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Test of AMS ^{14}C dating of pollen concentrates using tephrochronology

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ABSTRACT: Previous attempts to radiocarbon date sediments >10 kyr from the high rainfall region of Westland, New Zealand, a critical location for investigation of interhemispheric patterns of climate change, have been problematic. This study, building on recent work by Vandergoes and Prior (2003), shows that AMS ^{14}C dating of pollen concentrates has potential to provide more reliable ages than other sediment constituents, including plant macrofossils. The method was applied to sediments from three sites containing the 22.6k ^{14}C yr Kawakawa Tephra, which provided an independent test of the ^{14}C ages. Although some minor laboratory contamination was detected in tests on background standards, the modelled relationship between sample mass and measured ^{14}C content permitted an appropriate correction to be determined. Improved pollen concentrations derived by density separation between 1.4 and 1.2 specific gravity and sieving in the range 10–50 μm provided either older ages than other fractions of the same sample or, where *in situ* contamination was not evident, equivalent ages. Differences in degree of *in situ* contamination between depositional environments indicated that, in Westland, lake sites may be less susceptible to contamination by younger carbon than peat sites, where this process may be facilitated by root penetration into underlying sediments.
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KEYWORDS: AMS radiocarbon dating; pollen concentrates; Kawakawa Tephra; contamination; Westland, New Zealand.

Introduction

A simple technique for preparing near-pure pollen concentrations for AMS radiocarbon dating has produced encouraging results (Vandergoes and Prior, 2003). The method, involving heavy liquid separation (HLS) of various density fractions from bulk organic samples (Prior, 1998), builds on earlier work that demonstrated the advantages of using pollen concentrates as dating material (e.g. Brown *et al.*, 1989, 1992; Richardson and Hall, 1994). Using sediments from the high rainfall region of Westland, New Zealand, demonstrably prone to contamination by younger carbon (Hammond *et al.*, 1991), Vandergoes and Prior (2003) showed that sediment fractions containing high concentrations of pollen produced consistently older age estimates than bulk sediment, organic residue fractions, and plant macrofossils. They argued that these consistently older ages were likely to be closer to the true age of the sample (see also Vandergoes *et al.*, 2005). In outlining future work, Vandergoes and Prior recognised the need to evaluate AMS dating of pollen concentrates against independent time markers of established age. Using the ca. 22.6k ^{14}C yr Kawakawa Tephra as a stratigraphic benchmark and a modification of the pollen extraction method, this paper presents a further rigorous test of the method in the high rainfall region of Westland, a critical area for investigation of Quaternary climate change.

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Significance and rationale of this investigation

Westland occurs adjacent to the Southern Alps of New Zealand, one of only two regions at mid-latitudes in the Southern Hemisphere that has been extensively glaciated during the Quaternary (Fig. 1). As a result, glacial deposits in Westland provide a complex record of late Quaternary ice (Suggate and Almond, 2005), which has been linked to global

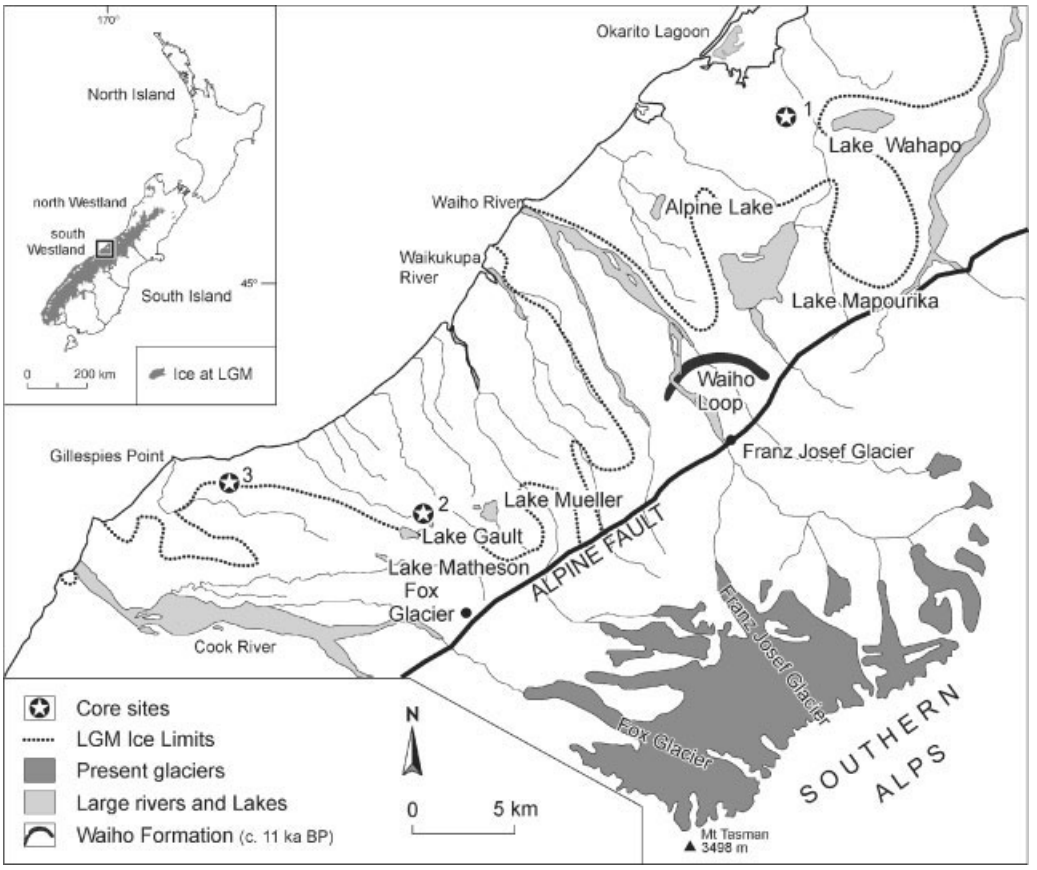

Figure 1 Geologic and geomorphic map of the study area showing location of sites, present and historic glacier extents and late Pleistocene glacial formations. 1, Okarito Pakihi; 2, Skiffington Swamp; 3, Galway Tarn (modified from Warren (1967))

climate change (Denton and Hendy, 1994; Lowell *et al.*, 1995; Vandergoes *et al.*, 2005; Newnham *et al.*, in press). Shrunken remnants of these glaciers survive today but they no longer extend into the Westland piedmont. Recent discussion of inter-hemispheric patterns of glaciation highlight the importance of this region to understanding global climate change mechanisms but, equally, stress the need for accurate dating of major periods of ice movement (Denton *et al.*, 1999, 2005; Broecker, 2003; Oerlemans, 2005).

Closely associated with the glacial deposits and landforms in Westland are depositional basins in which organic sediments began to accumulate soon after ice retreat (Moar and Suggate, 1996; Vandergoes and Fitzsimons, 2003; Vandergoes *et al.*, 2005; Newnham *et al.*, in press). These sediments therefore provide an opportunity to use radiocarbon dating to constrain accurately the timing of major pulses of ice retreat, wherever this occurred during the past ca. 50 kyr. As outlined below, however, previous efforts to apply this methodology have proved problematic (e.g. Moar and Suggate, 1996).

Westland precipitation is considerably higher than for any other region in New Zealand. From 1971 to 2000 mean annual rainfall recorded at Hokitika (Westland), at sea level, was 2875 mm; but this rises markedly with elevation (New Zealand National Climate Centre, 2006). For the same period mean annual rainfall at Milford Sound, the nearest climate station to the south of the study area, was 6749 mm. Precipitation is distributed fairly evenly throughout the year, for example at Hokitika both highest (278 mm; December) and lowest (172 mm; February) rainfall months occur in the summer.

Methodology

Radiocarbon dating in Westland

Previous work has demonstrated that serious errors may arise when peat and lake sediments are dated from the high rainfall region of Westland, New Zealand (Grant-Taylor and Rafter, 1971; Hammond *et al.*, 1991; Moar and Suggate, 1996). Following experimentation with different acid/alkali pretreatments and by dating soluble (fulvic and humic acids) and insoluble fractions from bulk peat and sediment samples, Hammond *et al.* (1991) concluded that samples from loess, silt/sands, or peat older than 10k ^{14}C yr typically became significantly contaminated by younger carbon particularly from humic and fulvic acids. On the other hand, Vandergoes and Prior (2003) showed from preliminary tests that AMS dating of pollen concentrates, separated from other organic constituents of a sample, has the potential to overcome this problem. These preliminary experimental results support the conceptual assertion that the pollen wall should be mostly impenetrable to humic and fulvic acids and indeed to other sources of contamination. In order to evaluate this assertion, it is essential that the accuracy and reproducibility of this method be tested rigorously.

In this investigation, experimental rigour is afforded by the use of material from an area in Westland where sediments are prone to contamination by younger carbon and of an age (Last Glacial Maximum, LGM) that makes it highly vulnerable to these effects. Accuracy is tested by sampling around a tephra layer of 'established' age, which additionally provides for

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reproducibility of results as it occurs at three sites to be tested. Our sampling strategy was to date separate pollen and organic residue fractions of sediment taken from several horizons above and below the tephra layer at each site. At two of the sites, plant macrofossils associated with tephra fall provided an additional dating material for comparison.

Study sites

Sediment cores were collected at three peat and lake sites in south Westland (Fig. 1), in January 1999 and January 2001 using a Russian D-section and modified square-rod Livingston corer. These sites, Skiffington Swamp (43° 25′ S, 169° 59′ 30″ E, 340 m a.s.l.), Okarito Pakihi (43° 14′ 30″ S, 170° 13′ E, 70 m a.s.l.) and Galway Tarn (43° 24′ 30″ S, 169° 52′ 24″ E, 130 m a.s.l.), were selected because they comprise sedimentary basins formed within moraine sequences believed to predate the LGM advances in the region (Fig. 1). All three contain Kawakawa Tephra. The catchments consist of non-carbonate lithologies and there are no indications of 'hardwater effect' in any previous ^{14}C dating reported for this region. Lateglacial to Holocene pollen records from two of these sites, Skiffington Swamp and Okarito Pakihi, have been reported (Vandergoes and Fitzsimons, 2003) and longer pollen records from all three sites have been produced (Vandergoes *et al.*, 2005; unpublished data; Newnham *et al.*, in press).

At Okarito Pakihi and Skiffington Swamp, Holocene peat overlies thick silts of variable organic content. Palynology of the sediments indicate that these basins persisted as lakes probably from their inception until the early Holocene when they became terrestrialised with extensive development of bog vegetation. Today these sites are dominated by the wire rush *Empodisma minus*, typically in association with *Gleichenia* ferns, the sedges *Baumea* and *Gahnia*, and various clubmosses (*Lycopodium*). *Leptospermum scoparium* shrubs are common at the drier margins and appear to be encroaching onto the bogs. Galway Tarn, by contrast, has maintained its lake form from inception to present in the centre of the basin, although terrestrialisation by a series of 'floating mats' of bog vegetation is occurring at the margins. These floating mats provided an effective platform for drilling into the underlying sediments, which confirmed the persistence of lacustrine sedimentation at the core site through to near present.

Kawakawa Tephra

Kawakawa Tephra represents distal fine ash deposited during the later phases of the ca. 22.6k ^{14}C yr Oruanui eruption from Taupo caldera volcano in the central North Island of New Zealand (Wilson, 2001). With the exception of the 74 kyr Toba eruption, the Oruanui event produced more deposits than any other eruption worldwide during the past 250 000 yr (Wilson, 2001). These deposits provide an unequivocal chronostratigraphic marker for the LGM which can be applied considerable distances from the source (Campbell, 1986; Pillans *et al.*, 1993). It is the most widespread Late Quaternary tephra layer in the New Zealand region and the only Quaternary tephra layer previously recorded in Westland (Robertson and Mew, 1982; Mew *et al.*, 1986, 1988; Almond, 1996; Almond *et al.*, 2001). No other macroscopic tephra layer has been observed at the study sites. Kawakawa Tephra is represented by a visible, discrete 1–2 cm thick layer in the Skiffington Swamp and Galway Tarn cores and by a high concentration of glass shards in the Okarito Pakihi core (Vandergoes *et al.*, 2005). We analysed glass shards from each of these sites using an electron microprobe (Table 1). The major element compositions of the glass shards are identical to each other and homogeneous (i.e. with low standard deviations), indicating that the same, single

Table 1 Electron microprobe analyses[a] of glass from Kawakawa Tephra[b] at Okarito Pakihi, Galway and Skiffington compared with glass from type localities and elsewhere

	Kawakawa Tephra						
Analysis no.[c]	Okarito Pakihi	Galway	Skiffington	1	2	3	4
SiO_2	78.04 (0.30)	77.75 (0.36)	77.88 (0.38)	78.55 (0.27)	78.69 (0.46)	78.74 (0.42)	77.89 (0.48)
Al_2O_3	12.65 (0.15)	12.59 (0.16)	12.55 (0.19)	12.03 (0.13)	12.25 (0.23)	12.53 (0.20)	12.63 (0.67)
TiO_2	0.14 (0.03)	0.13 (0.03)	0.15 (0.03)	0.12 (0.03)	0.12 (0.03)	0.10 (0.03)	0.13 (0.05)
FeO[d]	1.13 (0.10)	1.13 (0.13)	1.09 (0.13)	1.17 (0.05)	1.17 (0.10)	1.16 (0.12)	1.19 (0.11)
MnO	0.06 (0.06)	0.08 (0.05)	0.09 (0.05)	nd[e]	nd	nd	0.06 (0.09)
MgO	0.13 (0.02)	0.13 (0.03)	0.12 (0.03)	0.12 (0.02)	0.12 (0.02)	0.13 (0.02)	0.15 (0.03)
CaO	1.02 (0.07)	1.04 (0.06)	1.03 (0.07)	1.09 (0.06)	1.05 (0.09)	1.08 (0.10)	1.23 (0.10)
Na_2O	3.34 (0.41)	3.79 (0.24)	3.75 (0.28)	3.62 (0.11)	3.42 (0.29)	3.76 (0.11)	3.51 (0.22)
K_2O	3.27 (0.34)	3.06 (0.11)	3.13 (0.16)	3.10 (0.13)	3.05 (0.20)	2.49 (0.50)	3.06 (0.14)
Cl	0.20 (0.05)	0.23 (0.16)	0.18 (0.03)	0.21 (0.02)	0.18 (0.04)	nd	0.16 (0.05)
Water[f]	5.05 (1.42)	4.40 (1.62)	4.16 (1.19)	5.70 (0.74)	5.65 (1.96)	nd	5.92 (1.64)
n	20	20	20	24	275	32	10

[a]Means and standard deviations (in parentheses) of *n* analyses normalised to 100%-loss-free (wt%). Okarito Pakihi, Galway, and Skiffington glass analysed by wavelength-dispersive Jeol JXA-733 Superprobe at Analytical Facility, Victoria University of Wellington, using defocused beam diameter 10–20 µm, current 8 nA, and accelerating voltage 15 kV (Froggatt, 1983; Lowe *et al.*, 1999). Analyst: J. L. Horrocks.

[b]Eruptives have various names including Kawakawa Tephra Formation (comprising Oruanui Ignimbrite and Aokautere Ash members: Froggatt and Lowe, 1990), which we adopt here, and Oruanui (phases 1–10 comprising pyroclastic density current (ignimbrite) and fall deposits: Wilson, 2001). Distal Oruanui/Kawakawa deposits in northern South Island and on Chatham Is. (c. 800 km east of South Island) were mapped as (fall) phases 9 and 10 of the Oruanui eruption by Wilson (2001).

[c]Sources of analyses 1–4: 1, type locality for Aokautere Ash, Aokautere (Pillans *et al.*, 1993); 2, type locality for Kawakawa Tephra, Whangamata Rd, Taupo (Carter *et al.*, 1995); 3, Graham Terrace, Grey River, South Is. (Mew *et al.*, 1986); 4, Lake Poukawa, Hawkes Bay (Shane *et al.*, 2002).

[d]Total Fe as FeO.

[e]Not determined or not available.

[f]Difference between original analytical total and 100.

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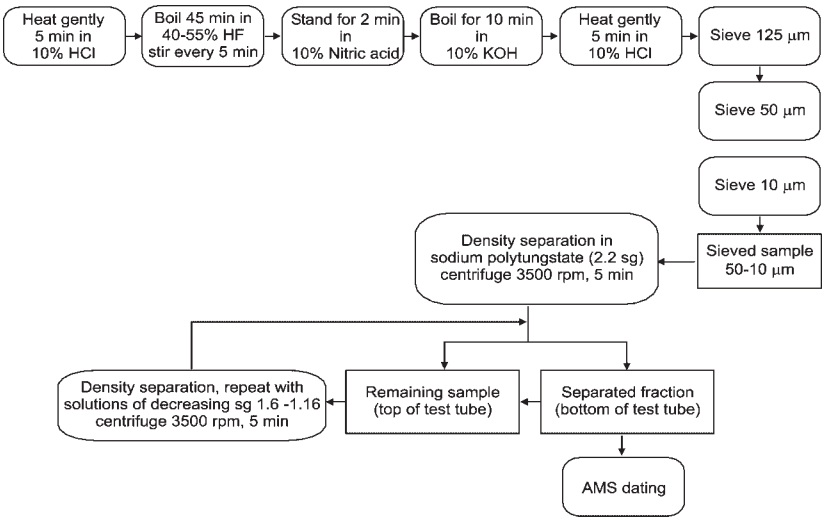

Figure 2 Summary flowchart of laboratory procedures used in preparation of pollen samples for AMS dating

layer of tephra is present at each site. The analyses closely match those for Kawakawa eruptives at type localities in North Island (Table 1, analyses 1–2), confirming that the tephra is a correlative of Kawakawa Tephra. Consequently, we are very confident that the same tephra isochron is present at each of our three study sites. These are the first glass-shard analyses to be obtained for Kawakawa Tephra in south Westland, the only previous analyses for South Island being obtained from Graham Terrace in north Westland (Table 1) and from several sites in eastern South Island and Marlborough (Eden *et al.*, 1992).

The best estimate for the age of the Kawakawa Tephra, as recommended by Froggatt and Lowe (1990), is an activity-weighted, pooled mean age of $22\,590 \pm 230$ ^{14}C yr BP ($n = 4$) from four determinations on small carbonised wood fragments embedded within the non-welded Oruanui ignimbrite emplaced by the Kawakawa (Oruanui) eruption (Wilson *et al.*, 1988). For several reasons outlined by Wilson *et al.* (1988), this age is considered to be superior to a pooled mean age of $20\,220 \pm 115$ ^{14}C yr BP ($n = 12$) based on ages obtained mainly on slices of peat: (1) the samples, from four separate sites, were of small carbonised branch fragments (up to 2 cm diameter) and so have negligible inbuilt age; (2) all four sites are remote from any geothermal contamination that might arise from old CO_2; (3) the fragments had fluidisation degassing 'pipes' rising from them and had stained the surrounding ignimbrite, showing that the branches were killed and pyrolysed by the enclosing flow and did not represent old, dead material; (4) sample preparation at the Godwin Radiocarbon Laboratory (Cambridge) included vigorous acid–base treatment to remove any possible contaminant; and (5) all four ages obtained were identical and so pooled tightly to provide a mean age. Clearly, the carbonised wood fragments represent material intimately associated with the eruption whereas the other ages are from material less closely associated with the eruption and of wider age range (see appendix 1 in Froggatt and Lowe (1990)). We therefore adopt here the age of Wilson *et al.* (1988), i.e. $22\,590 \pm 230$ ^{14}C yr BP, for Kawakawa Tephra.

Sampling strategy

A total of eight 1 cm thick bulk sediment slices were taken directly above and below the Kawakawa Tephra layer from each of the Skiffington Swamp and Okarito Pakihi cores and four 1 cm thick slices from the Galway Tarn core. For each sediment slice, pollen concentrates and organic material were separated into density fractions using the method outlined below (Fig. 2). At Galway Tarn and Skiffington Swamp, a layer of plant macrophyte stems is directly associated with tephra fall. Stem samples from these layers were hand-picked to provide three plant macrofossil samples (two at Galway Tarn). Prior to ^{14}C analysis, the macrofossils were subjected to an acid wash pretreatment (2M HCl at 80 °C); a more rigorous acid–alkali–acid treatment was not possible owing to the limited sample material available.

Method for concentrating pollen for AMS dating

The method used for the extraction of pollen from bulk samples is developed from techniques used by Brown *et al.* (1989) Regnéll (1992), Regnéll and Everitt (1996) and Prior (1998) (Fig. 2). Samples were processed 'wet', directly from the core, to avoid the possibility of contamination.

Chemical treatment and separation

Extraneous matter was removed according to standard methods (Faegri and Iversen, 1989), including removal of $CaCO_3$ by using HCl, removal of humic acids by using KOH and removal of silica by using HF. Dilute nitric acid was used to aid in the removal of organic residue. Sample separation by sieving (mesh size 125 and 6 μm) was undertaken to separate organic and inorganic matter both larger and smaller than most pollen. This method was refined by additional sieving steps (Fig. 2). Sieving at 50 μm was undertaken to separate more of the larger material from the samples while the mesh size of 6 μm was increased to 10 μm to eliminate more of the fine material.

Sieving was complemented by using a sodium polytungstate (SPT) heavy liquid separation at a specific gravity (sg) of 2.2, to separate most of the inorganic material from the lighter organic matter and pollen fraction. The subsequent procedure for pollen separation prior to AMS dating is summarised as follows.

The sample <50 μm was mixed thoroughly with 10 ml of SPT at a specific gravity of 1.62. The sample was centrifuged

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repeatedly for five minutes at 3500 rpm until a clear band of sample material was present at the top of the tube and the SPT was clear between the two separated samples:

1. The sample remaining at the top of the centrifuge tube was decanted then rinsed in distilled water and prepared for microscopic analysis (step 3). The remaining fraction from the bottom of the centrifuge tube was then washed with distilled water to remove any residual SPT.
2. The separation process was repeated sequentially with SPT solutions of specific gravity decreasing by 0.1 s.g. increments until all sample material remaining at the bottom of the test tube was separated into fractions or when density dropped below 1.10 s.g. At this specific gravity any material left floating is not likely to be pollen.
3. Small amounts of each sample fraction were mounted for microscopic analysis to determine which sample contained the most pollen for dating. Pollen percentages for each sample were determined by counting along slide traverses until a minimum of 100 objects were identified. The ratio of pollen versus other (organic and inorganic) objects formed the basis for percentage calculations. The samples were vacuum dried prior to dating.

^{14}C measurement

All plant macrofossil, organic residue, pollen concentrates and amalgamated samples were ^{14}C dated by AMS. For all samples, extraction of pollen concentrates was undertaken at the University of Plymouth. At the NERC Radiocarbon Laboratory (RCL) at East Kilbride, samples were combusted to CO_2 by heating with CuO in sealed quartz tubes and converted to graphite by Fe/Zn reduction (Slota *et al.*, 1987). ^{14}C analysis by AMS was undertaken at either the Center for AMS, University of California (sample code CAMS-) or at the University of Arizona NSF AMS facility (sample code AA-).

In addition to these core samples, we ran a series of standards to test the pollen-processing procedure. These consisted of background standards of kauri (*Agathis australis*) used for the Fourth International Radiocarbon Intercomparison (FIRI; Scott, 2003) and sediment samples from older horizons of the Okarito Pakihi cores, known to be >50k cal. yr (Vandergoes *et al.*, 2005).

Results

In keeping with international practice, all results are reported as conventional radiocarbon years BP (relative to AD 1950) and percentage modern ^{14}C, both expressed at the $\pm 1\sigma$ level for overall analytical confidence (all ^{14}C results, including the standards, having been corrected for routine processing background). Calibration of ^{14}C ages was not attempted as the tephra age and hence expected sample ages lie beyond the upper limit of the current calibration scheme (INTCAL04).

Standards

To test whether the pollen extraction procedure resulted in any contamination by carbon of a different age from that of the sample, we used this procedure to process a number of standard samples routinely used by NERC RCL for this purpose. Three samples were material older or close to the limit of radiocarbon dating: two samples were of (ancient) kauri (*Agathis australis*) wood (0.24% modern; Scott, 2003) and the other bituminous coal. Two samples of a standard of known age, also wood (IAEA-C5; 23.05 ± 0.02% modern; Rozanski *et al.*, 1992), were also processed. The results are shown in Table 2. The coal sample contained no more ^{14}C than the usual laboratory background and one IAEA-C5 sample (CAMS-82820) dated to within 1σ of the consensus value. The two ancient kauri wood samples gave finite age results, however, suggesting that these samples had acquired some contamination at some stage in the processing procedure (e.g. Hogg, 2004).

In addition to these standards, we processed sediment samples from one of the study sites, Okarito Pakihi, that were >50 kyr (Table 2). These samples also contained significantly more ^{14}C than the routine background level and are therefore younger than expected. Whilst this contamination may have occurred *in situ*, it may also have resulted from the processing procedure.

Table 2 Details of the first set of background (bituminous coal, pollen concentrates and kauri wood) and known age (IAEA-C5 wood) ^{14}C standards processed using the pollen concentration procedure. The entire sample processed through the pollen concentration procedure was used for ^{14}C dating except for samples marked #, for which sub-samples were dated. Owing to small sample size, the δ^{13}C value for samples marked * was estimated. Horizontal line separates first set of background and standards processed at the Center for AMS, University of California (sample code CAMS-) from the second set processed at the University of Arizona NSF AMS facility (sample code AA-)

Publication code	Material	Mass C recovered (mg)	Conventional radiocarbon age (BP $\pm 1\sigma$)	^{14}C enrichment (%modern $\pm 1\sigma$)	$\delta^{13}C_{PDB} \pm 0.1$‰
CAMS-82819	Bituminous coal#	—	46 630 ± 320	0.30 ± 0.01	−23.2
CAMS-82820	IAEA-C5 wood#	—	11 745 ± 45	23.17 ± 0.13	−26.3
CAMS-82822	Pollen concentrate (>50 ka)	2.09	29 560 ± 310	2.52 ± 0.01	−29.4
CAMS-82823	Pollen concentrate (>50 ka)	2.25	33 790 ± 530	1.49 ± 0.01	−29.2
CAMS-86749	Kauri wood	1.46	28 100 ± 120	3.02 ± 0.04	−23.8
CAMS-86750	Kauri wood	2.55	34 700 ± 100	1.33 ± 0.02	−23.8
CAMS-86751	IAEA-C5 wood	1.42	11 170 ± 45	24.90 ± 0.14	−25.3
AA-55242	Kauri wood	1.12	29 020 ± 440	2.70 ± 0.15	−23.5*
AA-55243	Kauri wood	1.77	30 650 ± 420	2.20 ± 0.12	−23.5
AA-55244	Pollen concentrate (>50 ka)	3.16	39 900 ± 1200	0.70 ± 0.11	−29.3
AA-55245	Pollen concentrate (>50 ka)	0.59	28 310 ± 330	2.95 ± 0.12	−29.2*
AA-55246	Pollen concentrate (>50 ka)	3.70	38 200 ± 1300	0.86 ± 0.14	−29.1

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In light of these results, we reviewed the processing procedure and identified one step where we considered contamination could be introduced. Following washing with acids, the concentrate is boiled for 10 minutes in 10% KOH and then sieved. As KOH absorbs carbon (CO_2) from the atmosphere, small residues of the KOH left with the pollen concentrates after this step may have been a source of contamination. Any such contamination is readily removed by introducing an additional step to the procedure, involving washing the sample again in acid, following KOH treatment.

To test this hypothesis, we processed a further five standards samples using this additional step: two further kauri wood samples and three additional sediment samples from the pre-50 kyr part of the Okarito Pakihi sequence (Table 2). Both kauri wood standards and the sediment samples had radiocarbon concentrations considerably above the background level, similar to the results from wood and sediment samples processed using the old method. These results suggest that the change in method has not removed the source of contamination.

Previous investigations using AMS dating of pollen concentrates have not reported a contamination problem of this nature (Brown *et al.*, 1989, 1992; Richardson and Hall, 1994; Vandergoes and Prior, 2003) although Kilian *et al.* (2002) suggest pollen concentrates may be susceptible to a reservoir effect, as yet not fully explained. The modification to the Vandergoes and Prior (2003) procedure that we report here is unlikely to be a source of contamination. It seems likely that an (as yet) unidentified source of younger C within the laboratory at University of Plymouth has contributed a small amount of contamination in both old and new pollen extraction procedures, making all sample ages younger than they should be.

Correction for laboratory contamination

Where it can be shown that systematic contamination within the laboratory has occurred, it is possible to correct for this using a mass balance approach:

$$M_t A_t = M_s A_s + M_c A_c \quad (1)$$

Where M represents the mass of carbon (in mg) and A the radiocarbon concentration (in % modern) of the total amount of recovered sample (t), uncontaminated sample (s) and contaminant (c).

Since $M_s = M_t - M_c$, substitution in equation (1) gives:

$$A_t = A_s + M_c(A_c - A_s)/M_t \quad (2)$$

which for a fixed mass of contamination takes the form of a straight line ($y = a + bx$) when A_t is plotted against the reciprocal of M_t, and A_c and A_s are constant. Thus the intercept (a) represents the radiocarbon concentration of the uncontaminated sample (A_s), and the gradient is expressed by the equation:

$$b = M_c(A_c - A_s) \quad (3)$$

Figure 3 plots the measured percentage modern values (A_t) against the reciprocal of sample size ($1/M_t$) for the background standards that were processed using the pollen concentration procedure. One background standard (CAMS-82819) was of much greater size than the others and had an acceptable percentage modern value, and has therefore not been plotted. A further background standard (AA-55245) was treated as an outlier and excluded, which greatly improved the r^2 value of the correlation from 0.498 ($p < 0.05$) to 0.732 ($p < 0.01$).

The strong correlation between percentage modern of the total recovered carbon and the reciprocal of sample size for the background standards in Fig. 3 provides support for the laboratory contamination of the samples being a constant mass and ^{14}C concentration. The regression derived from Fig. 3 ($y = 3.67624x - 0.00425$) can therefore be used to calculate the mass of the contaminant (M_c) by rearranging equation (3). Assuming that the contaminant had a ^{14}C activity equivalent to the contemporary atmosphere when the standards and samples were processed (i.e. 108% mod), and that the uncontaminated sample ^{14}C activity is 0 (which is supported by the regression in Fig. 3 passing almost exactly through the origin):

$$M_c = b/A_c \quad (4)$$

Using the above approach, the mass of contaminant has been calculated to be 0.0340 ± 0.0084 mg C (the error term being derived from the standard error of b, the gradient), which is equivalent to an average of ca. 2–3% of the total recovered carbon in the pollen concentrate and organic residue samples.

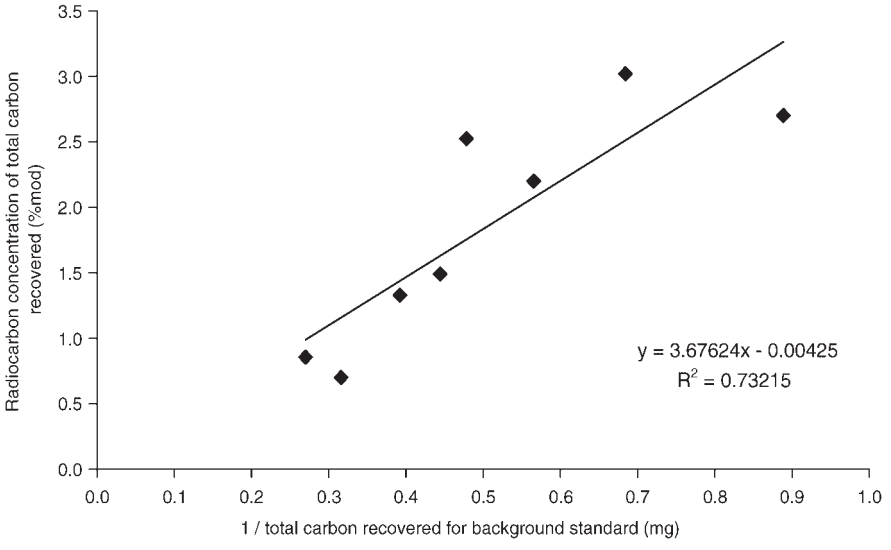

Figure 3 Plot of percentage modern ^{14}C concentration against reciprocal of total C recovered for background standards. The regression model derived from this relationship was used to correct for systematic contamination in subsequent results reported in this study

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Table 3 Details of radiocarbon results for pollen concentrate, organic residue and plant macrofossil samples. Owing to small sample size, the δ^{13}C values for samples marked * were estimated. R1 = organic residue (>50 μm and <125 μm), R2 = organic residue (>125 μm), P1 = Pollen concentrate (s.g. 1.3), P2 = pollen concentrate (s.g. < 1.3), P3 = pollen concentrate (s.g. 1.4), P4 = pollen concentrate (s.g. < 1.4). M1 = plant macrofossil (*Sphagnum* leaves and stems), M2 = unidentified plant macrofossils. Pollen percentages marked ♣ indicate the mean percentage of combined samples for the depth range. #The error associated with the corrected ^{14}C results was not equal on either side of the mean age, and only the maximum value is given

Publication code	Identifier	Material	Depth (cm)	^{14}C enrichment (%modern ± 1 σ)	^{14}C yr BP ± 1σ	$\delta^{13}C_{PDB}$ ± 0.1‰	Pollen %	Carbon recovered (mg)	Corrected ^{14}C yr BP ± 1σ#	Corrected ^{14}C yr BP 95% confidence intervals
Skiffington Swamp										
AA-55222	908 (1a)	R2	202–203	23.50 ± 0.25	11 634 ± 87	−28.7	—	1.39	12 391 ± 205	12 011–12 801
AA-55223	908 (1b, 2b, 3b)	R1	202–205	30.90 ± 0.40	9 440 ± 100	−27.9	—	1.58	9 888 ± 119	9 663–10 125
AA-55224	908 (1c, 2c, 3c)	P1	202–205	18.22 ± 0.32	13 680 ± 140	−27.6*	87.3♣	1.07	15 094 ± 408	14 366–15 922
AA-55225	908 (1d, 2d, 3d)	P2	202–205	11.90 ± 0.23	17 100 ± 160	−27.5	93.3♣	2.48	18 057 ± 259	17 576–18 576
AA-55226	908 (2a)	R2	203–204	30.04 ± 0.29	9 659 ± 79	−27.5	—	1.45	10 180 ± 137	9 921–10 453
AA-55227	908 (3a)	R2	204–205	26.74 ± 0.28	10 596 ± 86	−27.7	—	1.55	11 162 ± 150	10 880–11 461
AA-55228	908 (4a)	R2	205–206	23.79 ± 0.34	11 530 ± 120	−27.3	—	2.14	12 007 ± 124	11 773–12 252
AA-55229	908 (4b)	R1	205–206	34.55 ± 0.34	8536 ± 80	−27.0*	—	0.43	10 141 ± 501	9 292–11 177
AA-55230	908 (5a)	R2	207–208	27.80 ± 0.32	10 283 ± 92	−26.5	—	1.21	10 987 ± 190	10 633–11 367
AA-55231	908 (6a)	R2	208–209	34.47 ± 0.39	8 556 ± 92	−27.6	—	1.71	8 911 ± 92	8 735–9 094
AA-55232	908 (6b, 7b, 8b)	R1	208–211	34.33 ± 0.35	8 588 ± 81	−27.3	—	1.34	9 051 ± 122	8 821–9 294
AA-55233	908 (6c, 7c, 8c)	P1	208–211	26.53 ± 0.27	10 659 ± 82	−27.3*	79.3♣	0.64	12 172 ± 452	11 383–13 098
AA-55234	908 (6d, 7d, 8d)	P2	208–211	15.89 ± 0.18	14 774 ± 89	−27.1	93.3♣	1.39	16 037 ± 355	15 394–16 753
AA-55235	908 (7a)	R2	209–210	34.46 ± 0.24	8 559 ± 56	−27.3	—	1.29	9 038 ± 127	8 799–9 292
AA-55236	908 (8a)	R2	210–211	31.76 ± 0.23	9 213 ± 58	−27.3*	—	1.06	9 883 ± 182	9 547–10 247
AA-55237	908 (9)	M2	206–207	31.97 ± 0.23	9 161 ± 58	−26.6	—	—	—	—
Okarito Pakihi										
AA-55239	OK (5–8a)	P3	376–380	15.45 ± 0.18	15 004 ± 93	−29.3*	89♣	0.62	18 467 ± 1239	16 555–21 153
AA-55240	OK (5b, 7b, 8b)	P4	376–380	8.98 ± 0.16	19 360 ± 150	−29.3*	92.6♣	0.91	23 851 ± 1730	21 324–27 737
AA-55241	OK (6b)	P4	378–379	10.44 ± 0.17	18 150 ± 130	−29.3*	95	0.37	>27 445	23 087–Background
AA-55238	OK (1–4a, 1–4b)	P1 + P2	380–394	11.22 ± 0.16	17 570 ± 110	−29.3*	82.1♣	0.68	22 437 ± 1987	19 656–27 025
Galway Tarn										
AA-50509	0111 (3c)	R1	699–700	8.53 ± 0.17	19 780 ± 160	−27.9	—	2.29	21 326 ± 443	20 531–22 222
CAMS-86756	0111 (3a)	P4	699–700	8.16 ± 0.08	20 130 ± 80	−27.4	89	4.44	20 929 ± 212	20 531–21 350
CAMS-86757	0111 (3b)	R2	699–700	11.13 ± 0.08	17 640 ± 70	−27.2	—	1.09	20 289 ± 851	18 875–22 067
CAMS-86758	0111 (4a)	P4	700–701	8.60 ± 0.08	19 710 ± 80	−27.3	90	2.61	21 037 ± 371	20 362–21 784
CAMS-86759	0111 (4b)	R2	700–701	10.18 ± 0.08	18 350 ± 70	−27.3*	—	0.72	23 524 ± 2 171	20 549–28 622
AA-50510	0111 (4c + 4d)	R1 + R2	700–701	11.60 ± 0.17	17 300 ± 120	−28.0*	—	0.56	23 556 ± 3 034	19 837–31 470
CAMS-86760	0111 (7a)	P3	702.5–703	8.22 ± 0.09	20 070 ± 90	−27.4	90	2.60	21 480 ± 396	20 762–22 277
CAMS-86761	0111 (7b)	R2	702.5–703	8.38 ± 0.08	19 910 ± 80	−27.4	—	1.37	22 811 ± 940	21 262–24 786
CAMS-86762	0111 (8a)	P2	703–704	7.86 ± 0.08	20 430 ± 90	−27.5	81	2.44	22 030 ± 457	21 210–22 955
CAMS-86763	0111 (8b)	P2	703–704	7.95 ± 0.08	20 340 ± 80	−27.5	70	4.07	21 241 ± 241	20 790–21 722
CAMS-86764	0111 (8c)	R2	703–704	8.11 ± 0.08	20 180 ± 90	−28.8	—	1.74	22 452 ± 693	21 260–23 881
AA-50511	0111 (8e)	R1	703–704	8.74 ± 0.17	19 580 ± 160	−28.1*	—	0.62	28 345 ± 5 968	22 834–Background
AA-50512	0111 (8f)	R1	703–704	8.04 ± 0.15	20 250 ± 150	−28.1	—	1.39	23 247 ± 983	21 638–25 316
AA-47230	0111 (A)	M1	702–702.5	8.91 ± 0.14	19 420 ± 130	−27.6	—	—	—	
AA-47231	0111 (B)	M1	702–702.5	8.83 ± 0.14	19 500 ± 130	−27.8	—	—	—	—

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Table 4 Details of sampling strategy and sample amalgamation

(a) Skiffington Swamp

Depth (cm)	R2	R1	P1	P2	M
202–203	AA-55222				
203–204	AA-55226	AA-55223	AA-55224	AA-55225	
204–205	AA-55227				
205–206	AA-55228	AA-55231			
TEPHRA LAYER					AA-55237
207–208	AA-55230				
208–209	AA-55231				
209–210	AA-55235	AA-55232	AA-55233	AA-55234	
210–211	AA-55236				

(b) Okarito Pakihi

Depth (cm)	P1	P2	P3	P4	
376–377					
377–378					AA-55240
378–379			AA-55239	AA-55241	
379–380					
380–387					
387–388					
388–389	AA-55238				
389–394					

TEPHRA LAYER

(c) Galway Tarn

Depth (cm)	R2	R1	R1	P2	P3	P4	M
699–700	CAMS-86757	AA-50509				CAMS-86756	
700–701	CAMS-86759	AA-50510				CAMS-86758	
TEPHRA LAYER							AA-47230 AA-47231
702.5–703	CAMS-86761				CAMS-86760		
703–704	CAMS-86764	AA-50511	AA-50512	CAMS-86762 CAMS-86763			

Key to fractions (column headings)
R1 Organic residue (>50 μm and <125 μm)
R2 Organic residue—macro (>125 μm)
P1 Pollen concentrate (s.g. 1.3)
P2 Pollen concentrate (s.g. < 1.3)
P3 Pollen concentrate (s.g. 1.4)
P4 Pollen concentrate (s.g. < 1.4)
M Plant macrofossils
Empty cell indicates not enough sample for ^{14}C analysis

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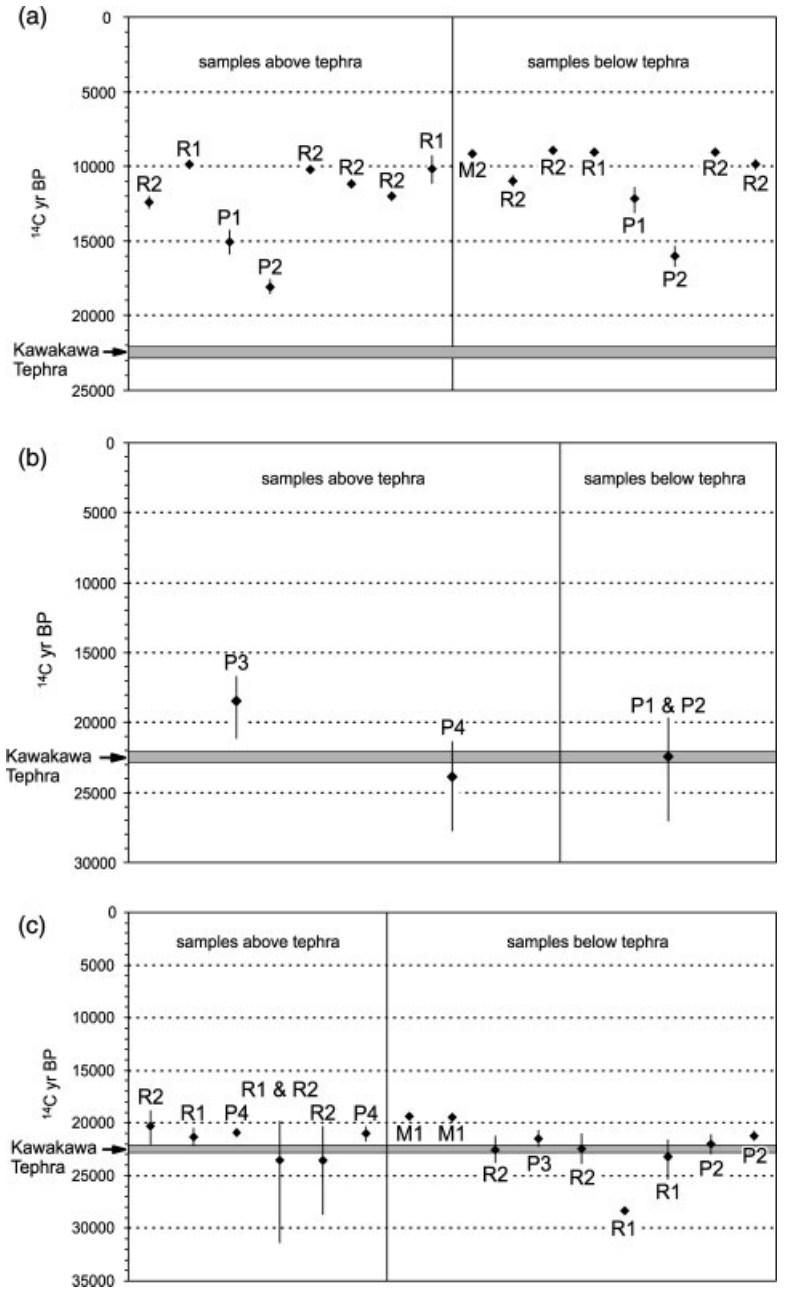

Figure 4 Plots of corrected ^{14}C ages at 2σ range for samples from (a) Skiffington Swamp, (b) Okarito Pakihi, (c) Galway Tarn. R1 = organic residue (> 50 μm and <125 μm), R2 = organic residue (> 125 μm), P1 = pollen concentrate (s.g. 1.3), P2 = pollen concentrate (s.g. < 1.3), P3 = pollen concentrate (s.g. 1.4), P4 = pollen concentrate (s.g. < 1.4). M1 = plant macrofossil (*Sphagnum* leaves and stems), M2 = unidentified plant macrofossils. Position of label abbreviation above or below age range indicates if sample was taken above or below the tephra layer, respectively. Age of Kawakawa Tephra is shown at 2σ range. Error ranges are not shown for sample AA-50511 (Galway Tarn) as these extend beyond the scale of this graph (cf. Table 3)

Corrected (uncontaminated) radiocarbon values have been calculated for all pollen concentrates and organic residue samples using mass balance (equation (1)) and assuming the fixed mass of contamination indicated by the background standards. Note that the conventional radiocarbon ages for the three plant macrofossil samples were not corrected in this way as they were not processed at University of Plymouth laboratories using the pollen extraction method. An independent check of the correction procedure was possible because a known age radiocarbon standard (CAMS-86751 IAEA-C5) had also been processed through the pollen concentration method. The uncorrected age for this standard was significantly too young, suggesting contamination, whereas the corrected age falls within 2σ of the known value for this standard.

The results from the south Westland samples are presented in Table 3 both as raw uncorrected values and with this correction applied, and corrected values are illustrated for each site in Fig. 4. The following discussion refers only to the corrected ages, as shown in Table 3, except for plant macrofossil samples, for which the conventional radiocarbon age is used. The minimum dry weight of 1 mg of sample recommended by the NERC RCL was not always achieved with the 1 cm thick sediment slices originally submitted. In these cases, when the weight of the pollen fractions proved to be too low, additional samples were taken adjacent to each sample point and combined with the first sample prior to dating, as described in the subsequent sections and in Table 4. Results for plant macrofossils are given in Table 3.

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Skiffington Swamp samples (Table 3; Fig. 4(a)); tephra depth 206–207 cm

Many of the 1 cm thick sediment samples at this site were found to contain insufficient sample carbon for analysis and were therefore combined as follows (Table 4):

Sample fraction R2 (organic residue >125 μm): 8 samples from 1 cm thick peat slices
Sample fraction R1 (organic residue >50 μm, <125 μm): 3 samples (202–205 cm, 205–206 cm, 208–211 cm)
Sample fraction P1 (pollen concentrate s.g. = 1.3): 2 samples (202–205 cm, 208–211 cm)
Sample fraction P2 (pollen concentrate s.g. < 1.3): 2 samples (202–205 cm, 208–211 cm)

All results from Skiffington Swamp, including the plant macrofossil sample, are considerably younger than the accepted age for the tephra (Fig. 4(a)). Furthermore the results for all fractions consistently exhibit age reversals whereby samples below the tephra typically give a younger ^{14}C age than corresponding samples taken from above the tephra. These results indicate that *in situ* contamination by younger carbon has been chronic at this site, at least for this section of sediments, and has affected all the fractions dated, including macrofossils. It is interesting to note that this contamination has apparently affected the organic residue and plant macrofossil samples to a far greater extent than the pollen concentrate samples (Table 3). Within the pollen concentrate ages, samples where pollen was separated at below 1.3 s.g. have a stronger concentration of pollen and gave older ages than corresponding samples where pollen was separated at specific gravity of 1.3.

In summary, all samples (including those of pollen concentrates) show strong contamination by younger carbon. The pollen concentrate samples consistently gave older ages and hence are less affected by contamination than are the organic residue and plant macrofossil samples. The least contamination is shown for the samples with highest pollen concentrations (with s.g. < 1.3).

Okarito Pakihi samples (Table 3; Fig. 4(c)); tephra depth 380 cm

These samples consistently contained very little pollen and no organic residue samples were available for analysis owing to the highly inorganic nature of the sediments. The pollen concentrate samples were combined as follows (Table 4):

Sample fraction P1 and P2 (combining pollen concentrates separated at s.g. < 1.3 and s.g. ≥ 1.3): 1 sample (depth 380–394 cm, directly below tephra)
Sample fraction P3 (pollen concentrates s.g. 1.4) and P4 (pollen concentrates s.g. ≤ 1.4): 2 samples (depth 376–380 cm, directly above tephra)
Sample fraction P3 (pollen concentrates s.g. 1.4): 1 sample (depth 378–379 cm)

At the 2σ level, these ages are similar to, or slightly younger than, the accepted age for the tephra. Sample AA-55241 (pollen concentrates s.g. 1.4) had extremely low C content (0.37 mg) and as a consequence extremely broad error ranges. It is not considered reliable for this analysis.

In summary, only three samples contained sufficient C for measurement and no organic residue or plant macrofossil ages are available for comparison with the pollen concentrate ages. As a consequence of low C content and the large errors generated by the correction procedure, the 2σ age ranges are extremely broad. The results nevertheless fall in line with, or are slightly younger than, the established age of the tephra.

Galway Tarn (Table 3; Fig. 4(c)); tephra depth 701–702 cm

The Galway Tarn samples show generally higher concentrations for both pollen and organic residues and so it was necessary to combine fewer samples than at the other two sites (Table 4). The results at this site show a greater degree of internal consistency than the Skiffington Swamp results and narrower errors than the Okarito Pakihi results. Two samples of plant macrofossils associated with tephra fall at this site gave identical uncorrected ages that are younger than the ages of pollen concentrates from above the tephra and ca. 3000 ^{14}C yr younger than the established tephra age.

In summary, the samples from this site gave generally more conformable age results with much less discrepancy between different fractions from the same horizon. All ages, above and below the tephra on both organic residue and pollen concentrates are in line with, or slightly younger than, the established tephra age. The two ages on macrofossils from directly beneath the tephra, however, are considerably younger than the established age of the tephra and the ages obtained from organic residues and pollen from the same or nearby horizons.

Discussion

In an earlier investigation, Vandergoes and Prior (2003) showed that pollen concentrate ages on sediment from Okarito Pakihi gave consistently older age estimates than ages derived from organic residue fractions of the same sample. They argued therefore that the main source of error, widely reported in radiocarbon dating sediments from this high rainfall region, is likely to be the organic residue and bulk organic fractions. They noted, however, that their density separation method for extracting the pollen concentrates was not successful in completely removing organic residue and plant fibres. This non-pollen component therefore may still be a potential source of contamination in pollen concentrate ages to an extent dependent upon the pollen concentration.

Our investigation built on the work of Vandergoes and Prior (2003) by: (a) introducing a new step in the pollen extraction procedure aimed at removing a greater proportion of the non-pollen component; (b) extending the study to two further sites with different depositional settings; and (c) testing the accuracy of the pollen concentrates method against an independent chronostratigraphic marker, the Kawakawa Tephra, present at all three sites. The next three sections discuss these three components in light of the results presented.

Pollen extraction procedure

The refinement of the pollen extraction procedure by adding additional sieving steps at 50- and 10-μm range resulted in effectively reducing the amount of larger and finer inorganic and organic residues and increasing the proportion of pollen present in each sample (Fig. 5). A comparison of dating samples prepared using the previous pollen extraction technique (e.g. Vandergoes and Prior, 2003) versus the refined procedure

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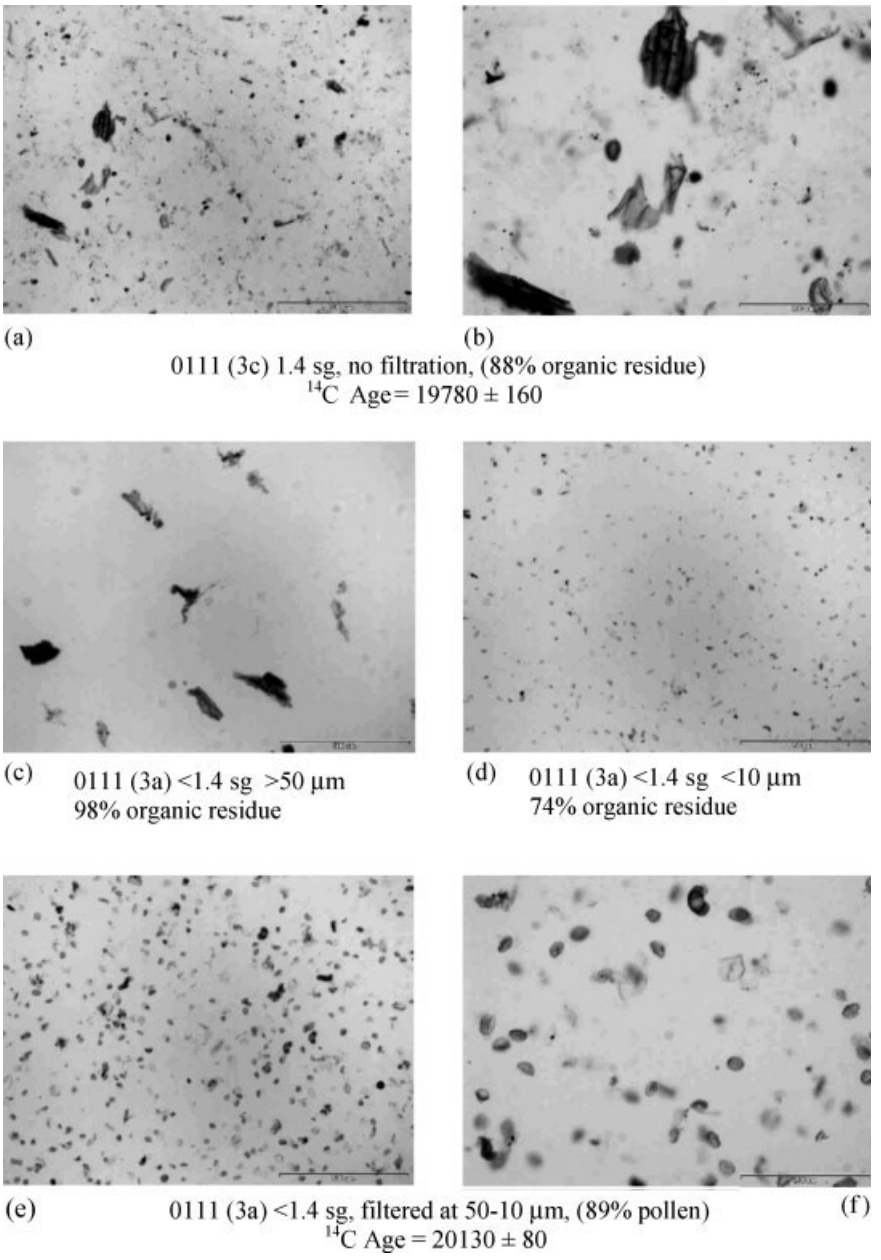

Figure 5 Examples of pollen and organic residue separations resulting from refined pollen extraction procedure and additional sieving steps at 50 and 10 µm. Sample separated from Galway Tarn (0111 (3c)) at 1.4 s.g. with no filtration shows increased amounts of large and fine organic residues ((a) and (b)). Sample separated from Galway Tarn (0111 (3a)) at <1.4 s.g. with filtration at >50 µm and <10 µm shows separation of large and fine organic residues ((c) and (d)). Sample separated from Galway Tarn (0111 (3a)) at <1.4 s.g. between 50 and 10 µm shows a more pure pollen concentrate with fewer organic residues and an increased relative pollen percentage for the sample. (Scale bar in (a), (c), (d), (e)) = 500 µm, in ((b) and (f)) = 200 µm)

reveals that the more pure pollen concentrate derived from the refined procedure consistently produces older age estimates (Fig. 6).

However, it should be noted that pre-sieving at 50 and 10 µm will probably result in some loss of pollen from the sample. This loss is almost certainly negligible in New Zealand sediment samples, where the vast majority of pollen encountered falls within this range; but it may be significant for other floras. It is important therefore to consider the size range of the most common pollen types in any sample and adjust the sieving criteria accordingly, before undertaking this additional step.

Depositional sites and contamination

The sampling strategy involving three sites from south Westland provides an opportunity to examine the reliability of AMS ^{14}C dating of pollen concentrates in different depositional settings. The results from Skiffington Swamp are clearly unreliable as all ages of pollen concentrates, organic residue and macrofossils are considerably younger than the tephra benchmark age and they exhibit high variability between different fractions. Contamination by younger carbon therefore has been severe at this site. The results from Okarito Pakihi are limited by pervasive low carbon concentration of these sediments, which results in only three reliable age determinations with broad error ranges. These ages nevertheless are broadly in line with expectations. The samples from Galway Tarn have higher carbon concentrations and so we have been able to obtain more ages with generally smaller error ranges. These results similarly are in line with expectations. The Skiffington Swamp results therefore are anomalous and require explanation.

It has been suggested previously that root penetration from certain types of bog vegetation into the peat substrate in some

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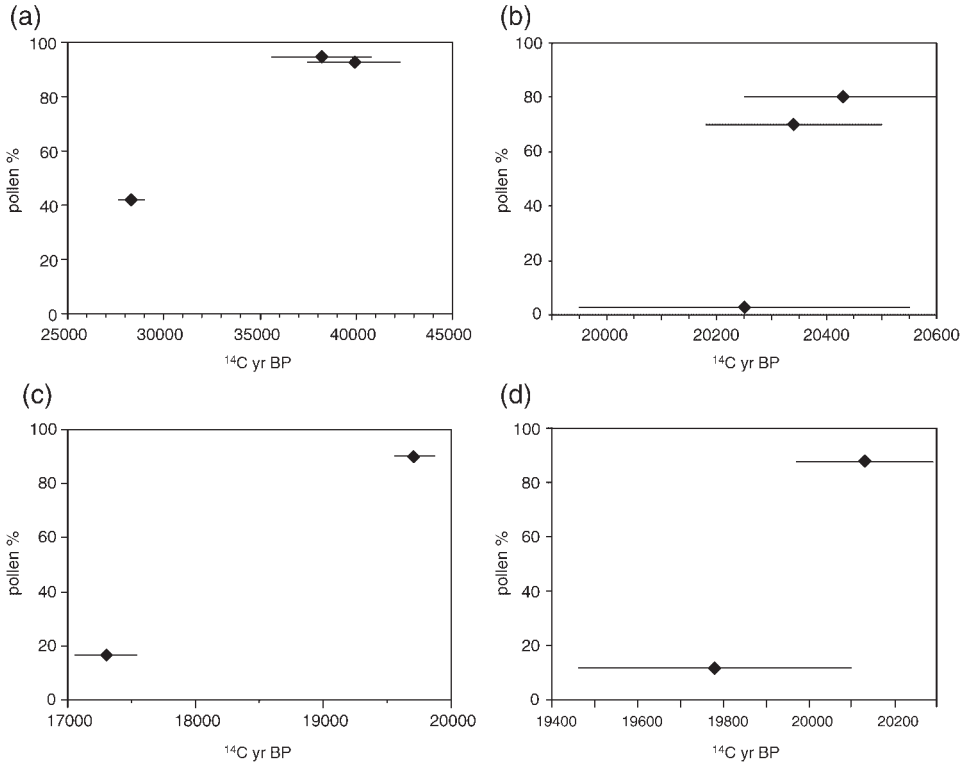

Figure 6 Comparison of conventional radiocarbon age and estimated pollen concentration (percentage of pollen in the sample) for samples from the same horizon: (a) Okarito 913 core at 750–755 cm depth; (b) Galway Tarn at 703–704 cm depth; (c) Galway Tarn at 700–701 cm depth; (d), Galway Tarn at 699–700 cm depth. Horizontal lines denote 2σ error range

settings could provide a vertical pathway for modern carbon and hence a source of contamination, accentuated in this high rainfall environment (Grant-Taylor and Rafter, 1971; Moar and Suggate, 1979; Hammond *et al.*, 1991; Vandergoes and Prior, 2003). The evidence presented here strongly supports this assertion. However, root penetration into underlying sediments is unlikely to have occurred at Galway Tarn as the core site has remained lacustrine through to the present day (Fig. 7). This site has limited age problems. In contrast, at both Skiffington Swamp and Okarito Pakihi sediment infilling of the lake basin and hydroseral succession resulted in the development of peatland commencing in the early Holocene. The vertical distance between the early Holocene peat and the Kawakawa Tephra layer is about 60 cm at Skiffington Swamp and about 95 cm at Okarito Pakihi. We suggest that the shorter vertical distance at Skiffington Swamp has made the underlying horizons dated here more susceptible to contamination by younger carbon via root penetration from the peatland plants. This could have resulted from roots directly contributing to the organic residue fraction carbon, including the small amount of non-pollen in the pollen concentrate samples, or from humic/fulvic acids that had migrated down root channels and which had not been completely removed in the sample preparations. The latter mechanism would probably be comparatively enhanced under the excessive precipitation regime of Westland. What is perhaps surprising is that, although this process can only have commenced at around 10 000 ^{14}C yr before present, when peat vegetation first developed, sediments as old as the LGM have been significantly affected.

If this explanation is correct, these results attest to the extent by which contamination by modern carbon may occur via root penetration in this high precipitation region, although it has not occurred consistently, as shown by the reliability of results from Galway Tarn and Okarito Pakihi. Together these results indicate that ^{14}C chronologies from peat sites in this high precipitation region should be used with caution and that lake sites may typically provide more reliable chronologies. It should be emphasised, however, that this recommendation does not necessarily apply to other regions. Radiocarbon chronologies from raised (ombrogenous) bogs in North Island, New Zealand, for example, have consistently shown strong coherence with tephrochronologies at the same site (e.g. Newnham *et al.*, 1995, 1998; Newnham and Lowe, 2000), while it has been demonstrated that catchment disturbance can result in inwashing of old carbon into lakes while peat sites can be unaffected (e.g. Newnham *et al.*, 1998; McGlone and Wilmshurst, 1999; Lowe *et al.*, 1999).

Accuracy of ages of pollen concentrates

Ignoring the Skiffington Swamp results, which are clearly unreliable, the ages of pollen concentrates from the other two sites generally fall into line with the established age of the tephra benchmark. A major exception is the two plant macrofossil ages from Galway Tarn which are some ca. 2500–3000 ^{14}C yr younger than both the established age for the tephra and the ages obtained for pollen concentrates and organic residue from the same or nearby horizons. It is also interesting to note that the single macrofossil age determination from Skiffington Swamp is significantly younger than all ages of pollen concentrates from the same or overlying horizons and from all organic residue ages from the overlying horizons. This suggests that the simple acid-wash pretreatment of macrofossil samples was less effective at removing contamination by younger carbon than was the more rigorous pretreatment of pollen concentrates and organic residue samples, or that the macrofossils were more susceptible to *in situ* contamination by younger carbon. Various problems encountered with the ^{14}C dating of peat

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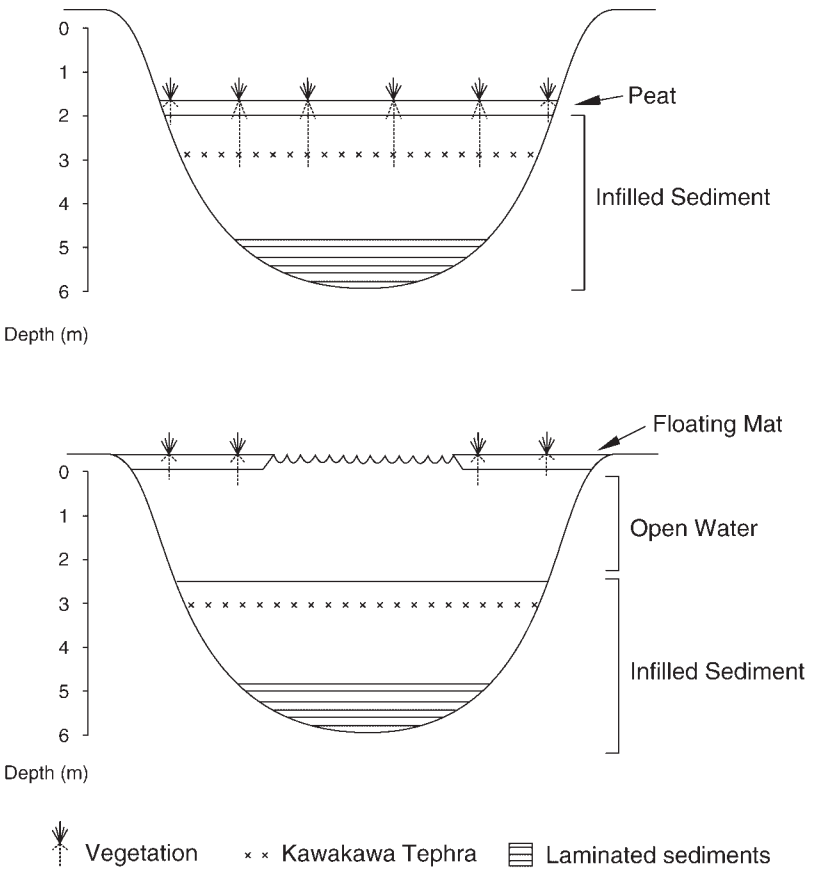

Figure 7 Schematic diagram showing model of contamination via root penetration at terrestrialised sites (e.g. Skiffington Swamp) compared with lake sites (e.g. Galway Tarn)

constituents, including plant macrofossils, have been reported previously (Shore *et al.*, 1995; Wohlfarth *et al.*, 1998; Nilsson *et al.*, 2001).

Are the ages of pollen concentrates more accurate than the ages of organic residue? This question can be addressed for the Galway Tarn and Skiffington Swamp results as low C levels at Okarito Pakihi restricted sampling at these sites to pollen concentrates only. At Galway Tarn the ages from pollen concentrates are statistically indistinguishable (at 95% confidence limits) from ages from organic residues at the same horizon (Fig. 4(c)). At Skiffington Swamp, where contamination by younger carbon has affected all samples, the ages of pollen concentrates are consistently older than their equivalent organic residue ages. This suggests that pollen concentrates are not immune from contamination but that they are less susceptible than organic residues.

Our results also show that samples of pollen concentrates with high carbon yields and a high proportion of pollen typically provide older ages (Fig. 6; Table 3) than samples from the same horizon with lower carbon or pollen content. This pattern suggests that the influence of contamination may be reduced by a sampling strategy that aims at improving both pollen concentration and carbon yield.

Conclusions

The work presented here provides a rigorous examination of AMS dating of pollen concentrates by applying the method to sediments with a known age of >20 kyr and hence comparatively low ^{14}C content, deposited in a high rainfall environment where radiocarbon dating of sediment samples is known to be prone to contamination by young carbon.

The results generally corroborate earlier work in showing that AMS ^{14}C dating of pollen concentrates can provide reliable age estimates. However, the small amount of contamination introduced in the pollen concentration procedure demonstrated the importance of testing these procedures with radiocarbon standards of known age or background ^{14}C levels. This is particularly the case because the technique had previously been shown not to introduce any contamination when samples were processed in another laboratory, and since the source of the contaminant at the Plymouth laboratory remains unknown, future work is clearly required to identify the source of this contamination.

The addition of sieving steps at 50- and 10-μm range, thereby reducing the amount of larger and finer inorganic and organic residues and hence increasing the relative pollen percentages for each sample, can provide more reliable age estimates. The results also suggest that at sites prone to contamination by younger carbon, pollen concentrate samples may be less susceptible to this process, particularly if an effort is made to increase carbon yield and pollen concentrations. Where contamination of samples of pollen concentrates has occurred, we concur with Vandergoes and Prior (2003) that residual organic matter in the pollen concentrates is a likely source.

These results also provide insight into the importance of site selection when ^{14}C dating is to be applied in high rainfall regions such as Westland. Our model to explain contamination associated with root penetration by bog vegetation suggests that in this region ^{14}C ages from peats or sediments underlying peats by up to ca. 60 cm, or perhaps more, should be treated

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with caution. By contrast, lake sites, or other depositional settings where root penetration can be discounted, would seem to pose a much lower risk of contamination by younger carbon. At the two sites not seriously affected by contamination, ages on both pollen concentrates and organic residues are generally in line with, or slightly younger than, the established age of the tephra benchmark, suggesting that, with careful site selection, reliable chronologies can be achieved in this region.

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