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MINIMALLY DESTRUCTIVE RADIOCARBON DATING OF CAPRINE DUNG

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ABSTRACT. Archaeological dung pellets are time capsules of ancient herbivore diets and gut flora, informing on past agropastoral activity, ecology, and animal health. Improving multi-proxy approaches is key to maximizing this finite archaeological resource. Through experiments with standard pretreatments used in radiocarbon (^{14}C) dating, we address a fundamental problem in maximal multi-proxy analysis: How to chronometrically date individual caprine pellets while conserving as much as possible for additional analyses? We applied acid-alkali-acid (AAA) or acid-only pretreatments to 37 samples of ancient and recent sheep/goat dung pellets from sites in the Negev desert, Israel, measuring weight-loss due to pretreatment. Shavings of outer surfaces and remaining inner pellets of four pairs were dated and compared. We found that (i) sample-specific factors affect pretreatment survivability, including preservation quality and initial sample size; (ii) given sufficient start weight, AAA can be used to pretreat sheep/goat coprolites; (iii) 100 mg appeared a desirable minimum sample weight before pretreatment; and (iv) shavings of coprolites' outer surface produced ^{14}C dates equivalent to dates obtained from inner coprolites. Whereas standard coprolite analysis protocols discard shavings removed from outer surfaces to avoid contamination, our findings indicate their efficacy for ^{14}C dating. This offers an important addition to workflows for multi-proxy coprolite analysis.

KEYWORDS: archaeology, coprolite, herbivore dung, multi-proxy method, pretreatment, radiocarbon.

INTRODUCTION

Coprolites, or ancient feces, are increasingly under investigation by researchers interested in records of past economy, environment, and evolution (Hunt et al. 2012; Qvarnström et al. 2016; Shillito et al. 2020). A variety of techniques are employed in coprolite analysis (e.g., Miller 1984; Poinar et al. 1998; Kühn et al. 2013; Linseele 2013; Camacho et al. 2018; Égüez and Makarewicz 2018; Sistiaga et al. 2014; Perrotti and van Asperen 2019; Zhang et al. 2019; Wood et al. 2020), and many studies apply multiple techniques to different coprolites in an assemblage (Reinhard and Bryant 1992; di Lernia 2001; Delhon et al. 2008; Shahack-Gross 2011; Marinova et al. 2013; Pineda et al. 2017; Baeten et al. 2018; Landau et al. 2020). Yet the full benefits of the multi-proxy approach will be realized when different complementary analyses are applied to each individual coprolite investigated, making the most of this finite archaeological resource (Fuks and Dunseth 2021). Meanwhile, multi-proxy approaches to analyzing individual coprolites are being employed and refined (Dunseth et al. 2019; Jouy-Avantin et al. 2003; Rifkin et al. 2020; Romaniuk et al. 2020; Polling et al. 2021; Velázquez et al. 2021). Human coprolites and those of other large mammals are often big enough to be subdivided such that each coprolite subsample is used for a different analysis or for a repetition of the same analysis, and much discussion concerns optimal subsampling strategies (Beck et al. 2019). Another standard procedure in coprolite studies is removal of the outer surface to reduce contamination (Wood and Wilmshurst 2016). However, these procedures present problems for multi-proxy analysis of individual livestock coprolites,

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particularly sheep/goat pellets, which are the most common type of dung in “Old-World” archaeology, and which have added research value as indicators of rangeland vegetation, seasonality, and pastoral practices (Akeret et al. 1999; Ghosh et al. 2008; Fuks and Dunseth 2021).

First, subdividing individual sheep/goat pellets for different analyses may sacrifice representativeness to the point of being counterproductive. Second, removing the outer surface significantly reduces the size of the starting sheep/goat pellet sample (as shown in this study), leaving even less material for subsampling and analysis. One solution is to maximize the number of analyses that can be applied *in series* to a single pellet. Thus, non-destructive analyses (description, weighing, imaging, NIR spectroscopy), could be followed by semi-destructive analyses (dissecting for plant macrofossils, FTIR spectroscopy) and fully destructive analyses in turn (pollen, phytolith, dietary fiber, lipid, protein, and DNA analyses). Yet this still leaves the sizable outer surface as unusable discard. Meanwhile, the richer and more interesting the information gleaned from coprolite analyses, the greater the need to establish its antiquity through direct radiocarbon dating. This creates a third problem in adopting a multi-proxy approach: there is no guarantee that an individual sheep/goat dung pellet can be directly dated *and* subjected to additional destructive analyses. Thus, *a priori* subdivision of individual caprine pellets for radiocarbon and other analyses risks sacrificing this scarce resource and producing no results.

We addressed these problems by exploring possibilities for minimally destructive radiocarbon dating of sheep/goat dung pellets preserved by desiccation in Israel’s Negev desert. Our primary research question was, how can an individual caprine pellet be chronometrically dated while preserving as much of it as possible for additional analyses? To answer this question, we conducted experiments on standard pretreatments used in radiocarbon analysis applied to desiccated dung pellets from three archaeological sites in the region. Our ultimate objective was to achieve minimally destructive reliable radiocarbon dating of dung pellet samples. The following specific research questions guided the experimental design:

- Which sample-specific factors are related to pretreatment losses and survivability?
- Which pretreatment (acid-alkali-acid or acid-only) best balances survivability and reliability?
- What is a minimal dung sample start weight for reliable radiocarbon dating?
- Can shavings of a coprolite’s outer surface be used to produce a reliable date?

METHODS

Sample Retrieval and Preparation

Analyzed coprolites derived from three sites in the Negev desert, Israel: Avdat (*Oboda, Abde*); Orhan Mor (*Moyat Awad*) and Nahal Omer (Table 1). The copious dung remains from these sites were variously preserved, often in semi-compacted dung layers or pulverized. We selected only uncharred intact pellets for analysis.

Archaeological coprolites from Avdat were retrieved in the 2016 excavation of the *Avdat in Late Antiquity Project* by Scott Bucking and Tali Erickson-Gini, which yielded hundreds of dung pellets (Bucking 2017; Bucking and Erickson-Gini 2020; Bucking et al. 2022; Erickson-Gini 2022). The particular coprolite assemblage used in this study was preserved by desiccation

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Table 1 Sample sites and contexts.

Label	Site	Collection date	Area	Locus	Basket	Context	Period
OBD-rec-2018	Avdat	2018	—	—	—	Acropolis ground collection	Modern
OBD-2016-L101-B4	Avdat	2016	A	101	4	Collapse layer	Late Islamic
OMR-2020-L103-B10033b	Nahal Omer	2020	A	103	10033b	Midden upper dung layer	Early Islamic
OMR-2020-L107-B17001	Nahal Omer	2020	A	107	17001	Midden lower dung layer	Early Islamic
OMR-2020-L203-B2031a	Nahal Omer	2020	B	203	2031a	Midden	Early Islamic
MOA-2020-L630-B6304	Orhan Mor	2020	F	630	6304	Mixed organic assemblage on slope	Roman(?)

Figure 1 Sheep/goat dung pellets from the late-medieval Avdat assemblage (OBD-2016-L101-B4).

and comes from a sealed collapse layer dated to the late-medieval, or local Late Islamic period (Table 1, Figure 1) by whole sheep/goat dung pellet (UBA-47071, 418 ± 22 BP, 1σ 1445–1470 cal CE; following acid-only pretreatment). In addition, modern dung pellets collected by the author (D.F.) in 2018 from the ground of Avdat's acropolis were used in the first batch of pretreatment experiments.

Coprolites from Orhan Mor and Nahal Omer were retrieved by the author (D.F.) in February 2022 during the Negev Camel Caravan Project excavation headed by Guy Bar-Oz and Roy Galili (Galili et al. 2021; Bar-Oz et al. 2022). The Nahal Omer pellets appeared exceptionally preserved by desiccation and derive from two different Early Islamic rubbish middens: Areas A and B of the 2020 excavations. The Orhan Mor coprolites come from a small hillside mixed organic assemblage whose ceramics suggest a 3rd c. CE terminus, or the local Roman period. Unlike the other contexts, however, this one was not well-stratified or sealed, and a later intrusion of dung pellets cannot be ruled out.

Over 100 pellets and pellet fragments from these contexts were individually prepared in the Pitt Rivers Laboratory of the McDonald Institute for Archaeological Research at the University of Cambridge. Each pellet/fragment was individually weighed and photographed, and observations of external preservation and color were recorded (Figure 2; Supplementary Table 1). Shaving of the outer surface, including any folds or cracks in contact with the encasing sediment, was performed on some of the fully intact pellets (Figure 3). This was conducted manually with a scalpel and tweezers, and all equipment was sprayed and wiped between pellets with an ammonium-chloride-based laboratory disinfectant. External shavings and the remaining inner part were stored in separate glass vials for each pellet and labeled accordingly.

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Figure 2 Intact sheep/goat dung pellet from late-medieval Avdat (OBD-2016-L101-B4-P8).

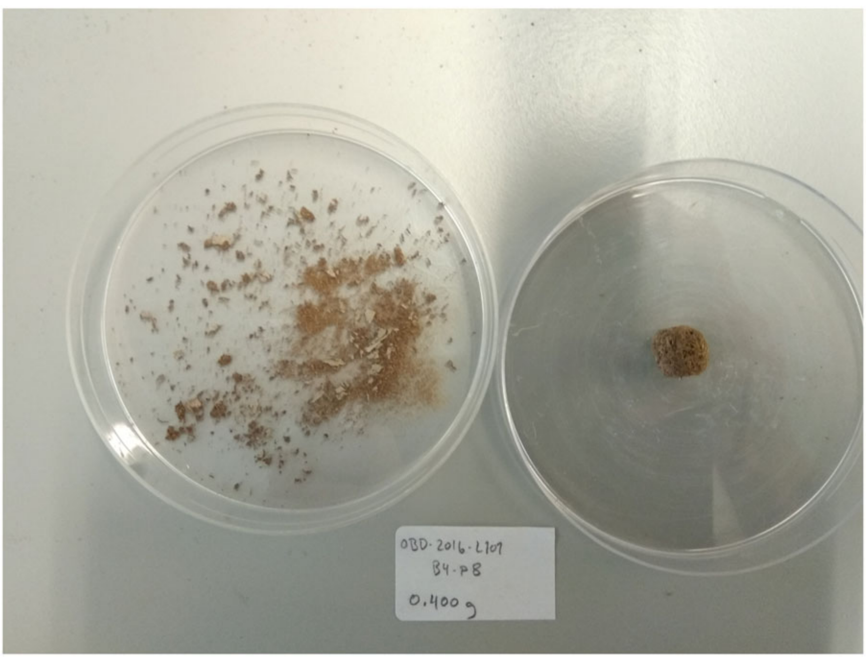

Figure 3 Outer shavings (left) and the remaining inner part (right) of a sheep/goat dung pellet from late-medieval Avdat (OBD-2016-L101-B4-P8-ex and OBD-2016-L101-B4-P8-in).

Pretreatment

Samples were brought to the ^{14}CHRONO Centre for Climate, the Environment & Chronology at Queen's University, Belfast, where they were further selected from among the originally intact pellets for pretreatment experiments (Supplementary Table 2). Shaving of the outer surfaces was performed on additional select pellets. Acid-alkali-acid (AAA) pretreatment was selected for Batches 1–3 because the alkali step removes potentially contaminating humic acids whereas acid-only pretreatment removes only carbonates. AAA consisted of the following steps:

- *Acid* – Sample placed in a polypropylene 50-mL test-tube solution of 0.1M HCl. Test-tubes placed in 80°C bath for 20 minutes.
- *Centrifuge and wash* – Test-tubes centrifuged using a SciQuip Sigma 4–5-L centrifuge at 3000 revloutions/min for 3 min. Supernatant fluid decanted and pellet/precipitate retained. Tubes then filled with deionized water, spun, and decanted 3 more times.
- *Alkali* – 25 mL of 0.25M NAOH solution in 80ºC bath.
- *Centrifuge and wash* – same as above. Note: Only one alkali rinse was needed as little color was removed in these samples.
- *Acid* – 1M HCl, 80ºC bath for 20 min.
- *Centrifuge and wash* – same as above.
- *Drying* – Samples were dried overnight at 75ºC.

In Batch 1, AAA pretreatments were conducted on six pairs of modern pellet samples (from OBD-rec-2018), where each pair included the external shavings and the remaining inner part of the pellet (P_{ex} and P_{in}). Preliminary observations at the alkali stage suggested sufficient survivability to continue using AAA.

In Batch 2, the experiment was repeated for one pair of late-medieval Avdat external pellet shavings (OBD-2016-L101-B4-P7-ex) and inner pellet (OBD-2016-L101-B4-P7-in). External shavings of five pellets from Roman(?) Orhan Mor (MOA-2020-L630-B6304) and five pellets from Early Islamic Nahal Omer, Area B (OMR-2020-L203-B2031a) were also tested. Preliminary observations at the Alkali stage suggested insufficient survivability for the Orhan Mor samples.

In Batch 3, a pair of external and internal pellet samples from an upper layer of Early Islamic Nahal Omer, Area A (OMR-2020-L103-B10033b) and from a lower layer (OMR-2020-L107-B17001) were tested with AAA pretreatment. Another pair of external and internal pellet samples from late-medieval Avdat (OBD-2016-L101-B4-P8-ex and OBD-2016-L101-B4-P8-in) was also tested.

In Batch 4, three pairs of whole pellets were selected from Orhan Mor and Nahal Omer to compare loss from acid-only against AAA pretreatments. These were performed with the same solutions described above but without hot baths.

Data was collected on start weights and end weights after drying for all samples, and qualitative observations of color and fibrousness were additionally considered to predict whether sufficient carbon content remained for radiocarbon measurement by AMS (Supplementary Table 2).

Table 2 Samples dated from Batches 2 and 3.

Excavation	Locus-Basket	Pellet	Internal	External
OMR-2020	L203-B2031a	P3	in	ex
OMR-2020	L103-B10033b	P1	in	ex
OMR-2020	L107-B17001	P1	in	ex
OBD-2016	L101-B4	P8	in	ex

AMS Dating

In order to test the reliability of dates retrieved from the outer surface of dung pellets, we dated eight samples from Batches 2 and 3 consisting of external shavings and the remaining inner part for four pellets (Table 2):

As a guide to the labeling system used below note that OBD-2016-L101-B4-P8, for example, refers to dung pellet 8 from Locus 101, Basket 4, of the 2016 Avdat (Oboda) excavations (see also Table 1). OBD-2016-L101-B4-P8-ex refers to that pellet's external shavings whereas OBD-2016-L101-B4-P8-in refers to its inner part (Figure 3).

The dried samples were weighed in pre-purified tin capsules and burned in oxygen with helium carrier gas in the element analyzer (Elementar Vario Isotope), then transferred to the AGE3 automated graphitization system, which uses the hydrogen reduction method (Němec et al. 2010). The prepared graphite was compressed into vacuum-cleaned aluminum holders and placed in an AMS magazine. The ratios $^{14}C/^{12}C$ and $^{13}C/^{12}C$ were measured using accelerator mass spectrometry (AMS) in the Ionplus Mini Carbon Dating System (MICADAS). The sample $^{14}C/^{12}C$ ratio was background corrected and normalised to the HOXII standard (SRM 4990C; National Institute of Standards and Technology). The radiocarbon ages were corrected for isotope fractionation using the AMS measured $\delta^{13}C$ which accounts for both natural and machine fractionation. The radiocarbon age and one standard deviation were calculated using the Libby half-life of 5568 years following the methods of Stuiver and Polach (1977).

RESULTS

Outer Shavings

Weights of the original intact pellets (P) and of the external shavings (P_{ex}) of 20 pellets used in this study appear in Table 3. The proportion of the external shavings' weight over whole pellet weight (P_{ex}/P), ranged from 18% to 64% with a mean of 37% and a standard deviation of 11% (n=20). These values varied among sample groups: For all recent and late-medieval pellets from Avdat, P_{ex}/P was under 35% whereas for all Early Islamic pellets from Orhan Mor it was above 35%. Three pellets from Orhan Mor had P_{ex}/P values of above 45% whereas the remaining two from Orhan Mor were 37% and 42%. P_{ex}/P ranged from 30–45% for all Nahal Omer pellets. These results reflect observed sample-specific differences in whole pellet preservation quality. In most of the recent pellets, the outer layer could be peeled off with the scalpel, whereas the Orhan Mor pellets had a tendency to crumble. Pellets from Nahal Omer and late-medieval Avdat were fairly rigid but not as easily shaven as the recent pellets.

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Table 3 Weights of whole pellets and external shavings.

Label	Batch	P wt (g)	P_{ex} wt (g)	P_{ex}/P
OBD-rec-2018-P25	1	0.22	0.073	33%
OBD-rec-2018-P26	1	0.20	0.068	34%
OBD-rec-2018-P27	1	0.24	0.082	34%
OBD-rec-2018-P11	1	0.36	0.108	30%
OBD-rec-2018-P12	1	0.35	0.095	27%
OBD-rec-2018-P8	1	0.38	0.093	24%
OBD-2016-L101-B4-P7	2	0.260	0.048	18%
MOA-2020-L630-B6304-P4	2	0.114	0.064	56%
MOA-2020-L630-B6304-P5	2	0.097	0.036	37%
MOA-2020-L630-B6304-P6	2	0.100	0.046	46%
MOA-2020-L630-B6304-P7	2	0.097	0.041	42%
MOA-2020-L630-B6304-P8	2	0.129	0.082	64%
OMR-2020-L203-B2031a-P1	2	0.145	0.044	30%
OMR-2020-L203-B2031a-P2	2	0.165	0.074	45%
OMR-2020-L203-B2031a-P3	2	0.320	0.127	40%
OMR-2020-L203-B2031a-P4	2	0.204	0.087	43%
OMR-2020-L203-B2031a-P5	2	0.193	0.077	40%
OMR-2020-L103-B10033b-P1	3	0.273	0.092	34%
OMR-2020-L107-B17001-P1	3	0.231	0.098	42%
OBD-2016-L101-B4-P8	3	0.397	0.114	29%

Pretreatment

Figure 4 presents weight loss due to pretreatment by sample (see also Supplementary Tables 3–4). Of 37 pretreated samples, two yielded end weights larger than those of the original sample and were rejected as measuring or recording errors. Of the samples undergoing AAA pretreatment, weight-loss ranged from 58–100%, with a mean of 78% and standard deviation of 13% (n=32). As with the external shavings' relative weights, weight losses due to pretreatment varied by assemblage:

For the recent Avdat pellet samples used in Batch 1, weight losses ranged from 58–76%, with a mean of 65% and standard deviation of 6% (n=10; based on 6 inner pellets and 4 associated external shavings). To formulate a working assumption regarding minimum datable sample size, we used a previously AMS-dated late-medieval Avdat dung pellet (UBA-47071) where carbon content measured 60.54% (Table 4). At this carbon content, we estimated a minimum sample weight for radiocarbon dating following pretreatment as 1 mg for compatibility with the AGE3 regular sample size setup, but we considered 2–4 mg to be preferable in the event of higher weight loss in pretreatment. In Batch 1, end weights were all well above this threshold ($\geq$ 20 mg) and we therefore continued to experiment with AAA pretreatment in Batches 2 and 3. However, subsequent batches displayed different pretreatment survivability ranges and means, which varied according to site and starting weight.

Four late-medieval Avdat pellet sample losses ranged from 63–79%, within the range of the recent Avdat pellets. By contrast, pellets from Orhan Mor undergoing AAA pretreatment had effective total losses in four out of five AAA pretreatments ($\geq$97%, with end weights of

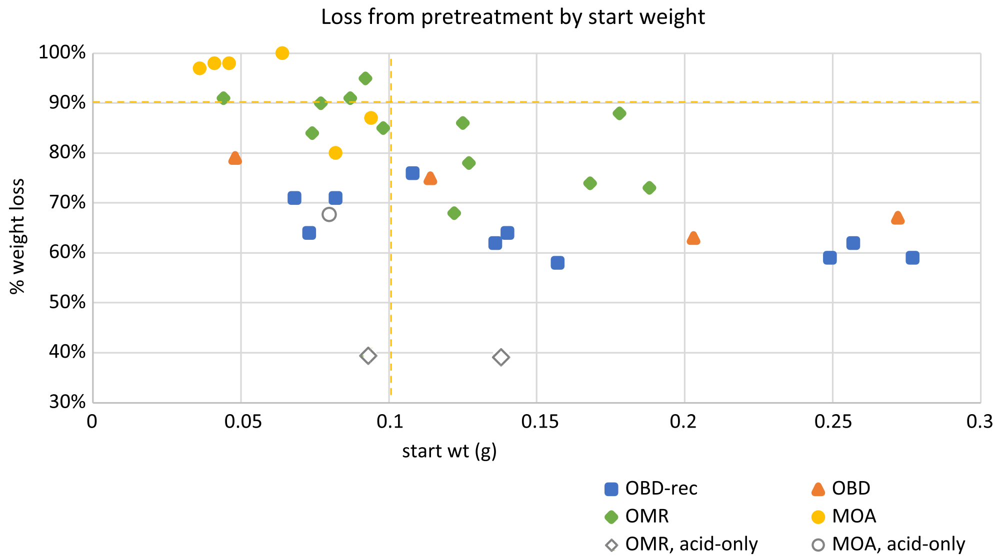

Figure 4 Loss from pretreatment by start weight.

0.001 g or less). In the fifth sample, an 80% loss was recorded, with 16 mg remaining out of the initial 82 mg. However, on inspection with a stereo microscope the surviving material appeared to be almost entirely composed of quartz granules with a couple pieces of microcharcoal, and the sample was deemed non-datable.

Nahal Omer pellet samples fared in between the Orhan Mor and Avdat pellets, with a range of 68–95% losses due to AAA pretreatment, a mean of 84% and standard deviation of 8% (n=12). End weights ranged from 4–28 mg for the external shavings (n=7) and 18–51 mg for the inner pellets (n=3). The surviving material was light yellow in color and appeared to be highly fibrous under the stereo microscope.

We observed that washing of samples with deionized water after each pretreatment stage accounts for some of these losses, especially among the lighter samples. However, most loss appeared to have occurred at the alkali stage of pretreatment. This suggested that acid-only would yield lower losses. To test this hypothesis, we compared acid-only to AAA pretreatments on pairs of pellets from three different assemblages in Batch 4, one from Orhan Mor and two from Nahal Omer. Each pair consisted of two pellets from the same archaeological locus-basket, where one whole pellet underwent acid-only pretreatment and the other underwent AAA (Figure 5). Comparison of weight losses demonstrates much greater loss under AAA: for the Orhan Mor pair, loss was 87% under AAA compared with 68% under acid-only. For the Nahal Omer pairs, losses were 74% and 68% under AAA compared with only 39% for each of the two acid-only treated pellets.

A final factor observed to affect pretreatment survivability is starting weight. Pretreatment losses by starting weight appear in Figure 4. All samples with start weights >200 mg exhibited weight losses <70%, while all weight losses >90% derived from samples with start weights <100 mg.

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Figure 5 Dried results of whole pellet pretreatment in acid-only (left) and AAA (right). Dung pellets shown come from Orhan Mor (MOA-2020-L630-B6304-P9 and MOA-2020-L630-B6304-P10).

AMS Dating

To test the reliability of radiocarbon-dating external pellet shavings, pairs of AAA pretreated inner and external pellet were separately dated by AMS from four pellets. None of the Orhan Mor pellet external shavings were deemed datable due to pretreatment weight losses and observations of surviving content. Samples were drawn from each of the four remaining archaeological loci used in this study, including one pellet from late-medieval Avdat and three from Early Islamic Nahal Omer (see Tables 1 and 4). Carbon content ranged from 21.15%–50.27%. In each case, the radiocarbon date obtained from the external shavings closely matched that obtained from the inner part of the same pellet, and all pairs pass the chi-squared test at 95% confidence level (Table 4). Although dated at a preliminary stage using acid-only pretreatment, data for UBA 47071 is presented at the end of Table 4 for comparison with the other late-medieval Avdat pellet (UBA 47567, 47568). Unlike the other samples, weight presented for UBA 47071 refers to its whole pellet weight prior to pretreatment.

DISCUSSION

Information obtained from each of the three stages of this study offers useful insights for radiocarbon dating of coprolites. This has particular relevance to minimally destructive analysis of sheep/goat dung pellets. We discuss findings from each stage.

Outer Shavings

Data on relative weights of external shavings suggest that the proportion of pellet weight lost from removing the outer layer to avoid contaminants is on the order of ⅓ to ½ for ancient

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Table 4 AMS dates from dung pellets and Chi-squared test for external-internal pellet pairs.

UBA	Sample ID	Pretreatment	Sample wt (g)	Graphite (mg)	% carbon	^{14}C BP	1σ	T’	χ_i (.05)	Mean ^{14}C BP
47436	OMR-2020-L103-B10033b-P1-in	AAA	0.022	0.992	37.96	1326	24			
47437	OMR-2020-L103-B10033b-P1-ex	AAA	0.005	0.754	26.88	1324	22	0.004	3.84	1325
47438	OMR-2020-L107-B17001-P1-in	AAA	0.018	0.855	28.43	1180	22			
47439	OMR-2020-L107-B17001-P1-ex	AAA	0.015	0.642	21.15	1197	21	0.312	3.84	1189
47566	OMR-2020-L203-B2031a-P3-ex	AAA	0.028	0.800	41.64	1261	22			
47565	OMR-2020-L203-B2031-P3-in	AAA	0.051	0.985	29.49	1309	21	2.491	3.84	1286
47567	OBD-2016-L101-B4-P8-in	AAA	0.09	0.979	50.27	304	27			
47568	OBD-2016-L101-B4-P8-ex	AAA	0.029	0.979	44.74	320	24	0.196	3.84	313
47071	OBD-2016-L101-B4-P6	Acid-only	0.325	1.005	60.54	418	22	—	—	—

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sheep/goat pellets. This is a significant proportion of the dung pellet which is lost in rigorous coprolite analysis and can probably only be reduced slightly through finer instrumentation. This certainly justifies checking whether such external coprolite shavings can be reliably used for any component of multi-proxy analysis. Differences between samples in the proportion of pellet weight lost from removing the outer layer are related to coprolite preservation quality and might be used as a proxy for general preservation. Qualitatively speaking, we observed that the way a pellet sample performs under handling at this stage may indicate how it will perform in pretreatments and subsequent analyses.

Pretreatment

Pretreatment weight loss of dung pellet samples was found to be correlated with start weight (Spearman rank correlation $\rho = 0.763$) and with site (Figure 4). Variation in sample loss according to site and start weight may well be linked to a third common factor, namely, preservation. Preservation in this sense is a qualitative factor based on observable characteristics. Visible traits which we associate with good preservation include a minimum of nicks and dents in the pellet, pellet rigidity, lightness of color, visible fibers and a greater propensity for macroscopic plant remains within the pellet. Poorly preserved pellets are associated with external nicks and dents, a greater propensity to crumble under light pressure, darker hue, few or no visible plant remains, and a sandier rather than fibrous internal structure.

Using these criteria, the best-preserved study samples were the recent pellets from Avdat, which were also the heaviest and exhibited the lowest losses in these experiments. Hence, we cannot disentangle their start weight and preservation quality as factors affecting percent loss. On the other hand, Orhan Mor pellets were generally lighter than the rest, their preservation was observably poorer with a sandy texture, no visible fiber and a tendency to crumble, and their losses due to pretreatments were higher than samples of comparable start weight from Nahal Omer. These findings support the observation made by Dunseth et al. (2019) that weight may be a proxy for organic preservation in dung pellets. Nevertheless, one way that small starting weight independently contributes to high percentage losses during pretreatment is through the greater suspension of light crushed pellet solids in water during the washing stages, which are poured out. In theory, additional centrifuging or longer settling times for suspended particles could help, but this is usually impractical in a busy radiocarbon lab. Instead, pellet weight and observations of preservation quality such as internal fibrousness, may be used to select pellets for radiocarbon dating.

The differences between weight losses under acid-only and AAA pretreatments in Batch 4 demonstrate that the greatest losses resulted from the alkali stage. This indicates the presence of undigested biomolecular compounds such as plant waxes, lipids and proteins as well as potentially some humic acids, despite the dry conditions. We would expect the plant-derived compounds to have been consumed as part of the diet and therefore unlikely to be a concern for radiocarbon dating. However, humic acids can be derived from younger, or occasionally older, organic material in sediments, which can affect radiocarbon measurements. Indeed, the date obtained from an acid-only pretreated whole pellet from late-medieval Avdat (418 BP ± 22) was older by about 100 ^{14}C yrs when compared to the AAA pretreated samples from the same assemblage (Table 4). This suggests the importance of using alkali as part of pretreatments for dung pellets. The effect of either humic acids or biomolecular compounds on stable isotope analysis should be considered. C:N measurements may be useful indicators of the presence of these additional sources of carbon.

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AMS Dating

We found that AMS radiocarbon dating of external pellet shavings yielded essentially the same results as dating the inner part of the same pellet. This is significant because coprolites' outer surfaces are removed and discarded to reduce contamination in other analyses (e.g., pollen, phytolith, sedimentary and biomolecular analyses) because the extraction process would not remove the contaminating material. Our findings show that external pellet shavings may be reliably used for radiocarbon dating, at least for some assemblages, as most contamination would be removed by the AAA pretreatment.

By capitalizing on this otherwise useless coprolite component, reliable radiocarbon dating can be performed without sacrificing material used in other analyses, presenting a new addition to multi-proxy coprolite analysis workflows. Future research on minimally destructive coprolite dating could investigate the taphonomic mechanisms underlying carbon preservation in dung pellets, in concert with soil chemistry and micromorphology. First, if reliable radiocarbon measurements can be obtained from external shavings, can other isotopic measurements be reliably obtained from the same source? Second, more experiments could be performed to quantify the significance of humic acids and the differences between coprolite radiocarbon dates after acid-only versus AAA pretreatments. Meanwhile, our success in dating external shavings which underwent AAA pretreatment suggests a practical yet ideal protocol in which rigorous pretreatment is applied in the radiocarbon dating of an otherwise useless coprolite component. The main thing to test in the future is its applicability to a wider variety of samples and contexts.

CONCLUSIONS

This study enabled us to answer the following research questions concerning minimally destructive radiocarbon dating of sheep/goat dung pellets, based on samples from archaeological sites in the Negev desert:

Which sample-specific factors are related to pretreatment losses and survivability?

Site and start weight were correlated with weight-based pretreatment survivability. In addition, observable preservation features—including external surface, rigidity, color, fibers and other macroscopic plant remains within—appear to be correlated with survivability.

Which pretreatment (AAA or acid-only) best balances survivability and reliability?

Our results demonstrate that AAA can be used as a pretreatment for sheep/goat dung pellets, above a certain minimal start weight. Acid-only pretreatment is less destructive but should only be used after humic acid contamination is ruled out.

What is a minimal dung sample start weight for reliable radiocarbon dating?

Our results suggest that an initial weight of 100 mg is a desirable minimum threshold for dating samples of sheep/goat dung from the Negev desert.

Can outer shavings of dung pellets be used to produce a reliable date?

Yes. Our findings indicate that it is just as reliable to date the external shavings of a dung pellet as it is to date the remaining inner pellet. This suggests an important addition to multi-proxy coprolite analysis workflows, certainly for Negev sheep/goat dung pellets, and likely for those of other regions and species.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2023.70

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AUTHOR CONTRIBUTIONS

D.F., N.O.M. and P.J.R. designed the research. D.F. and N.O.M. conducted the experiments. D.F. wrote the manuscript with substantial contributions by N.O.M. and P.J.R. Samples and information on archaeological context were provided by T.E.G., S.B., R.G. and G.B.O.

COMPETING INTERESTS DECLARATION

The authors declare that there are no competing interests associated with this paper.

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