An Icelandic freshwater radiocarbon reservoir effect: Implications for lacustrine ^{14}C chronologies

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Abstract

A freshwater radiocarbon (^{14}C) reservoir effect (FRE) is a ^{14}C age offset between the atmospheric and freshwater carbon reservoirs. FREs can be on the order of 10,000 ^{14}C years in extreme examples and are a crucial consideration for ^{14}C dating of palaeoenvironmental and archaeological samples. Correction for a FRE may be possible, provided the FRE and the proportion of FRE-affected carbon within a sample can be accurately quantified. However, although such correction is desirable for affected samples, it is essential that such correction is accurate in order to produce useful chronological information. Accuracy of FRE correction can be limited by spatial variation in FRE within a freshwater system, but despite this there is currently a paucity of information to identify and quantify such

variability within affected systems. Here we present results of a study that investigates the effects of spatial FRE variation upon dating accuracy within the freshwater system of Lake Mývatn, northern Iceland. A substantial FRE (>10,000 ^{14}C years) has previously been identified in archaeological and modern samples from the region, which shows the potential for considerable spatial variability. The study also assesses the use of δ^{13}C and δ^{15}N in age correction of affected samples. The results show that benthic detritus and organisms at primary trophic levels from locations within the lake are affected by a FRE of at least 3500 ^{14}C years, with clear spatial variation resulting in ^{14}C age differences of up to 7670 ^{14}C years between samples. There is a broad correlation between stable isotope values and FRE within the dataset. However, large associated uncertainties currently preclude highly accurate and precise stable isotope-based quantification of the proportion of FRE-affected carbon within archaeological and palaeoenvironmental samples from Mývatn and the surrounding region.

1. **Introduction**

Radiocarbon (^{14}C) dates underpin Holocene chronologies, providing absolute chronological information for carbonaceous sample materials. The method is applicable to a vast range of material types, due to the small sample sizes required for accelerator mass spectrometry (AMS) measurement, and is invaluable in palaeoenvironmental and archaeological research. However, a key assumption in ^{14}C dating is that the sample ^{14}C content at the time of death or final formation was equal to that of the contemporaneous atmospheric carbon (C) reservoir. While this is true for the fast-cycling terrestrial biospheric C reservoir, the ^{14}C content in other reservoirs, notably the marine and some freshwater reservoirs, is offset from that of the atmosphere. This is due to differences between these reservoirs and the atmosphere in terms of C residence times and/or the ^{14}C age of carbon inputs. The net result is a ^{14}C age offset (known as a reservoir effect) between carbon in the atmosphere-terrestrial biosphere reservoir and that of the marine or freshwater C reservoir (Stuiver and Braziunas, 1993). Reservoir effects are also transferred up the food chain from non-terrestrial to terrestrial organisms. For example, prehistoric human communities with a freshwater dietary component frequently reflect bone ^{14}C ages older than contemporaneous terrestrial material (e.g. Cook *et al*., 2001; Culleton, 2006; Fischer *et al*., 2007).

The marine reservoir effect (MRE) results from a universal, primary, underlying mechanism; the 'ageing' of water masses as they are separated from atmospheric CO_2 during extended deep ocean circulation. Therefore, oceanic response to atmospheric ^{14}C variations can be modelled and a correction for the global average surface water MRE is available (Stuiver *et al*., 1986). Despite this, local deviations from the global MRE (termed ΔR) arise due to regional oceanographic conditions, and must be empirically quantified (Stuiver and Braziunas, 1993; Ascough *et al*., 2005). However,, in freshwater

systems a number of underlying factors can be responsible for a freshwater ^{14}C reservoir effect (FRE). Carbon with a ^{14}C activity equivalent to that of the atmosphere enters freshwater systems via gaseous atmospheric CO_2 exchange and breakdown of modern terrestrial organic matter. This ^{14}C activity can be reduced by admixture with inputs of carbon from dissolution of geological carbonates or from high-temperature geothermal water-rock interactions. Such carbon is '^{14}C dead' (i.e. the activity is indistinguishable from background ^{14}C levels). Other freshwater C sources have ^{14}C activities intermediate between modern and background, including CO_2 from glacial melt-water or oxidation of ancient organic material, including that stored within soils and sediments (Abbott and Stafford, 1996; Hall and Henderson, 2001; Moreton *et al*., 2004). Physical isolation of C within a freshwater body (e.g. by density stratification or ice cover) can also result in a FRE (Abbott and Stafford, 1996). A further complication is that the sources of old carbon to a freshwater setting may not be immediately obvious. For example, Hutchinson *et al*. (2004) state that the underlying mechanism behind FREs of up to 680 ± 65 ^{14}C yr affecting basal sediments of lakes and bogs in the Georgia Basin and Puget Lowland is not readily apparent.

Documented FRE values show a wide range, and can be considerable, e.g. FRE values in some sub-glacial Antarctic lakes range up to $20,720 \pm 100$ ^{14}C yr BP (Hodgson *et al*., 2009). However, despite documentation of the occurrence of FREs in a range of settings, their underlying formation mechanisms and their implications for ^{14}C chronologies are comparatively much less well understood. It is obviously desirable in situations where a FRE has been demonstrated to be able to correct ^{14}C ages of samples from this setting. This is theoretically achievable if the FRE offset within the system is homogeneous and measurable, and the proportion of FRE-affected C within a sample can be accurately determined. Stable isotope values of carbon and nitrogen (δ^{13}C and δ^{15}N) have previously been used to quantify the FRE within archaeological samples (e.g. Cook *et al*., 2001).. The δ^{13}C signatures of

ecosystems differ due to physical and biochemical fractionation effects, while enrichment in $\delta^{15}N$ of 1.3-5.3‰ occurs with successive trophic levels (Minagawa and Wada, 1984; Cabana and Rasmussen, 1994; 1996). The $\delta^{15}N$ values of aquatic organisms are frequently higher than terrestrial organisms due to the greater complexity of aquatic food webs (Schoeninger and DeNiro, 1984). Therefore, if C from terrestrial versus aquatic environments has significantly different isotopic values, it is possible to discriminate between the two, and hence determine the proportion of FRE-affected C within a sample. For example, Cook *et al.* (2001) successfully used a combination of $\delta^{13}C$ and $\delta^{15}N$ values with ^{14}C measurements to assess the proportion of freshwater C consumed by Mesolithic and Neolithic inhabitants of the Iron Gates Gorge region of the Danube. The ^{14}C ages of these individuals were subsequently corrected for a substantial FRE. However, growing evidence suggests the FRE within an individual system is not necessarily homogeneous. Potential sources of variation are differences in the proportion and ^{14}C activity of carbon inputs to the system, and varying proximity of organisms to C inputs of differing ^{14}C age (e.g. Geyh *et al.*, 1998; Stein *et al.*, 2004; Bronk-Ramsey, 2008). Such variability in FRE within a system would mean that a single FRE correction factor for ^{14}C ages was inappropriate, and indeed application of such a factor may compound, rather than reduce, the FRE-derived inaccuracies in ^{14}C ages. Despite this, the potential for spatial variation in FRE values remains poorly studied.

This paper assesses the potential for spatial variation in FRE values within lacustrine systems by analysis of samples from Lake Mývatn, a large (37 km^2), shallow lake in the interior highlands of Iceland (65° 35'N, 17° 00'W; Figure 1). Lake Mývatn is almost entirely fed from groundwater springs, and a substantial FRE has been attributed to input of ^{14}C-depleted carbon within the spring waters (Ascough *et al.*, 2007; 2010). This FRE is present in archaeological samples from the period 868-968 cal AD, and appears to vary by over 1500 ^{14}C years during a calibrated calendar period of ~100 years

(McGovern *et al*., 2007; Ascough *et al*., 2010). An important question therefore is whether this variation reflects temporal changes in an otherwise homogeneous FRE, or spatial variability in the Mývatn FRE at a single point in time. This study is relevant not only for settings where the FRE may be derived from input of geothermally-sourced carbon, but also for settings where ^{14}C-depleted carbon is derived from a variety of other sources.

2. **Methods**

2.1. *Sample material*

Lake Mývatn comprises a North Basin (8.5 km^2) and a South Basin (28.2 km^2) (Figure 1), and water inputs are almost exclusively from cold (c.5ºC) and warm (geothermal, ~20ºC) springs along the eastern shore (Ólafsson 1979). Water depth is a maximum of 3-4 m in the South Basin and 2-2.5 m in the North Basin. Material was obtained from nine separate locations within Lake Mývatn in July 2008 including, (i) zones of groundwater inflow (Helgavogur and Grjotavogur) and (ii) mixing zones away from groundwater inflow, in both the North and South Basins. These were chosen in order that samples from locations in close proximity to previously-identified inputs of strongly ^{14}C-depleted carbon (Ascough *et al*., 2010) could be compared with samples from locations within the South Basin at distance from these sources.

The main aim of this investigation was quantification of spatial variation in FRE within the lake. It was therefore important that samples represented only the primary lake ecosystem levels, and that biota represented localized lake water ^{14}C within a few meters of the sample site. This avoided any interpretative difficulties due to the presence of many trophic levels within the sample group, or the use of more mobile organisms at higher trophic levels (e.g. fish), whose ^{14}C activity potentially represented an average of several sites within the lake. Therefore sample material comprised benthic detritus,

primary producers and primary consumers. Eight different sample materials were obtained overall (Table 1), although due to biota abundances it was not possible to obtain samples of all eight materials at each site. Benthic detritus (top 5 cm of sediment) and chironomid (*Tanytarsus gracilentus*) larvae were obtained by drop-corer at six locations. Green algae (*Cladophora spp.*) were obtained by scraping rock surfaces, and aquatic plants (*Potamogeton filiformis – Slender-leaved pondweed*) were hand sampled from a boat. Caddis fly larvae (*Apatania zonella*), freshwater molluscs (*Radix peregra*) and blackfly larvae (*Simulium vittatum*) were obtained by brushing and picking animals from stones by hand. Zooplankton were collected by plankton net, from which *Daphnia longispina* were separated in the laboratory under microscope. All samples were thoroughly cleaned in distilled water following collection. Invertebrates were placed in distilled water in order to ensure emptying of gut contents prior to analysis. Following collection, all samples were air-dried at 30°C, followed by freeze-drying and storage in pre-combusted glass vials or clean plastic bags prior to analysis. Molluscs were separated from their carbonate shells prior to analysis.

2.2. *Sample pre-treatment and measurement*

Individual dried samples were homogenized by grinding using an agate mortar and pestle. In the case of aquatic plants it was possible to obtain sufficient material for analysis from a single organism. However, it was necessary to bulk together several individuals for analysis of the invertebrate specimens. This is advantageous as it ensures that a population average is obtained in the case of these smaller organisms. In the case of *Tanytarsus gracilentus* and *Simulium vittatum*, 10 individuals were bulked for each measurement. For *Radix peregra* and *Apatania zonella* three individuals were bulked for each measurement.

Bulk elemental analyses of carbon (C) and nitrogen (N) were made together with $\delta^{13}C$ and $\delta^{15}N$ measurements using continuous-flow isotope ratio mass spectrometry on a Costech elemental analyser (EA -Milan, Italy) fitted with a zero-blank auto-sampler. The EA was coupled via a ConFloIV to a ThermoFinnigan Delta[plus] XL isotope ratio mass spectrometer (Thermo Finnigan GmbH, Bremen, FRG) as described in Werner *et al*. (1999). Each sample was measured in duplicate together with a mix of laboratory standards and blanks. External reproducibility was better than ± 0.2‰ (1σ) for $\delta^{13}C$ and better than ± 0.3‰ (1σ) $\delta^{15}N$. Stable isotope values are reported as per mil (‰) deviations from the VPDB and AIR international standards for $\delta^{13}C$ and $\delta^{15}N$, respectively.

CO_2 for ^{14}C measurement was obtained from the solid samples by combustion in sealed quartz tubes using the method of Vandeputte *et al*. (1996). The evolved CO_2 was then cryogenically purified and a 3 ml sub-sample of the purified sample CO_2 was converted to graphite using the method of Slota *et al*. (1987). Sample $^{14}C/^{13}C$ ratios were measured by AMS at 245 keV on the SUERC SSAMS with carbon in the 1^+ charge state. For normalization of sample $^{14}C/^{13}C$ ratios, an aliquot of CO_2 was obtained for off-line $\delta^{13}C$ determination on a VG SIRA 10 isotope ratio mass spectrometer, using NBS 22 (oil) and NBS 19 (marble) as standards.

3. **Results**

Results of stable isotope and ^{14}C measurements (both fraction modern carbon (Fm) and ^{14}C age BP) are presented in Table 2. The off-line $\delta^{13}C$ values used for normalization of the sample $^{14}C/^{13}C$ ratios for Fm and ^{14}C age BP are also presented. Benthic detritus $\delta^{13}C$ varied by 2.7‰, (from -16.5‰ to -19.2‰). The $\delta^{15}N$ of benthic detritus varied by 9.4‰ (between -3.1‰ and +6.3‰). Detritus ^{14}C age varied by approximately 3480 ^{14}C years, from 3965 ± 30 ^{14}C years BP (Station 128) to 7445 ± 30 ^{14}C years BP (Helgavogur). The $\delta^{13}C$ of aquatic plants (*Potamogeton filiformis*) varied by 5.0‰ (-16.9‰ to

-11.9‰), and the majority of *P. filiformis* δ^{15}N values varied by 6.3‰ (between -4.3‰ and +2.0‰).

However, one *P. filiformis* sample (from the N. Basin Deep site) had a δ^{15}N of -16.0‰. The

explanation for this depleted value is not readily apparent, but could reflect a difference in nitrogen

source to plants at this site arising from human activities (i.e. diatomite mining), as is documented

elsewhere (Collier *et al.*, 2002). Additionally, the δ^{15}N of aquatic plants can show seasonal variations

of >10‰ at single sites (Boon and Bunn, 1994). The ^{14}C age of *P. filiformis* ranged by ~7670 ^{14}C

years; from 3545 ± 30 ^{14}C years BP (Station 128) to 11, 215 ± 35 ^{14}C years BP (Helgavogur).

The δ^{13}C and δ^{15}N values of algae (*Cladophora spp.*) from Helgavogur (-10.1‰ and +3.4‰,

respectively) were enriched relative to algae at Grjotavogur (-14.8‰ and -1.3‰, respectively). Algae

from Helgavogur had a ^{14}C age of 10,925 ± 30 ^{14}C years BP, whereas algae from Grjotavogur had an

age of 7160 ± 30 ^{14}C years BP. Caddis fly larvae (*Apatania zonella*) from Grjotavogur also had a high

^{14}C age of 7255 ± 30 ^{14}C years, δ^{13}C of -19.0‰, and δ^{15}N of -0.9‰.

Zooplankton (*Daphnia longispina*) samples from near the island of Hrútey had a δ^{13}C of -

17.0‰ and δ^{15}N of +1.2‰. The ^{14}C age was 3795 ± 30 ^{14}C years. The blackfly larva (*Simulium

vittatum*) from the river Laxá outflow had a δ^{13}C value of -15.4‰ and δ^{15}N of +1.2‰, with a ^{14}C age of

4260 ± 30 ^{14}C years. Chironomid larvae (*Tanytarsus gracilentus*) had a δ^{13}C range of 5.6‰, from -13.7

(Station 95) to -19.3‰ (N. Basin deep). The δ^{15}N range of these samples was 6.5‰ (-0.4‰ to +6.1‰).

The large range in ^{14}C ages in *Tanytarsus gracilentus* samples (5355 ^{14}C yr) reflects the high ^{14}C age of

material from Helgavogur (9530 ± 30 ^{14}C years BP) relative to that from other sites (4175 ± 30 ^{14}C yr

BP to 4760 ± 30 ^{14}C yr BP).

The mollusc (*Radix peregra*) from Helgavogur is depleted in δ^{13}C (-22.6‰), enriched in δ^{15}N

(+5.5‰), and depleted in ^{14}C (10,655 ± 30 ^{14}C years BP) relative to the other samples. At the two other

sites (Dragsey - Laxá and Station 128), mollusc δ^{13}C showed a 2.3‰ range (-13.4‰ to -15.7‰), a 3.1‰ δ^{15}N range (+0.5‰ to +3.6‰) and a ^{14}C age range of 815 years (3655 ± 30 to 4470 ± 30 ^{14}C years BP). The δ^{15}N value of +3.6‰ for *Radix peregra* in the river Laxá was somewhat higher than expected for a grazer. However, this value is similar to that found in invertebrate-feeding fish and ducks in the lake and river (unpublished data) and is probably an indication that the snails feed on the river's dense population of Hydra (cf. Cuker and Mozley 1981).

4. **Discussion**

The results firstly show that, without exception, all sampled materials from Lake Mývatn are affected by a FRE of at least 3500 ^{14}C years. Secondly, this FRE shows clear spatial variation in the lake, resulting in ^{14}C age differences of up to 7670 ^{14}C years between organic carbon at different locations. Spatially-dependant differences in FRE are particularly clear between samples from the groundwater inflow locations (i.e. Helgavogur and Grjotavogur) versus samples from other sites in the lake (Figure 2A). When material from Helgavogur and Grjotavogur is excluded, sample ^{14}C age still varies between locations (Figure 2B). The ^{14}C age of samples decreases overall in the order Helgavogur > Grjotavogur > Station 33 > Laxá > Station 95 > North Basin Deep > Station 13 > Station 128 > Near Hrútey. Samples in the current study include primary producers and consumers within the Lake Mývatn ecosystem. The results therefore imply that the FRE and variation in FRE will also be apparent in the ^{14}C ages of both aquatic organisms at higher lake trophic levels (e.g. fish), and terrestrial organisms consuming aquatic-derived carbon.

The FRE in Mývatn appears due to the influx of ^{14}C-depleted carbon to the lake from groundwater springs. Seasonal ice cover and thermal stratification are unlikely to influence lake carbon ^{14}C age, as the water column is shallow, well-mixed by wind-driven wave action in the summer and

spring-fed areas are permanently ice-free (Ólafsson 1979; 1991; Thorbergsdóttir et al., 2004). The ^{14}C age of water inflow at the warm spring of Helgavogur has a ^{14}C age of ~10,000 years, apparently as a result of carbon derived via water-rock interactions in the Námafjall field, within a fissure swarm across the Krafla geothermal center (Kristmannsdóttir and Ármannsson, 2004; Ascough et al., 2010). Biota at this site have ^{14}C ages similar to that of the spring water, ranging from 9530 ± 30 to $11,215 \pm 35$ [14]C yr BP (Table 2, Figure 2A), substantially in excess of those from other sampling sites. However, the ^{14}C age of detritus from Helgavogur (7445 ± 30 ^{14}C yr BP) is slightly lower. Wind induced re-suspension of sediment occurs frequently within the lake, together with substantial bioturbation from the actions of chironomid larvae and ducks (Kjaran et al., 2004). The ^{14}C age of Helgavogur detritus may therefore reflect the admixture of less strongly ^{14}C-depleted carbon, circulated by benthic sediment transport from other zones within the lake.

Water at the cold spring of Grjotavogur originates in the interior highlands and has a ^{14}C age of ~7000 ^{14}C years (Ascough et al., 2010), most likely derived from carbon within glacial melt-water and water-rock interactions at distance from Lake Mývatn. Both of these factors contribute to high ^{14}C ages in Icelandic groundwater from a variety of locations (Sveinbjörnsdóttir et al., 1995; 2000). Algae and caddis fly larvae at Grjotavogur also have ^{14}C ages similar to previously published bulk water measurements; these range from 7160 ± 30 to 7255 ± 30 ^{14}C yr BP (Table 2, Figure 2A). [14]C measurements of samples from the spring sites in Lake Mývatn suggests that biota at these locations incorporated carbon largely from ^{14}C-depleted dissolved CO_2 and bicarbonate (HCO_3^-) in the spring water influx. In contrast, the ^{14}C ages of samples from other sites are significantly lower, ranging from 3545 ± 25 ^{14}C yr BP to 4760 ± 30 ^{14}C yr BP (Table 2, Figure 2A and Figure 2B). Therefore, although biota at these locations incorporates a proportion of strongly ^{14}C-depleted carbon from the spring sources, a significant fraction of sample carbon is also derived from sources with higher ^{14}C content.

This may originate via gaseous transfer of CO_2 at the air-water interface, or oxidation of organic material transported into the lake from the surrounding terrestrial zone.

The FRE variation between samples from the spring sites (Helgavogur and Grjotavogur) versus samples from other sites can be attributed predominantly to spatial factors (i.e. proximity to the influx of ^{14}C-depleted carbon in groundwater inputs). However, although it is possible that the variation in FRE between non-spring sampling sites (Figure 2B) is also spatially-determined, it is also possible that a proportion of this variability is related to trophic level differences between samples. In some samples both isotope values and FRE could plausibly be explained by the feeding strategy of the species in question. For example, *Daphnia longispina* has low δ^{13}C (-17.0‰) and young ^{14}C age (3795 ± 30 ^{14}C yr BP) relative to other samples (Table 2). This may result from the consumption by *Daphnia longispina* of food resources depleted in δ^{13}C and enriched in ^{14}C content, relative to those of other organisms. These could be either phytoplankton in the pelagic zone that incorporate carbon derived from modern atmospheric CO_2 at the air-water interface, or detrital material that included a proportion of modern terrestrial organic material. The latter seems more plausible, as the high alkalinity of waters within lake Mývatn (pH of 8.2 to 10.2 (Dickman *et al.*, 1993)) reduces the likelihood of substantial atmospheric CO_2 influx to the lake.

If FRE were correlated with δ^{13}C or δ^{15}N within lake Mývatn, it would be possible to use stable isotope values as a predictor for FRE in the Mývatn ecosystem, and hence derive a correction factor for sample ^{14}C ages. This requires that differences in habitat location, or trophic level between samples result in a significant offset between FRE and at least one stable isotope. At Helgavogur δ^{13}C values reported for geothermally-influenced (i.e. high ^{14}C age) water are >2‰ heavier than water at Grjotavogur or Station 33 (Ascough *et al.*, 2010). This is in accordance with published data showing

heavier $\delta^{13}C$ values in Icelandic groundwater correlated with higher apparent water ^{14}C age; for example carbon release during sub-glacial volcanic eruptions results in groundwater $\delta^{13}C$ enrichments of up to 3.8‰ and ^{14}C age increases of ~20,000 years (Sveinbjörnsdóttir et al., 2000). In results presented here, the relative $\delta^{13}C$ enrichment of water at Helgavogur does appear to be reflected in the $\delta^{13}C$ value of algae from this site, which is almost 5‰ heavier than algae at Grjotavogur (Table 2). However the $\delta^{13}C$ of other samples (detritus, aquatic plant, mollusc and chironomid larvae) from Helgavogur are within the range of values for other sampling locations (Table 2; Figure 3). This is despite the fact that all samples from Helgavogur incorporate a higher proportion of geothermally-derived ^{14}C-depleted carbon relative to samples from other locations. It is not possible therefore to correlate FRE with $\delta^{13}C$ within this dataset (see Figure 4A).

Examination of the $\delta^{15}N$ values also shows considerable intra-site variation, although the $\delta^{15}N$ of material from the warm spring site (Helgavogur) appears significantly enriched relative to equivalent samples from other locations. (Figure 3). It is likely that the enrichment at Helgavogur results from nitrate inputs within inflowing groundwater (Ólafsson 1979; 1991), and nitrogen from groundwater inflow only comprises ~4% of overall nitrogen for primary lake productivity, with the remainder originating via internal nutrient cycling and N-fixation (Jonasson, 1979; Jonasson and Adalsteinsson, 1979; Ólafsson, 1979). Therefore, it appears that the $\delta^{15}N$ enrichment drops off rapidly away from the groundwater inflow site. The offset in $\delta^{15}N$ between Helgavogur and other sample sites in Lake Mývatn, coupled with the high ^{14}C age of samples from Helgavogur, results in an overall correlation between $\delta^{15}N$ and FRE (see Figure 4B). However it is important to note that the $\delta^{15}N$ enrichment appears localized to the Helgavogur site, and at other sample locations there is no clear pattern in $\delta^{15}N$. This means that $\delta^{15}N$ is not overall a strong predictor of sample ^{14}C age for organisms at the same

trophic level, particularly given that the samples from Grjotavogur have high ^{14}C ages, yet are relatively depleted in δ^{15}N .

Given the above discussion, it is not possible within the current dataset to confidently ascribe a variable FRE correction to samples from Lake Mývatn on the basis of stable isotope measurements. This is due to the fact that overall isotopic differences between sample types and species do not appear sufficiently large, and there is considerable variability in stable isotope values within any single species. It must be noted that the latter point may be a function of the size of the current sample, and that finer-scale isotopic detail may be forthcoming from a larger sample group than in the present study.

The present study provides strong evidence that in freshwater settings with a point source of ^{14}C-depleted carbon, it is likely that there will be a spatial dependence in the ^{14}C age of benthic detritus and biota within the freshwater body. Previous variation is observed in FRE offsets of over 1500 ^{14}C years for archaeological samples from the Lake Mývatn region (Ascough *et al.*, 2010). The results of this study show that this variation could well result from spatial variability in FRE at a single point in time, rather than temporal changes in FRE during the period 868-968 cal AD. It is conceivable that for multiple archaeological or palaeoenvironmental samples that are demonstrably of equivalent calendar age, but variable ^{14}C age, such information could be of use to provenance the location where the sample was formed. However it is important to note that this is only applicable where multiple samples are available and the relative calendar age of these can be confidently assigned. Further, such an approach is more appropriate for sedentary organisms, rather than those such as fish, that integrate the ^{14}C signature of several different areas.

The data presented demonstrate that, along with temporal changes in the ^{14}C age of carbon inputs to a freshwater system, spatial FRE variation is a crucial concern. Spatial variation is particularly likely to influence settings where a large influx of ^{14}C-depleted groundwater exists. Such groundwater could be derived from a range of sources besides geothermal influence, including carbonate dissolution via water flow through calcareous geology. In affected systems, the ^{14}C content of identical samples can vary by several thousand years, depending upon the proximity of sampling location to high ^{14}C age carbon inputs. Hence, in such settings, if FRE quantification is attempted, sample location is clearly a critical consideration, and it is preferable to obtain samples from more than one location in order to assess whether there is significant spatial FRE variation in the system.

The results of this study emphasize that in freshwater settings, samples composed of terrestrially-sourced carbon (e.g. plant macrofossils) should be preferred, unless investigators can be confident that freshwater carbon ^{14}C content is not affected by a FRE. In settings where a FRE is present (or suspected) there may be an absence of suitable terrestrial material for dating, in which case other dating methods should be considered (e.g. Hutchinson *et al*., 2004). Correction of sample ^{14}C ages for a FRE is practical only if the FRE is constant, and the proportion of FRE-affected carbon within a sample can be determined accurately. Stable isotope values can provide an accurate proxy for the latter, provided there is sufficient isotopic offset between carbon (δ^{13}C) of different ^{14}C ages within a freshwater system. However, in Mývatn, complexity within the system means it is unlikely that highly accurate correction of FRE values based upon stable isotopic measurements will be possible. This difficulty is compounded by the fact that there is spatial variability in FRE within Lake Mývatn of up to several thousand ^{14}C years. Therefore, if any correction for a FRE is to be attempted, a careful assessment of the freshwater system should be made to ensure that variations in FRE within the system are not likely to exceed measurement precision.

5. **Conclusions**

A large FRE exists in Lake Mývatn, as a result of carbon inflow derived from geothermally-mediated water-rock interactions and possibly glacial meltwater at hot and cold springs along the lake edge. At present, samples of detritus, primary producers and primary consumers from all locations within Lake Mývatn have a ^{14}C age of at least 3500 ^{14}C years, extending to ~10,000 ^{14}C years at points close to the influx of geologically-sourced ^{14}C-depleted carbon. Along with temporal variation in FRE, there is clearly large spatial variation (of up to 7670 ^{14}C years) in the ^{14}C age of aquatic carbon in different lake locations. Although these variations are extreme, it is highly likely that spatial variation exists within many other freshwater systems, particularly in lacustrine spring-fed settings. Therefore, the results presented here have implications for ^{14}C dating of samples, including archaeological and palaeoenvironmental materials from freshwater systems within which a FRE is either likely or has previously been identified, and where there is potential for heterogeneous spatial distribution of ^{14}C-depleted carbon. In such settings, terrestrial samples should be preferentially selected for ^{14}C dating, or alternative dating methods considered, wherever possible. If FRE correction is to be attempted in any setting, it is important that investigators are confident that it is possible to accurately quantify an appropriate FRE value for the freshwater system and that additional uncertainty due to any spatial FRE variation within the system is recognized.

Acknowledgements

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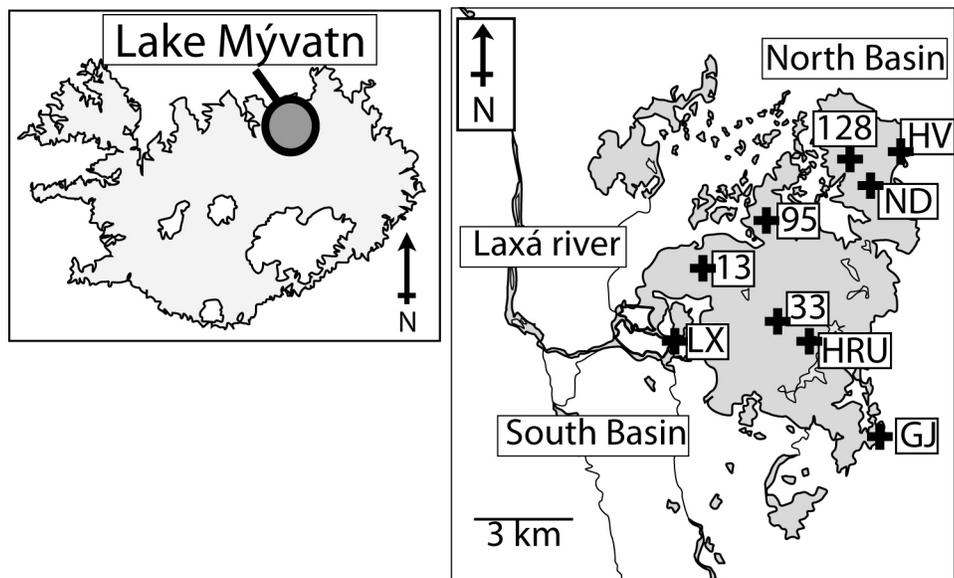
Figures

Figure 1: Location of study site within Iceland (left), and location of sampling stations at Lake Mývatn (right). HV = Helgavogur; 128 = Station 128; ND = North Basin Deep; 95 = Station 95; 13 = Station 13; 33 = Station 33; HRU = Near Hrútey; LX = Laxá; GJ = Grjotavogur.
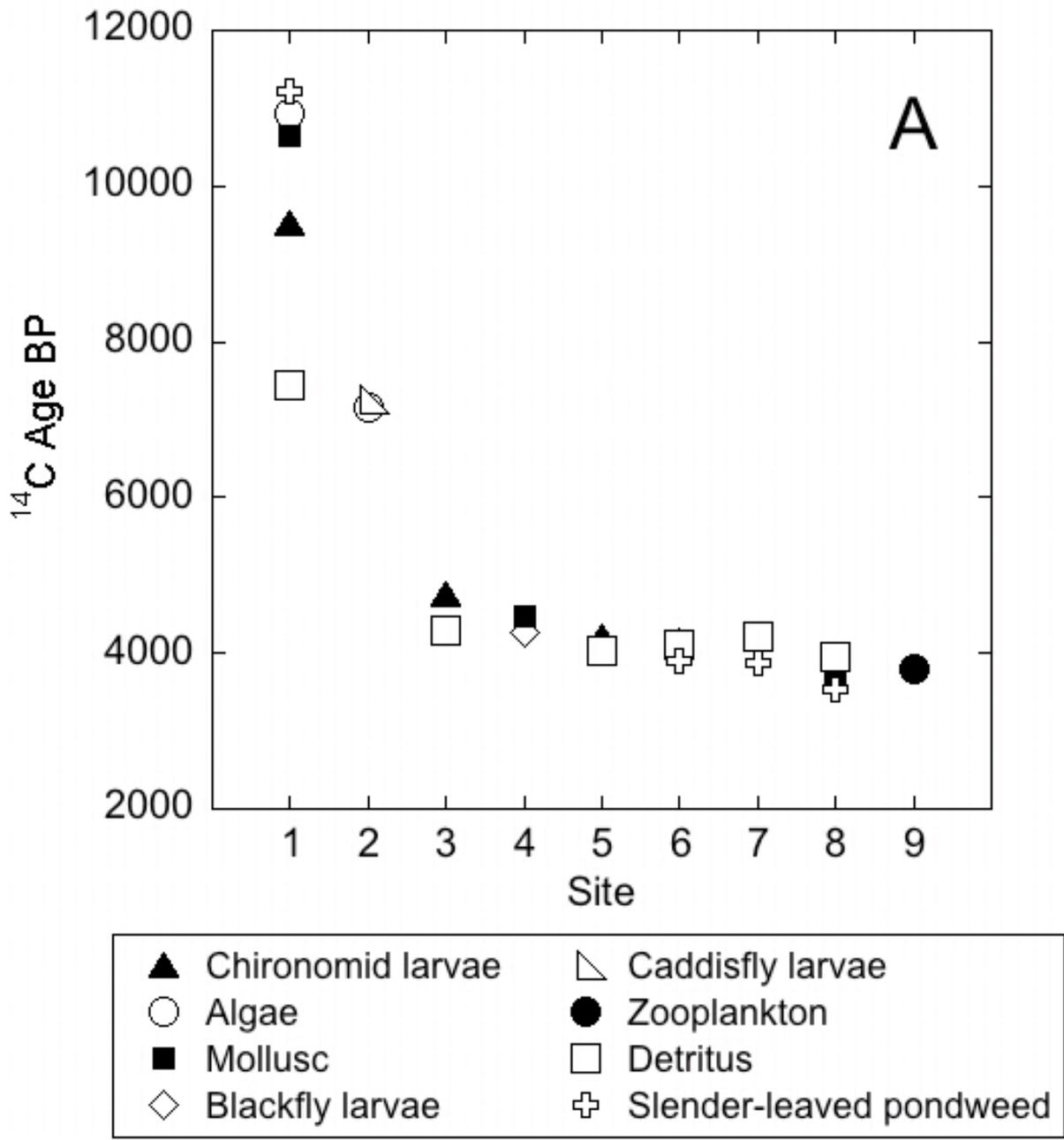
Figure 2A: Relationship of FRE value versus sampling location for all sample sites. Sites: 1 = Helgavogur; 2 = Grjotavogur; 3 = Station 33; 4 = Laxá; 5 = Station 95; 6 = North Basin Deep; 7 = Station 13; 8 = Station 128; 9 = Near Hrútey.
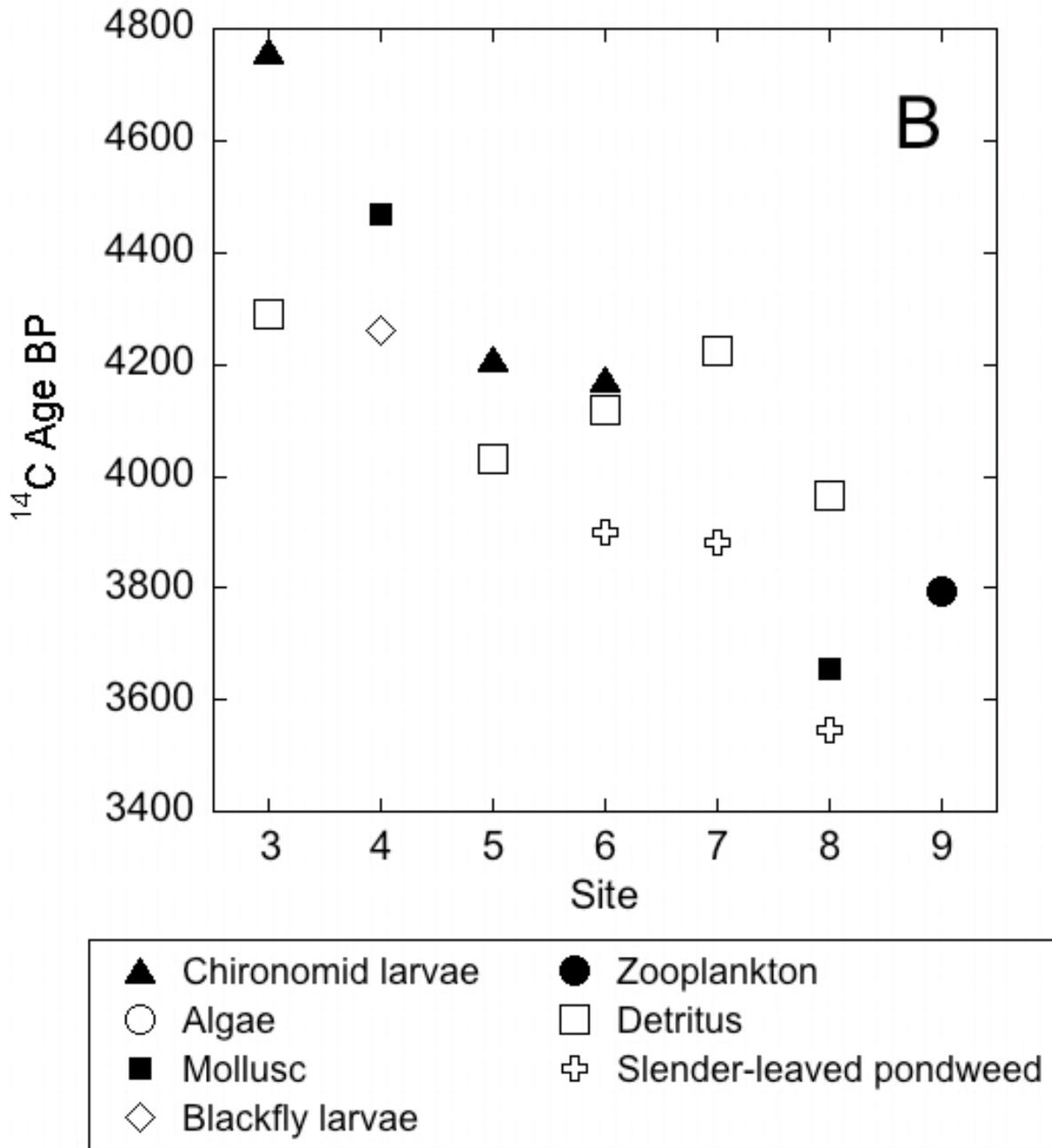
Figure 2B: Relationship of FRE value versus sampling location for sample sites excluding groundwater spring sites (i.e. Helgavogur and Grjotavogur). Sites: 3 = Station 33; 4 = Laxá; 5 = Station 95; 6 = North Basin Deep; 7 = Station 13; 8 = Station 128; 9 = Near Hrútey.
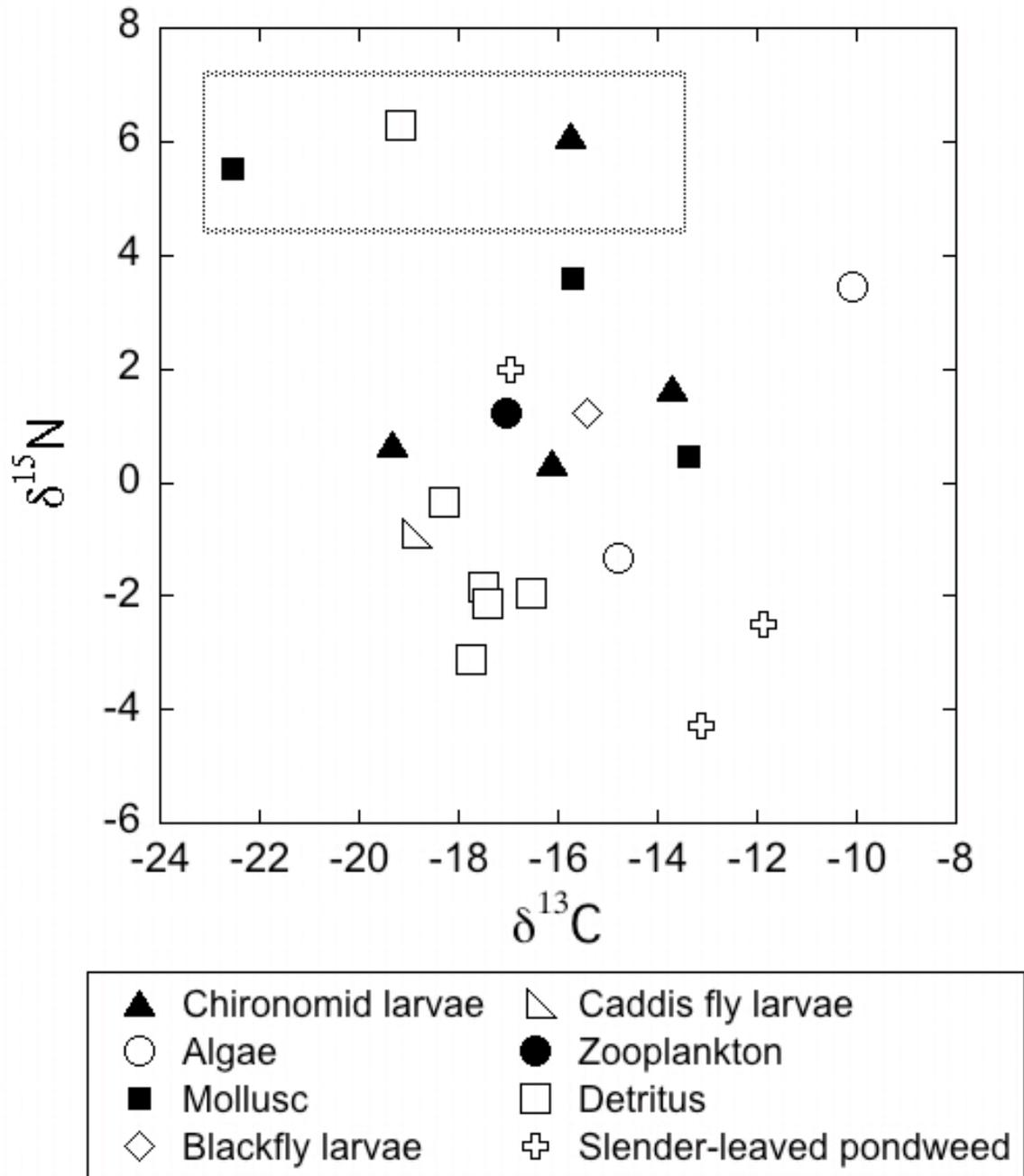
Figure 3: δ^{13}C versus δ^{15}N for samples, dashed box highlights the high δ^{15}N values for Helgavogur relative to those of material from other sampling locations. The extreme low δ^{15}N value for slender-leaved pondweed from the N. Basin deep site is excluded for clarity.
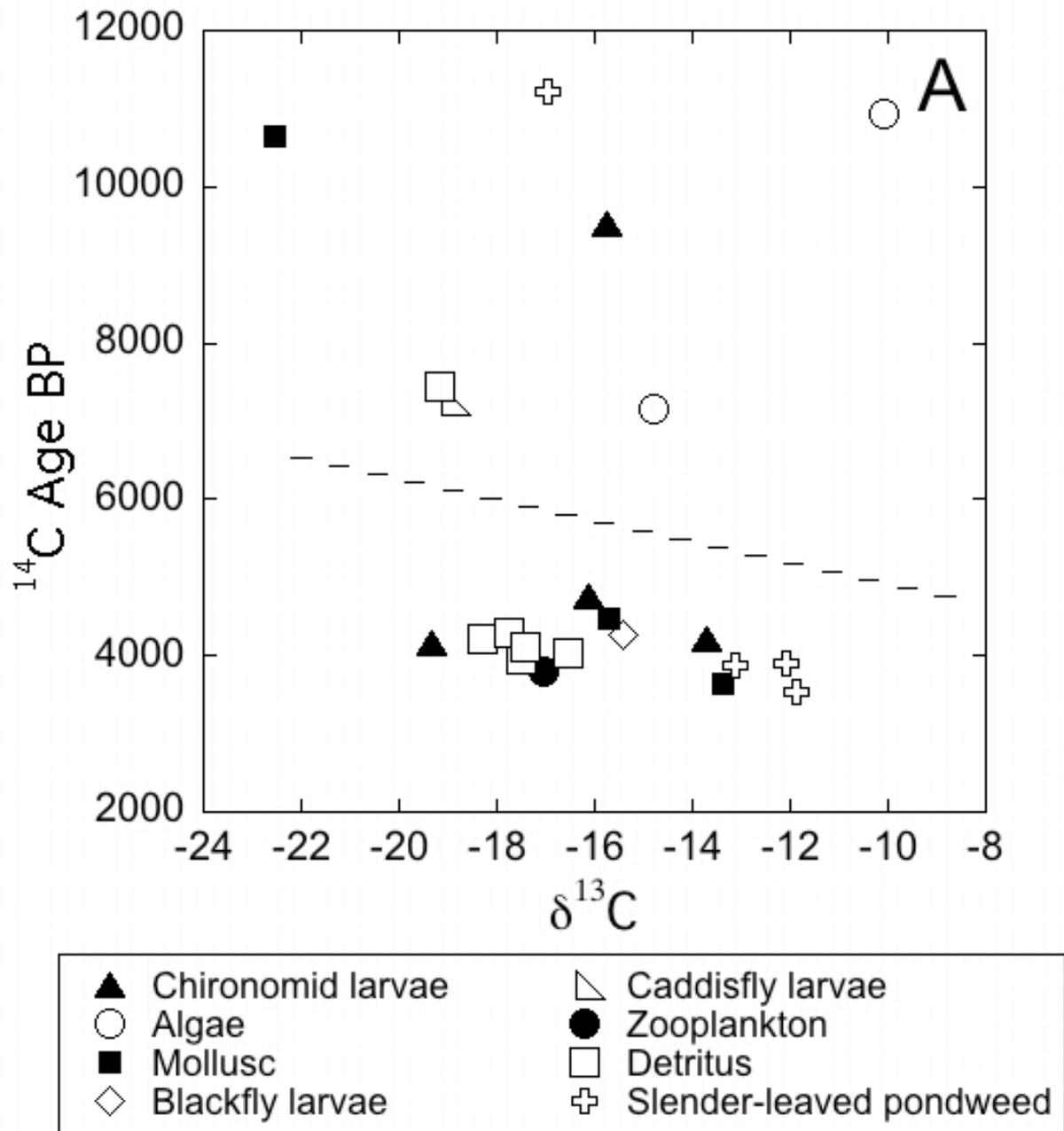
Figure 4A: Relationship of FRE versus δ^{13}C for all sample sites. Dashed line shows linear regression. (R = 0.17, N.S).
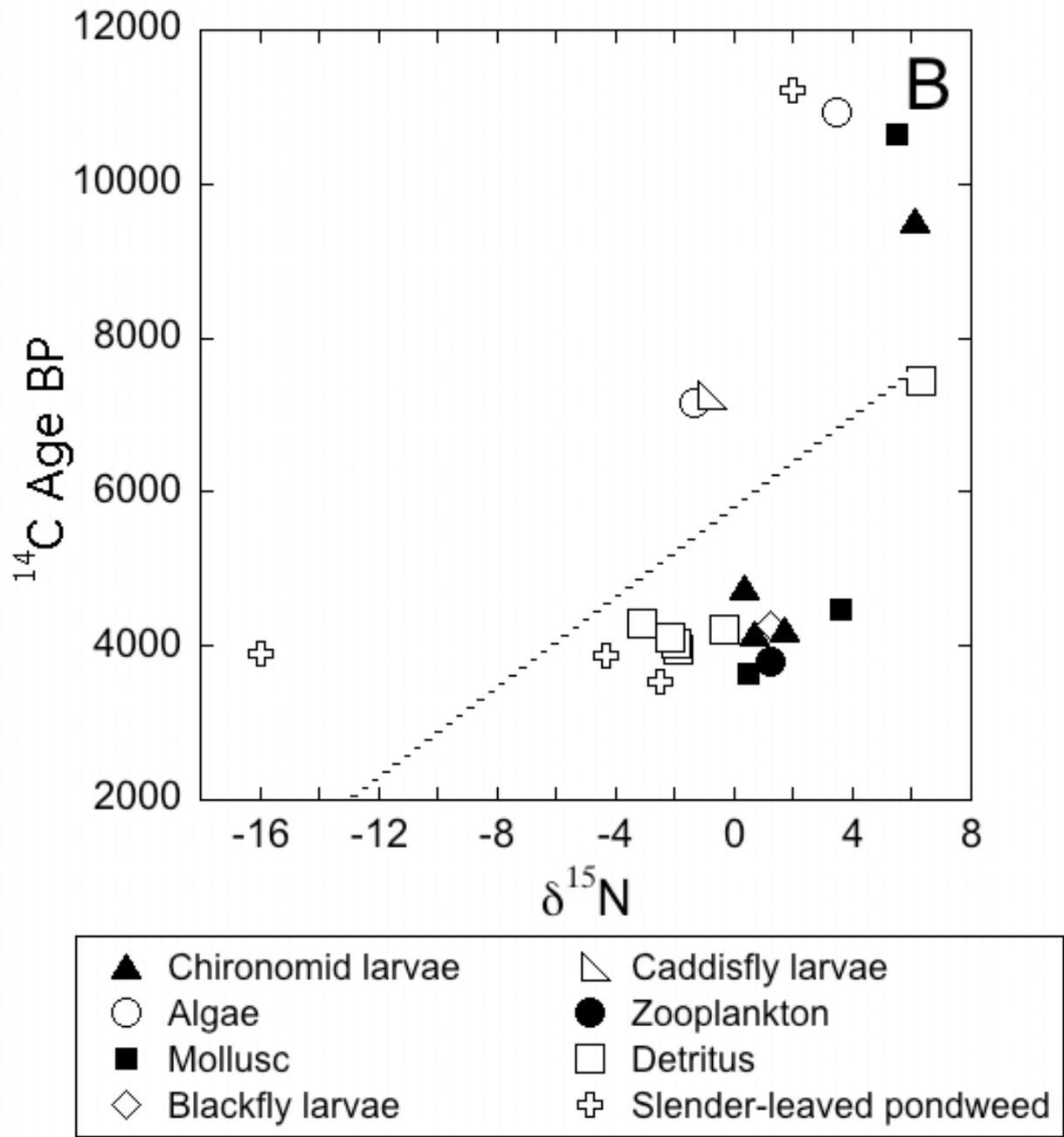
Figure 4B: Relationship of FRE versus $\delta^{15}N$ for all sample sites. Dashed line shows linear regression, (R = 0.51, P <0.05).

Material	Sampling sites	Collection method
Lake benthic detritus	Station 128	Drop-coring
	Station 13	
	Station 33	
	Station 95 Helgavogur	
	N. Basin deep	
Algae (*Cladophora spp.*)	Grjotavogur	Scraping from rocks
	Helgavogur	
Aquatic plant (*Potmogeton filiformis*)	Helgavogur	Hand-collected
	N. Basin deep	
	Station 13	
	Station 128	
Caddis fly larvae (*Apatania zonella*)	Grjotavogur	Brushing and picking by hand
Blackfly larvae (*Simulium vittatum*)	Dragsey (Laxá)	Brushing and picking by hand
Chironomid larvae (*Tanytarsus gracilentus*)	Helgavogur	Drop-coring
	N. Basin deep	
	Station 33	
	Station 95	
Zooplankton (*Daphnia longispina*)	near Hrútey	Zooplankton net
Mollusc (*Radix peregra*)	Helgavogur	Brushing and picking by hand
	Station 128	
	Dragsey (Laxá)	

Table 1: Summary of samples collected for analysis

Reporting Number	Sample Type (common)	Latin name	Site	Sample	Gas aliquot δ^{13}C (‰)*	Fm** ± 1σ	^{14}C Age ± 1σ	δ^{13}C (‰)	δ^{15}N (‰)
SUERC-27059	Detritus	-	Station 128	M-68	-17.5	0.6106 ± 0.0019	3965 ± 30	-17.5	-1.9
SUERC-27056	Detritus	-	Station 13	M-65	-17.4	0.5909 ± 0.0015	4225± 30	-18.3	-0.4
SUERC-27057	Detritus	-	Station 33	M-66	-17.7	0.5863 ± 0.0018	4290 ± 30	-17.7	-3.1
SUERC-27058	Detritus	-	Station 95	M-67	-16.0	0.6056 ± 0.0018	4030 ± 30	-16.5	-2.0
SUERC-27060	Detritus	-	Helgavogur	M-69	-18.5	0.3958 ± 0.0012	7445 ± 30	-19.2	+6.3
SUERC-27061	Detritus	-	N. Basin deep	M-70	-17.2	0.5989 ± 0.0018	4120 ± 30	-17.4	-2.1
SUERC-27067	Algae	Cladophora spp.	Grjotavogur	M-83	-14.5	0.4101 ± 0.0011	7160 ± 30	-14.8	-1.3
SUERC-27066	Algae	Cladophora spp.	Helgavogur	M-81	-10.4	0.2567 ± 0.0009	10925 ± 35	-10.1	+3.4
SUERC-27079	Slender-leaved pondweed	P. filiformis	Helgavogur	M-139	-16.6	0.2475 ± 0.0009	11215 ± 35	-16.9	+2.0
SUERC-27080	Slender-leaved pondweed	P. filiformis	N. Basin deep	M-143	-12.0	0.6153 ± 0.0017	3900 ± 30	-12.1	-16.0
SUERC-27077	Slender-leaved pondweed	P. filiformis	Station 13	M-133	-12.3	0.6169 ± 0.0015	3880 ± 30	-13.1	-4.3
SUERC-27078	Slender-leaved pondweed	P. filiformis	Station 128	M-134	-11.3	0.6431 ± 0.0015	3545 ± 25	-11.9	-2.5
SUERC-27072	Caddisfly larvae	Apatania zonella	Grjotavogur	M-124	-18.7	0.4054 ± 0.0011	7255 ± 30	-19.0	-0.9

SUERC-27062	Blackfly larvae	Simulium vittatum	Dragsey (Laxá)	M-77	-15.1	0.5883 ± 0.0018	4260 ± 30	-15.4 +1.2
SUERC-27070	Chironomid larvae	Tanytarsus gracilentus	Helgavogur	M-115	-15.8	0.3054 ± 0.0010	9530 ± 35	-15.8 +6.1
SUERC-27071	Chironomid larvae	Tanytarsus gracilentus	N. Basin deep	M-120	-20.9	0.5946 ± 0.0015	4175 ± 30	-19.3 +0.7
SUERC-27068	Chironomid larvae	Tanytarsus gracilentus	Station 33	M-103	-15.5	0.5528 ± 0.0017	4760 ± 30	-16.1 +0.4
SUERC-27069	Chironomid larvae	Tanytarsus gracilentus	Station 95	M-111	-14.6	0.5922 ± 0.0016	4210 ± 30	-13.7 +1.7
SUERC-27076	Zooplankton	Daphnia longispina	near Hrútey	M-125	-16.5	0.6233 ± 0.0017	3795 ± 30	-17.0 +1.2
SUERC-27082	Mollusc	Radix peregra	Helgavogur	M-146	-22.8	0.2654 ± 0.0008	10655 ± 30	-22.6 +5.5
SUERC-27086	Mollusc	Radix peregra	Dragsey (Laxá)	M-149	-15.6	0.5731 ± 0.0018	4470 ± 30	-15.7 +3.6
SUERC-27081	Mollusc	Radix peregra	Station 128	M-145	-13.0	0.6346 ± 0.0017	3655 ± 30	-13.4 +0.5

Table 2: Results of stable isotope (δ^{13}C and δ^{15}N) and radiocarbon (^{14}C) analysis on samples from sites within Lake Mývatn. Note that the δ^{13}C values used for normalization of the ^{14}C AMS measurements are also provided.