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INVESTIGATING POTENTIAL C14-CONTAMINANTS DURING PROCESSING AND STORAGE OF ARCHAEOLOGICAL PLANT AND INSECT SAMPLES

Becky Briant, Department of Geography, Birkbeck, University of London, Malet Street, London, WC1E 7HX b.briant@bbk.ac.uk
Philippa Ascough, Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF Philippa.ascough@glasgow.ac.uk
Fiona Brock, Cranfield Forensic Institute, Cranfield University, Defence Academy of the United Kingdom, Shrivenham, SN6 8LA f.brock@cranfield.ac.uk
David Smith, Classics, Ancient History and Archaeology, University of Birmingham, Edgbaston, Birmingham, B15 2TT d.n.smith@bham.ac.uk

Background and rationale

There is concern in the archaeological community to reduce the use of chemicals that contain carbon compounds in plant and insect sample processing and storage. This is to avoid contamination of samples that are otherwise valuable for ^{14}C measurement. These chemicals (e.g. paraffin, ethanol, glycerine) potentially introduce carbon that has a different ^{14}C age to that of the sample into the sample matrix. If this carbon cannot be removed during pretreatment, it will compromise the accuracy of a sample ^{14}C measurement. Yet, these chemicals have significant value for processing and storage (e.g. Rousseau, 2011), significantly reducing sample preparation time and enabling archive samples to be stored and studied at a later date. Whilst individual projects have both successfully dated material after periods of storage (e.g. Zazula *et al.*, 2009) and removed other preservatives (e.g. Brock *et al.*, 2018; Dee *et al.*,

Figure 1. Fieldwork at a) Windsor Great Park; b) Dunham Massey.

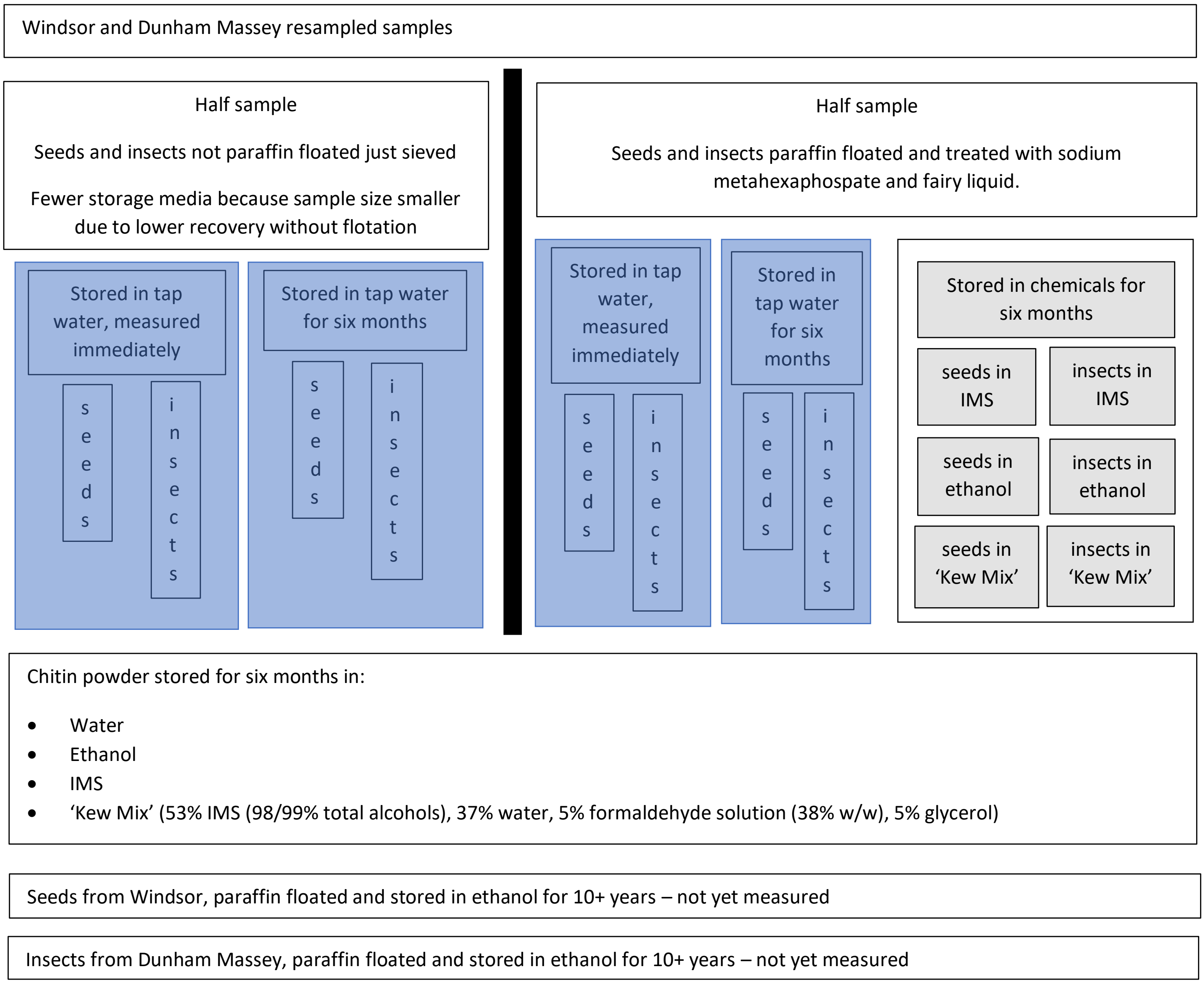

Figure 2. Experimental workflow. Paraffin flotation after Kenward *et al.* (1980) and Rousseau (2011) and 'Kew Mix' mixed as in Natural Science Collections Association (2019).

2011), there has been no systematic chemical analysis of this particular problem.

We have undertaken a series of experiments on modern-day seeds and insects designed to address this problem. Samples that have been paraffin-floated (after Kenward *et al.*, 1980; Rousseau, 2011) and stored in ethanol for c. 10 years (since work reported in Smith *et al.*, 2010) will be compared with recently resampled material from identical locations that have been subjected to a range of controlled treatment and storage protocols. Fieldwork was undertaken in July 2022 at Bears Rails Pond, Windsor Great Park and Smithy Pond, Dunham Massey to resample these locations (Figure 1). Samples have been processed and stored as shown in Figure 2.

After the various periods of storage, Fourier transform infrared (FTIR) spectroscopy was undertaken on these samples and on chitin soaked in each relevant chemical, to determine whether traces of processing chemicals are retained in the sample matrix. In this way we aimed to fully characterise the spectra and monitor the removal of processing chemicals. This technique was trialled on previous archive samples before undertaking this project and it suggested both that FTIR could be used for investigation and that there was significant loss of solvents after only 10-15 minutes of air drying.

Initial results

Whilst not all samples and treatments have yet been assessed, initial results suggest that paraffin is the chemical used on the samples that is most likely to be detectable on samples using FTIR, possibly because it is less volatile than the solvents used for storage. The key area of interest in all spectra is between 3000 and 2700 cm^{-1}. Figure 3a shows clearly that paraffin has three distinctive peaks in this region that are

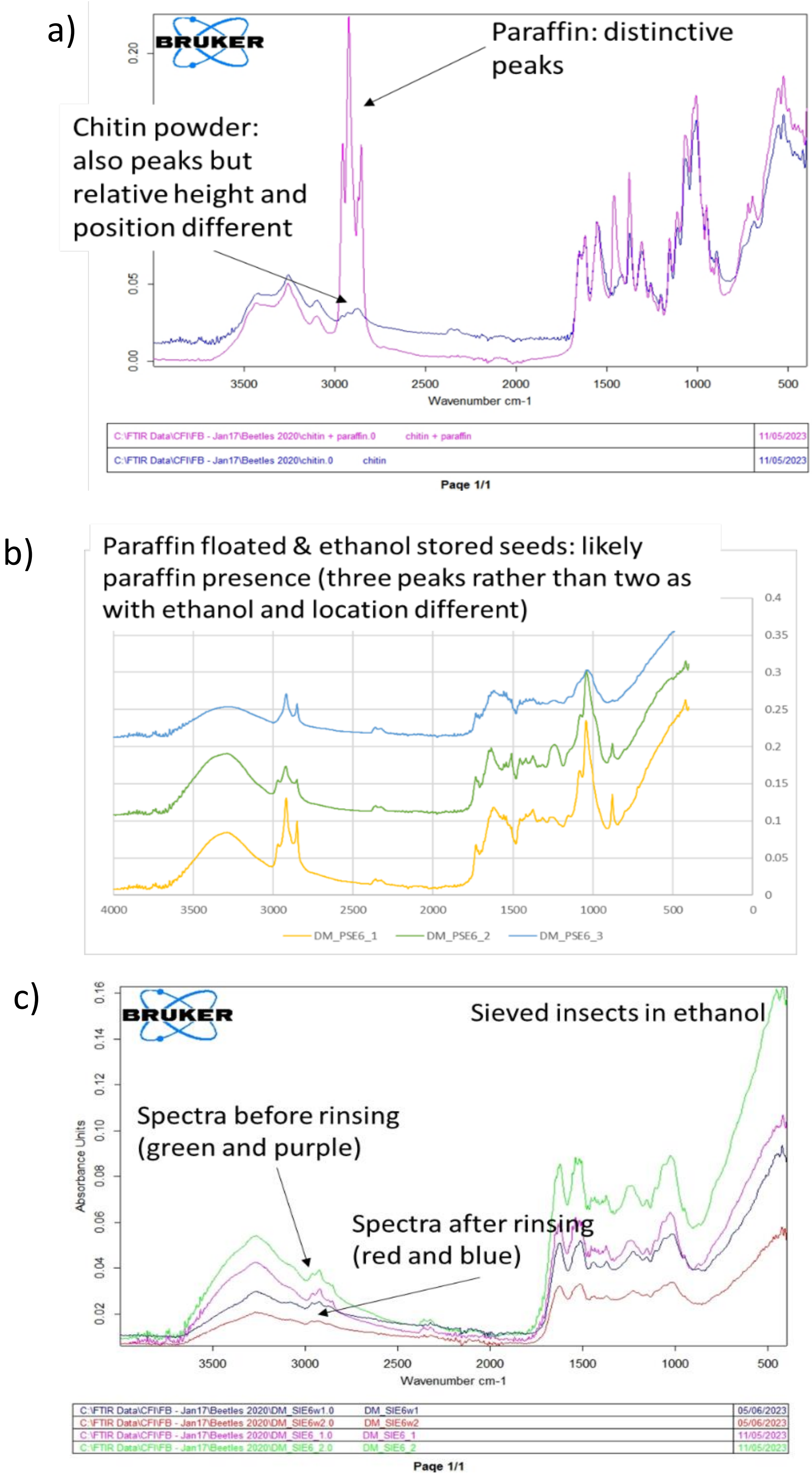

Figure 3. Initial results from FTIR spectroscopy on samples from Dunham Massey: a) baseline spectra for chitin powder (used to replicate insects) and paraffin, b) spectra for seeds sieved with paraffin flotation and stored in ethanol, c) spectra for insects water rinsed and freeze dried after sieving and storage in ethanol.

different from those seen in the chitin powder. These peaks are also different from those in ethanol, which has only two peaks in the same region. Similar peaks are sometimes seen in samples that have been paraffin floated (Figure 3b), although not all samples show evidence of retained paraffin. More experiments and measurements are planned, but Figure 3c suggests that the water rinse and subsequent freeze dry used in all radiocarbon dating preparation protocols is very effective at removing excess chemicals.

Further work remains to be done on samples from Windsor (although recovery rates were lower from this location) and also on these samples from Dunham Massey, based on the initial findings presented above. However, these findings presented already show the power of FTIR spectroscopy in accurately tracking potential contamination.

Significance

This project has important implications for the workflows used in environmental archaeology. If researchers can be confident that paraffin-floated samples of seeds are not contaminated and can still be ^{14}C dated it will significantly increase the efficiency of sample processing. It is possible based on these initial results that this might be the case, but more work is needed to conclude this robustly.

Acknowledgments

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