurrently with the small samples and used to diagnose the modern and dead carbon contamination amounts which were then used to correct the ^{14}C results. The overall uncertainty in these small samples in much larger than for > 0.3 mgC samples, not only because fewer ^{14}C counts are obtained, but because the relative contribution of contamination is larger and the amount of contamination is also uncertain.

RESULTS AND DISCUSSION

^{14}C content, mass loss during pretreatment and other results are shown in Figure 2 and Table 3.

In all cases, there is a clear progression towards increased mass loss with more aggressive pretreatment. As might be expected, the fragile heath and leaf samples lost substantially greater mass than the twigs or wood fragment. In some cases, 85–90% of sample mass was removed during STD AAA and Aggro AAA pretreatments, both of which involve heating the sample to 85°C. This dramatic mass loss meant that those samples had to be treated as small samples during AMS measurement, resulting in much larger measurement uncertainties than for the larger samples (Figure 2).

STD AAA (85°C) also resulted in substantially more mass loss than RT AAA, even though only one alkali wash was required in all cases. The most fragile sample, BST Leaf, lost substantially more mass in RT AAA than in acid only pretreatment, but for the other samples the mass loss was similar for RT AAA and acid only pretreatments. We hypothesize that performing the acid only pretreatment at room temperature rather than 85°C would result in smaller mass loss, but insufficient material from these samples was available to test this.

The acid only pretreatment gives younger ages than the various AAA pretreatments in several, but not all, cases. This is most apparent in the case of the H3B heath, for which the acid only pretreatment gives a CRA four standard deviations younger than the weighted mean of the other three pretreatments. This result is reasonable given that the H3B heath has a much lower ^{14}C content (21,000 yr BP) than any of the other samples (5000–9000 BP), and therefore the effect of unremoved, younger contamination will be more apparent in this sample than in the others. The MAV Leaf and OK Twig also show slightly, but not significantly, younger ages for the acid only pretreatment than for the other pretreatments. All three of these samples came from swamp settings, where there is greater potential for vertical movement of humic laden fluids of different age than the sample.

There is some variability amongst results for the various AAA methods, but none show statistically significant differences, and there is no consistent pattern amongst the different samples. The largest difference is in the Aggro AAA for the OK Wood sample, which is 53 ± 37 yr BP older than the weighted mean of the other three pretreatments of the same sample. In all other cases, the differences between AAA pretreatment methods for a given sample are within one standard deviation of each other.

It is apparent from the greater mass loss in the STD AAA and Aggro AAA pretreatments, that more material was removed than in the RT AAA pretreatment, yet the ^{14}C content is similar after any of these treatments. We suspect that while the alkali step is intended to remove

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

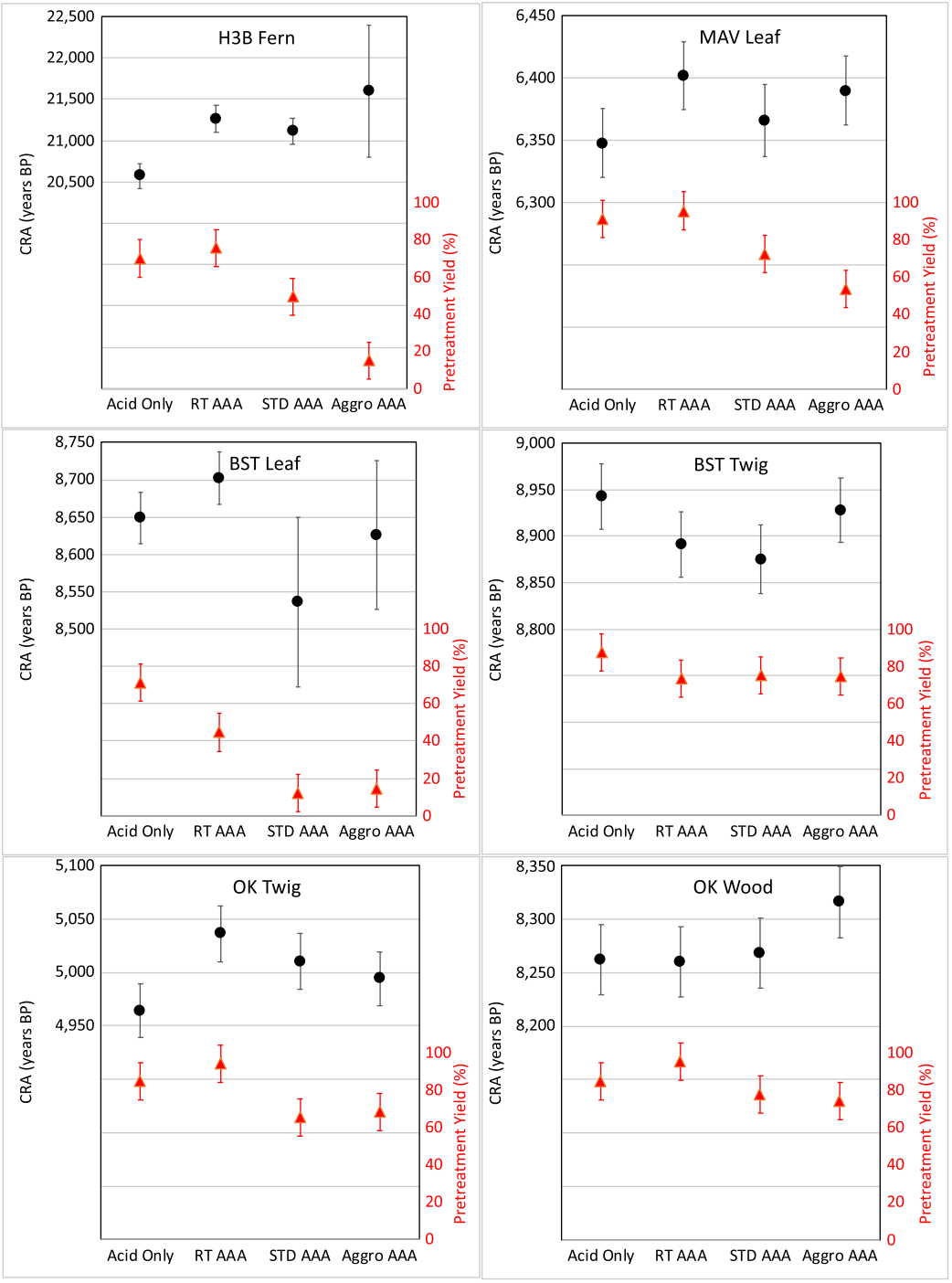


Figure 2 ^{14}C results presented as conventional ^{14}C age (left axis) and pretreatment yields (right axis) for macrofossil samples pretreated by various methods. Error bars are as described in the text.

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

Table 3 Results for pretreatment test samples. NZA is the unique Rafter Radiocarbon Laboratory measurement identifier. Initial mass is the mass prior to the beginning of chemical pretreatment. Pretreatment yield was determined from the initial mass and dry mass after pretreatment. Graphite mass not directly related to pretreatment yield but is included to indicate where samples needed to be treated as small samples (see text). ^{14}C results are given as conventional radiocarbon age (CRA), and ^{13}C content as $\delta^{13}C$.

NZA	Sample name	Pretreatment	Initial mass (mg)	Alkali washes	Pretreatment yield (%)	Mass graphite (mg)	$\delta^{13}C$ IRMS	CRA (^{14}C yr BP)	CRA error
63040	H3B Heath	Acid only	2.4	0	70	0.8	–23.2	20,570	150
63041	H3B Heath	RT AAA	2.2	1	75	0.8	–22.5	21,260	160
63042	H3B Heath	STD AAA	2.1	1	38	0.5	–22.5	21,110	160
63216	H3B Heath	Aggro AAA	2.4	4	5	0.2	N/A	21,590	800
63043	MAV Leaf	Acid only	2.3	0	90	0.7	–29.8	6348	28
63044	MAV Leaf	RT AAA	2.3	1	95	0.7	–29.7	6402	28
63045	MAV Leaf	STD AAA	2.2	1	75	1.2	–29.7	6366	29
63046	MAV Leaf	Aggro AAA	2.6	4	55	1.0	–29.6	6390	28
66347	BST Leaf	Acid only	2.6	0	70	0.6	–27.3	8649	34
66356	BST Leaf	RT AAA	2.7	1	45	0.8	–26.9	8702	35
66423	BST Leaf	STD AAA	2.6	1	10	0.3	N/A	8536	113
66424	BST Leaf	Aggro AAA	2.8	3	15	0.3	N/A	8626	100
66357	BST Twig	Acid only	3.0	0	90	0.7	–24.8	8943	35
66358	BST Twig	RT AAA	2.9	1	75	0.5	–24.7	8891	35
66422	BST Twig	STD AAA	4.0	1	75	1.0	–24.8	8875	37
66359	BST Twig	Aggro AAA	3.7	2	75	1.0	–24.8	8928	35
66348	OK Twig	Acid only	1.8	0	85	0.8	–24.4	4964	25
66349	OK Twig	RT AAA	2.0	1	95	0.8	–24.1	5036	26
66350	OK Twig	STD AAA	2.1	1	65	0.8	–24.3	5010	26
66351	OK Twig	Aggro AAA	2.0	3	70	0.7	–24.1	4994	25
66352	OK Wood	Acid only	4.5	0	85	0.9	–25.3	8262	33
66353	OK Wood	RT AAA	3.2	1	95	0.5	–25.6	8260	33
66354	OK Wood	STD AAA	3.7	1	80	0.8	–25.6	8268	33
66355	OK Wood	Aggro AAA	3.6	3	75	0.8	–25.8	8316	33

contaminating humic material, in fragile and degraded samples, it also breaks down the sample material itself. Some of this may remain in solution as small particulates that are lost during subsequent rinsing and/or sample transfer.

CONCLUSIONS

This study focused on AAA pretreatment methods for fragile terrestrial plant macrofossils and did not consider the well-known reservoir effects that may be encountered with aquatic macrofossils. Nor have we attempted to address the more rigorous pretreatments for more robust wood samples for which there is ample evidence that isolation of the cellulose component may give more reliable ages (e.g. Olsson 1980; Hoper et al. 1998; Gaudinski et al. 2005; Southon and Magana 2010).

Our results indicate that for terrestrial plant macrofossil samples from sediment and peat bog contexts, room temperature acid-alkali-acid (RT AAA) pretreatment is likely to be sufficient to remove contaminating materials and produce a reliable ^{14}C age. In many cases, a simple acid wash (acid only) is likely to be sufficient, but in some samples it appears that alkali washes may be needed to effectively remove contamination. Heating the solutions, and repeating the alkali washes multiple times often results in substantial sample mass loss but does not significantly change the measured ^{14}C age. Therefore, we recommend use of RT AAA for sediment and swamp macrofossil pretreatment. Our samples span Holocene ages and into the Last Glacial Maximum. Although all are from New Zealand, they are from a range of paleo-archive contexts. These results can therefore be expected to be generalizable for pretreatment of fragile terrestrial plant macrofossils from geological contexts.

ACKNOWLEDGMENTS

Thanks for the support of the Rafter Radiocarbon Laboratory staff for assistance with sample preparation and measurement. Thank you to two reviewers for their helpful comments that have improved the paper.

REFERENCES

Andree M, Oeschger H, Siegenthaler U, Riesen T, Moell M, Ammann B, Tobolski K. 1986. ^{14}C dating of plant macrofossils in lake sediment. Radiocarbon 28(2A):411–416.

Baisden WT, Prior CA, Chambers D, Canessa S, Phillips A, Bertrand C, Zondervan A, Turnbull JC. 2013. Radiocarbon sample preparation and data flow at Rafter: Accommodating enhanced throughput and precision. Nuclear Instruments and Methods in Physics Research B 294:194–198.

Bradley L-A, Stafford TW. 1994. Comparison of manual and automated pretreatment methods for AMS radiocarbon dating of plant fossils. Radiocarbon 36(3):399–405.

Brock F, Higham T, Ditchfield P, Ramsey CB. 2010. Current pretreatment methods for AMS radiocarbon dating at the Oxford Radiocarbon Accelerator Unit (ORAU). Radiocarbon 52(1):103–112.

Callard SL, Newnham RM, Vandergoes MJ, Alloway BV, Smith C. 2013. The vegetation and climate during the Last Glacial cold period, northern South Island, New Zealand. Quaternary Science Reviews 74:230–244.

Clark KJ, Hayward B, Cochran UA, Wallace LM, Power W, Sabaa A. 2015. Evidence for past subduction earthquakes at a plate boundary with widespread upper plate faulting: Southern Hikurangi Margin, New Zealand. Bulletin of the Seismological Society of America 105(3): 1661–1690.

Cochran UA, Clark KJ, Howarth JD, Biasi GP, Langridge RM, Villamor P, Berryman KR, Vandergoes MJ. 2017. A plate boundary earthquake record from a wetland adjacent to the Alpine Fault in New Zealand refines hazard estimates. Earth and Planetary Science Letters 464:175–188.

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

Crann CA, Murseli S, St-Jean G, Zhao X, Clark ID, Kieser WE. 2017. First status report on radiocarbon sample preparation techniques at the A.E. Lalonde AMS Laboratory (Ottawa, Canada). Radiocarbon 59(3):695–704.

De Vries H, Barendsen G. 1954. Measurements of age by the carbon–14 technique. Nature 174:1138–1141.

Donahue DJ, Linick T, Jull AT. 1990. Isotope-ratio and background corrections for accelerator mass spectrometry radiocarbon measurements. Radiocarbon 32(2):135–142.

Dunbar E, Cook GT, Naysmith P, Tripney BG, Xu S. 2016. AMS ^{14}C dating at the Scottish Universities Environmental Research Centre (SUERC) Radiocarbon Dating Laboratory. Radiocarbon 58(1):9–23.

Gaudinski JB, Dawson TE, Quideau S, Schuur EAG, Roden JS, Trumbore SE, Sandquist DR, Oh S-W, Wasylishen RE. 2005. Comparative analysis of cellulose preparation techniques for use with ^{13}C, ^{14}C and ^{18}O isotopic measurements. Analytical Chemistry 77(22):7212–7224.

Hajdas I, Bonani G, Zolitschka B, Brauer A, Negendank JF. 1998. ^{14}C ages of terrestrial macrofossils from lago grande di monticchio (Italy). Radiocarbon 40(2):803–807.

Hajdas I, Hendriks L, Fontana A, Monegato G. 2017. Evaluation of preparation methods in radiocarbon dating of old wood. Radiocarbon 59(3):727–737.

Hoper S, McCormac G, Hogg AG, Higham TF, Head MJ. 1998. Evaluation of wood pretreatments on oak and cedar. Radiocarbon 40(4):45–50.

Howarth JD, Fitzsimons SJ, Norris RJ, Langridge RM, Vandergoes MJ. 2016. A 2000 Yr rupture history for the Alpine Fault derived from Lake Ellery, South Island, New Zealand. Geological Society of America Bulletin 128(3–4):627–643.

Kitigawa H, Fukuzawa H, Nakamura T, Okamura M, Takemura K, Hayashida A, Yasuda Y. 1995. AMS ^{14}C dating of varved sediments from lake Suigetsu, central Japan and atmospheric ^{14}C change during the Late Pleistocene. Radiocarbon 37(2):371–378.

Knowles TDJ, Monaghan PS, Evershed RP. 2019. Radiocarbon sample preparation procedures and the first status report from the Bristol Radiocarbon AMS (BRAMS) Facility. Radiocarbon 61(5):1541–1550.

Kretschmer W, Anton G, Bergmann M, Finckh E, Kowalzik B, Klein M, Leigart M, Merz S, Morgenroth G, Piringer I. 1997. The Erlangen AMS facility: status report and research program. Nuclear Instruments and Methods in Physics Research B 123:93–96.

Maxwell JJ, Howarth JD, Vandergoes MJ, Jacobsen GE, Barber IG. 2016. The timing and importance of arboriculture and agroforestry in a temperate East Polynesia Society, the Moriori, Rekohu (Chatham Island). Quaternary Science Reviews 149:306–325.

McGlone MS, Bathgate J. 1983. Vegetation and climate history of the Longwood Range, South Island, New Zealand; 12,000 BP to present. New Zealand Journal of Botany 21:293–315.

McWethy DB, Whitlock C, Wimshurst JM, McGlone MS, Fromont M, Li X, Dieffenbacher-Krall AC. 2010. Rapid landscape transformation in South Island, New Zealand, following initial Polynesian settlement. Proceedings of the National Academy of Sciences 107(50):21343–21348.

Newnham RM, Vandergoes MJ, Hendy C, Lowe DJ, Preusser F. 2007. A terrestrial palynological record for the last two glacial cycles from southwestern New Zealand. Quaternary Science Reviews 26(3/4):517–535.

Oldfield F, Crooks PRJ, Harkness DD, Petterson G. 1997. AMS radiocarbon dating of organic fractions from varved lake sediments: An empirical test of reliability. Journal of Paleolimnology 18:87–91.

Olsson IU. 1976. The importance of the pretreatment of wood and charcoal samples. In: Berger R, editor. 9th International Conference on Radiocarbon Dating, La Jolla, CA.

Olsson IU. 1980. ^{14}C in extractives in wood. Radiocarbon 22(2):515–524.

Olsson IU. 1986. A study of errors in ^{14}C dates of peat and sediment. Radiocarbon 28(2A):429–435.

Santos GM, Southon J, Griffin S, Beaupre S, Druffel E. 2007. Ultra small-mass AMS ^{14}C sample preparation and analyses at KCCAMS/UCI Facility. Nuclear Instruments and Methods in Physics Research B 259(1):293–302.

Santos GM, Ormsby K. 2013. Behavioral variability in ABA chemical pretreatment close to the ^{14}C age limit. Radiocarbon 55(02):534–544.

Southon JR, Magana AL. 2010. A comparison of cellulose extraction and ABA pretreatment methods for AMS ^{14}C dating of ancient wood. Radiocarbon 52(3):1371–1379.

Stuiver M, Polach HA. 1977. Discussion: Reporting of ^{14}C data. Radiocarbon 19(3):355–363.

Taylor RE. 1987. Radiocarbon dating: An archaeological perspective. Orlando (FL): Academic Press, Inc.

Tornqvist TE, Jong D, Oosterbaan WA, Borg VD. 1992. Accurate dating of organic deposits by AMS ^{14}C measurement of macrofossils. Radiocarbon 34(3):566–577.

Turnbull JC, Zondervan A, Kaiser J, Norris M, Dahl J, Baisden WT, Lehman SJ. 2015. High-precision atmospheric $^{14}CO_2$ measurement at the Rafter Radiocarbon Laboratory. Radiocarbon 57(3):377–388.

Turner G, Howarth JD, de Gelder G, Fitzsimons SJ. 2015. A new high-resolution record of Holocene geomagnetic secular variation from New Zealand. Earth and Planetary Science Letters 430:296–307.

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press

Vandergoes MJ, Fitzsimons SJ, Newnham RM. 1997. Late Glacial to Holocene vegetation and climate change in the eastern Takitimu Mountains, western Southland, New Zealand. Journal of the Royal Society of New Zealand 27(1): 53–66.

Vandergoes MJ, Newnham RM, Preusser F, Hendy CH, Lowell TV, Fitzsimons SJ, Hogg AG, Kasper HU, Schlüchter C. 2005. Regional insolation forcing of late Quaternary climate change in the Southern Hemisphere. Nature 436(7048):242–245.

Vandergoes MJ, Dieffenbacher-Krall AC, Newnham RM, Denton GH, Blaauw M. 2008. Cooling and changing seasonality in the Southern Alps, New Zealand during the Antarctic Cold Reversal. Quaternary Science Reviews 27(5):589–601.

Vandergoes MJ, Hogg AG, Lowe DJ, Newnham RM, Denton GH, Southon J, Barrell DJA, Wilson CJN, McGlone MS, Allan ASR et al. 2013a. A revised age for the Kawakawa/ Oruanui tephra, a key marker for the Last Glacial Maximum in New Zealand. Quaternary Science Reviews 74:195–201.

Vandergoes MJ, Newnham RM, Denton GH, Blaauw M, Barrell DJA. 2013b. The Anatomy of Last Glacial Maximum climate variations in South Westland, New Zealand, derived from pollen records. Quaternary Science Reviews 74:215–229.

Vandergoes MJ, Howarth JD, Dunbar GB, Turnbull JC, Roop HA, Levy RH, Li X, Prior C, Norris MW, Keller ED et al. 2018. Integrating chronological uncertainties for annually laminated lake sediments using layer counting, independent chronologies and Bayesian age modelling (Lake Ohau, South Island, New Zealand). Quaternary Science Reviews 188:104–120.

Zondervan A, Hauser T, Kaiser J, Kitchen R, Turnbull JC, West JG. 2015. XCAMS: The compact ^{14}C accelerator mass spectrometer extended for ^{10}Be and ^{26}Al at GNS Science, New Zealand. Nuclear Instruments and Methods in Physics Research B 361:25–33.

https://doi.org/10.1017/RDC.2020.8 Published online by Cambridge University Press