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LABORATORY PROCEDURES FOR THE PREPARATION OF SOIL AND SEDIMENT SAMPLES FOR RADIOCARBON DATA

(also includes procedures for preparation of charcoal and wood)

by

William C. Johnson
Salavatore Valastro

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Kansas Geological Survey
1930 Constant Avenue
University of Kansas
Lawrence, KS 66047-3726

LABORATORY PROCEDURES FOR THE PREPARATION OF SOIL AND SEDIMENT SAMPLES FOR RADIOCARBON DATING

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William C. Johnson[1] and Salavatore Valastro[2]

[1] Department of Geography, 213 Lindley Hall, University of Kansas, Lawrence, KS 66045
[2] Radiocarbon Laboratory, Balcones Research Center, The University of Texas, Austin, TX 78712

Introduction

Radiocarbon dating has been a valuable tool in late-Quaternary studies for more than 40 years. The numerical age control on stratigraphy provided by radiocarbon dating permits determination of the timing of various erosional and depositional events and affords the opportunity to calculate the rate and magnitude of environmental and geomorphic change. In particular, radiocarbon dating has, in recent years, become critical to geoarchaeological research. Materials for radiocarbon dating are, however, limited in late-Quaternary deposits of the central Great Plains. Late-Pleistocene vegetative cover of the region has produced only scattered wood and charcoal in loess and alluvium, and grass cover of the Holocene resulted in even fewer datable macrofossils. Earth scientists and archaeologists frequently use organic carbon preserved in buried soils and sediments for radiocarbon age control. There is, however, considerable debate about the accuracy of ages determined from buried soils and sediments, despite general acceptance of radiocarbon dating. Some argue that resulting age determinations are fraught with problems (e.g., Polach and Costin, 1971; Gilet-Blein et al., 1980; Geyh et al., 1983; Forman and Miller, 1989; Hammond et al., 1991), while others maintain that ages provide relatively reliable age control (e.g., Matthews and Dresser, 1983; Haas et al., 1986, Martin and Johnson, 1995). Radiocarbon dating of organic carbon in soils and sediments has become routine in recent years and is producing results comparable to charcoal and wood. Dating such materials does, however, require greater care in collection, preparation, and interpretation.

Quality of radiocarbon ages

Various factors affect the quality, or accuracy of radiocarbon ages obtained from soils or sediment. The first area of potential problems relates to sample collection. Where the sample is collected in the stratigraphic sequence determines what event it represents temporally; this is especially true for buried soils. One may collect samples from the top, bottom, and middle parts of a soil, or draw a composite sample integrating the entire sampled horizon. The latter is the least desirable from most perspectives. W.C. Johnson and his students typically collect from 2 to 5 cm-thick layers in the bottom and top of the buried A horizon, with the intent of estimating the onset

and termination, respectively, of pedogenesis. In buried alluvial soils, the difference between the top and bottom of the A horizon can range up to 1000 years (Johnson and Martin, 1987; Johnson and Logan, 1990). In contrast, the cumulic A horizon of the Gilman Canyon soil developed within middle-Wisconsinan loess deposits of the central Great Plains has yielded a range of approximately 10,000 years (Johnson, 1993; Johnson et al., 1993). Consequently, radiocarbon ages obtained from soils can be incorrectly interpreted without appropriate collection strategies or incomplete information on the same. The quantity of sample collected also relates to the accuracy of the age. In order to have a sufficient sample size for conventional radiocarbon analysis, as done at the University of Texas Radiocarbon Laboratory, approximately 8 kg (4 one-gallon *Ziploc* heavy duty freezer bags) are collected. Less is required if the sample is collected from a buried soil with a relatively high organic matter content, and more if from sediments expressing minimal or no pedogenesis. If an insufficient amount of ^{14}C-containing gas is produced, the standard deviation associated with the age will increase.

Contamination is a major problem when dating soils and sediments. Because of the nutrient reservoir and water-holding capacity of buried soils, modern roots tend to congregate in buried A horizons that are within reach, thereby creating a major source of contamination. Likewise, carbonates often accumulate immdiately above and below buried soils, providing a source of carbon often appreciably older or younger than the soil. During the sampling of a buried soil or sediments, krotovinas (infilled animal burrows) must be avoided since they represent an intruded source of either older (from below) or younger (from above) organic carbon. All of the above sources of contamination can be eliminated through a combination of good field and laboratory techniques.

Two adjustments, correction and calibration, should be made in radiocarbon ages to improve the quality and interpretibility of the ages. Because the carbon pathway differs among plants, ratios among the isotopes of carbon in plant tissue vary, which in turn results in ^{14}C determinations which may not represent the true radiocarbon age. This process, isotopic fractionation, may produce anomolously young ages (Taylor, 1987), particularly in the central Great Plains, where many of the grass species tend to over-represent the ^{14}C actually in the atmosphere. A procedure based on a standardized ^{13}C concentration corrects radiocarbon ages for the effects of isotopic fractionation. If an age determination is not corrected, it may be inaccurate by hundreds to thousands of radiocarbon years, resulting in potential interpretation problems. Another adjustment involves

changes in the concentration of radiocarbon in the atmosphere through time; this change has resulted in a disparity between radiocarbon and calendar years. As a consequence, radiocarbon ages younger than about 18,400 years B.P. can be calibrated to calendar ages using a relationship established with tree rings and corals. Calibrated ages are easily derived using software (CALIB ver. 3.0) developed by Stuiver and Reimer (1993).

Each radiocarbon laboratory has its own method for pretreating and processing samples for radiocarbon dating (Taylor, 1987). Although the procedures may be very similar from one laboratory to another, significant differences in ages can result from the subtleties. Martin and Johnson (1995) noted that radiocarbon ages of the three organic fractions (total, humic acid, and humin) isolated from late-Quaternary buried soils in the central Great Plains displayed considerable differences between two radiocarbon laboratories; these differences probably reflect, in part, variations in preparation techniques.

Why prepare your own samples for dating?

If carried out properly, there are a number of advantages to preparing your own samples, particularly soil and sediment, for radiocarbon dating. There are at least four advantages, one of which is that the scientist becomes aquainted with the sample which he or she is submitting for dating. Various physical and chemical attributes become much more apparent as one works with the sample: particle size composition and heavy mineral content during the wet sieving, rootlet size and concentration while skimming, carbonate content when treating with HCl, initial color and color change during preparation, etc. This intimacy takes on more importance if a suite of samples is being prepared from one or more associated stratigraphic columns. Another advantage of preparing your own samples is that the exact mode of preparation is known, i.e., one less variable is present when it comes to interpreting the resulting radiocarbon assays. This knowledge is most important when two or more radiocarbon laboratories are used; because of the variation in final age determination due to interlaboratory differences in preparation techniques, evaluation of laboratory ages is somewhat more complicated when two or more laboratories are involved (Martin and Johnson, 1995). Also, by preparing his or her own sample, the scientist has the opportunity to split the sample for submission to two or more radiocarbon laboratories for comparative purposes. A

third advantage could be a reduction in the cost of the radiocarbon dating procedure, especially if the humic acid and/or humin fractions are being submitted for dating. Most radiocarbon laboratories charge an additional fee for the preparation of soil and sediment; a fee of $100 to $150 is common for total humate sample preparation alone. Even if the scientist employs a student technician to prepare the samples, a saving should still be realized. The fourth advantage, a reduction in turn-around time, is often an important factor. By preparing the sample prior to submission, the scientist saves the radiocarbon laboratory appreciable time because the sample is ready to burn for gas production upon receipt.

Facilities

The preparation precedure described below was developed several years ago at the University of Texas Radiocarbon Laboratory by S. Valastro. For the past few years, W.C. Johnson and students in the University of Kansas Department of Geography have been applying the procedure to a variety of soil and sediment types. At the University of Kansas, the procedure has been easily adapted to a laboratory facility typically found in most geography, geology and archaeology departments.

Laboratory requirements for the preparation of radiocarbon samples are relatively few. The laboratory room needs a 4-foot or larger fume hood, acid-proof sink (sediment trap-equipped best), a faucet equipped with an aspirator filter pump, distilled water supply (tap water filtered for organics is an alternative), and a modest amount of counter space. Equipment needs include a floor-style centrifuge and a rotor head with one-liter cups and bottles (optional), 20-quart aluminum or stainless steel cooking pots with lids (9 or more), 4-liter beakers (*Kimax* heavy duty best; 12 or more), long glass stirring rods, 8-inch sieves in 60, 230, and 270 Tyler designation (stainless steel best), large perforated spoon (stainless steel), glass siphoning wand (old pipet?) and tubing, mortar and pestle (6-8 inch diameter), soil grinder (optional), large/heavy duty coffee grinder (optional), and large capacity mechanical convection oven. Supplies required for the preparation include heavy duty aluminum foil, plastic cling wrap, concentrated HCl, NaOH, pH test paper (e.g., Hydrion 152), sponges, *Ziploc* heavy duty one-gallon bags, and laboratory wear (apron, gloves, safety glasses, etc.).

Preparation of Soils and Sediment

The procedure outlined below for soil and sediment samples is easily mastered. To a large extent, it is an art form acquired through the application of common sense and simple laboratory technique. Several basic tenets of laboratory work must be kept in mind. For example, all wet treatment activity is to be done wearing rubber gloves and a laboratory apron or coat; the former protects the hands and keeps skin oil out of the sample, and the latter protects street clothes and reduces the potential for clothing lint contamination. Attire should include headwear to minimize the possibility of contamination from hair. Also, keep paper and cloth laboratory towels away from the sample, and do not wipe gloved hands with the towels because fibers and lint tend to adhere to some types of laboratory gloves. The above guidelines are not inclusive - the scientist must simply bear in mind that prevention of contamination is paramount during all phases of the procedure.

The procedure for preparation of soil and sediment samples is presented in two stages: first, isolation of the total humate fraction and second, isolation of the humic acid and humin (residue) fractions. Procedures for preparing charcoal and wood samples are also included.

Stage 1: Isolation of the Total Humate Sample

1) Disaggragating the sample:

(a) Place one bag (e.g., one-gallon *Ziploc*) of the sample collected into one of the 20-quart cooking pots; add distilled water; using the large perforated stainless steel spoon, stir well to disaggregate; cover and let stand overnight or longer to allow for complete disaggragation (the sample may require repeated stirring).

(b) Repeat for all bags of the sample; be certain to mark all pots if disaggregating more than one sample - confusion would be catastrophic.

2) Sieving to remove floating debris and sand-size particles:

(a) Stir well; skim off floating debris with 60-mesh sieve until clear; keep water running in sink for flushing the sieve; repeat several times (stir-skim, stir-skim, ...).

(b) Pass the sample through the 230-mesh sieve held over a clean 20-quart pot; transfer the

sediment -water mixture to the sieve with a 500-1000 ml beaker or facsimile; frequently stir or aggitate the original pot using plunge from the beaker and/or stirring with the spoon to keep silt and clay in suspension; add distilled water to the pot as necessary. Use running tap water to flush the sieve over the sink. Gauge the transfering and sieving such that two full pots result. Discard the water and sediment (sand and larger) remaining in the bottom of the original pot.

(c) Slowly/gently skim the two new pots with a 230- or finer (e.g., 270) sieve, if required.

(d) Repeat for all other pots containing disaggregated sample.

(e) Cover and let stand overnight or until settling has occurred. If the sample does not settle, add a few drops of concentrated HCl or a squirt of dilute HCl to the water surface; do not stir - any carbonates present in the bottom sediment will neutralize the acid. Avoid using HCl at this stage, if possible, because it will dissolve aluminum and discolor stainless steel.

Note: Centrifugation may be used to settle the sediment rather than standing, but several runs are required given the volume of sediment-water mixture.

3) Transferring the sample to beakers:

(a) Siphon the pots (or decant the centrifuge bottles) slowly since sediment in the bottom will slump and flow easily (Fig. 1). Flush the sediment into the 4-liter beakers using a distilled water jet; fill the beakers to within 2 inches of the top; if you overfill, there will be too much sediment to insure adequate acid treament, especially when stirring. Upon settling, there should be no more than 1½ inches of sediment in the bottom.

4) Removal of carbonates:

(a) With the beakers in the fume hood, add 1-2 ml of concentrated HCl to check for carbonates; if not reactive, acidify to a pH of 4 to 5 (monitor with pH paper). If there is a reaction, add HCl in small amounts (c. 5 ml), stirring thoroughly. Use a distilled water jet to kill any foam from going to the beaker lip. Wipe exposed interior beaker walls with a small clean sponge rinsed in distilled water to remove any possible non-acidified sediment. The small sponge may be kept in a beaker filled with distilled water. Cover with plastic wrap.

(b) After the reaction has apparently stopped, let stand acidified one ot two days in the fume

hood to ensure neutralization of any dolomite that may be present. Keep the beakers covered with plastic wrap.

5) Rinsing:

Rinsing the sample may be accomplished in the beakers or with the centrifuge.

Rinsing in the 4-liter beakers -

(a) Siphon the supernatant water from the beakers after the clay has settled. Refill with distilled water and stir thoroughly. Allow to settle again and repeat the siphoning and stirring two more times. Continually monitor the pH; if it rises above 5 (sample must stay slightly acid to avoid absorbsion of atmospheric CO_2), acidify by adding a few drops of concentrated HCl, followed by stirring. After each stirring, wipe sediment from the exposed beaker walls. As before, beakers should be covered with plastic wrap while settling.

Rinsing with the centrifuge -

(a) Stir and transfer the sample to wide-mouth, 1-liter centrifuge bottles; centrifuge (15 min at 1000-1500 rpm) and decant, discard the supernatant.

(b) Add distilled water, shake, and centrifuge to rinse the sediment; repeat three more times; maintain a pH of 5. If the pH rises above 5, add a few drops of concentrated HCl.

(c)Transfer the sediment, with a spatula and minimum amount of distilled water, from the centrifuge bottles into 4-liter beakers. Wipe the beaker walls clean with the distilled-water rinsed sponge. Let stand until the sediment settles; siphon off the supernatant.

6) Oven drying:

(a) Siphon the supernatant from the beakers.

(b) Cover the beakers with aluminum foil; vent with slits. Place the beakers in the oven (mechanical convection) at 100° C until the sediment has dried completely, forming a cake(Fig. 3). Complete drying should occur with 3 to 4 days.

7) Pulverizing:

(a) Remove the dry cake from the beakers; scrape the beakers to remove as much of the sediment as possible. The sample may be pulverized with a large mortar and pestle, but this is time

consuming and fatiguing, especially if the sample is clay-rich. The process goes faster if the cake is first broken into dime size chunks in the mortar, ground to 2 mm or less in a soil grinder, and then powdered in a coffee mill/grinder. Work with the sample on foil and **do not touch with hands** - use a spatula to load the mortar and grinders. Be certain to wash and rinse (distilled water) the mortar and pestle and contact grinder elements thoroughly prior to use and between different samples.

8) Sample packaging or Stage 2:

(a) Store the pulverized sample in aluminum foil or a plastic (*Ziploc*) bag with the proper identification data for shipping to the radiocarbon laboratory. If the humic acid and/or humin fractions will be dated, proceed to Stage 2 prior to packaging for submission.

Note: Several different samples may be in progress at one time. When preparing a suite of samples for total humate dating, there can be one sample disaggregating in pots, one sieved sample settling in pots, one in beakers in the fume hood (HCl treatment and rinsing), one drying in the oven, and another being pulverized. An individual can maintain progress by rotating from one sample, or stage to another.

Stage 2: Isolation of Humic Acid and Humin Fractions

1) Spliting the total humate sample:

(a) Mix and quarter the total humate sample: place on aluminum foil, mix with the corner roll method, spread and smooth with a large cake spatula, quarter with a small spatula. Place opposite quarters into 4-liter beakers (1 quarter/beaker), and retain the other two quarters for total humate dating.

2) NaOH extraction:

(a) Add hot (not boiling) 2% NaOH (5% if especially organic-rich) to within about one inch of the beaker top. Note: when mixing the NaOH solution from pellets, place beaker in running cold water or ice (an exothermic reaction).

(b) Stir well repeatedly. Allow to sit a few hours or overnight until settled, or centrifuge. Be

certain to cover with plastic wrap if allowed to settle overnight.

3) Precipitation of humic acid:

(a) Decant into another beaker and acidify with concentrated HCl, a ml or so at a time, while stirring; check for precipitation (look for a color change). Check the pH - it should be about 1.

(b) Let stand to precipitate several hours. Transfer to centrifuge bottles and centrifuge. Discard the supernatant and carefully wash the precipitated humic acid fraction into a clean collection beaker.

Repeat the NaOH extraction until a weak coffee color is achieved when hot NaOH is added to the sample. Continue to precipitate with HCl.

4) Rinsing of the precipitate/humic acid fraction:

(a) Rinse the precipitate (in the collection beaker) with distilled water two times (centrifugation best), keeping it slightly acid.

5) Oven drying of humic acid fraction:

(a) Cover the beaker with foil and oven dry slowly (70°C or less).

6) Pulvering the cake:

(a) Powder the cake with the motar and pestle, and wrap securely in foil, then place in a *Ziploc* bag. (Note: about 3 grams are required for a full sample)

7) Acidification and rinsing of humins (residue fraction):

(a) Acidify the sediment remaining in the beakers with HCL and distilled water. Centrifuge or let settle and decant/siphon.

8) Oven drying of humin fraction:

(a) Cover the beakers with foil (vented) and place in oven to dry (100°C).

9) Pulverizing the cake:

(a) Remove the cake from the oven and pulverize; place prepared humin sample in foil and *Ziploc* bag with the proper sample identification data.

Preparation of Charcoal and Wood

Charcoal

1) HCl digestion:

(a) Place the charcoal sample in a beaker and add 2% HCl; if the charcoal pieces are large, first break them up with a knife.

(b) Boil the mixture on a hot plate: 10-15 minutes if a small sample, 30-60 minutes if large.

(c) Allow the HCl to digest overnight.

2) NaOH treatment:

(a) Decant/siphon the acid solution and rinse the charcoal with distilled water until diluted to about pH 5. Transfer the charcoal into a clean beaker.

(b) Add 2% NaOH and boil about 15 minutes (30-60 minutes if large pieces). Allow to digest overnight.

3) Separation of the humic acid fraction (if desired):

(a) Decant the NaOH (humic acids) into a beaker and proceed as in Stage 2 above if this fraction is to be dated separately or if insufficient charcoal remains for conventional dating (c. 10 grams), otherwise discard it.

4) HCl treatment (acidification):

(a) Rinse with distilled water and add 2% HCl. Stir.

(b) Wash the charcoal into a beaker through a sieve small enough to remove the finest particles.

5) Oven drying:

(a) Cover the beaker with foil and place in the oven (100°C).

6) Rootlet removal:

(a) After the charcoal sample has dried, pick out rootlets on a clean plate glass panel (with white underlayment) using a magnifying light fixture or binocular dissecting microscope.

7) Packaging:

(a) Wrap the prepared sample in foil and then place in an appropriately-sized *Ziploc* bag with proper identification data.

Wood

Prepare using the same procedure outlined for charcoal except:

1) Cut wood up into shavings prior to step 1) above.

2) After the NaOH treatment, extract the lignin with household bleach by boiling until the wood is white. Rinse prior to the HCl treatment.

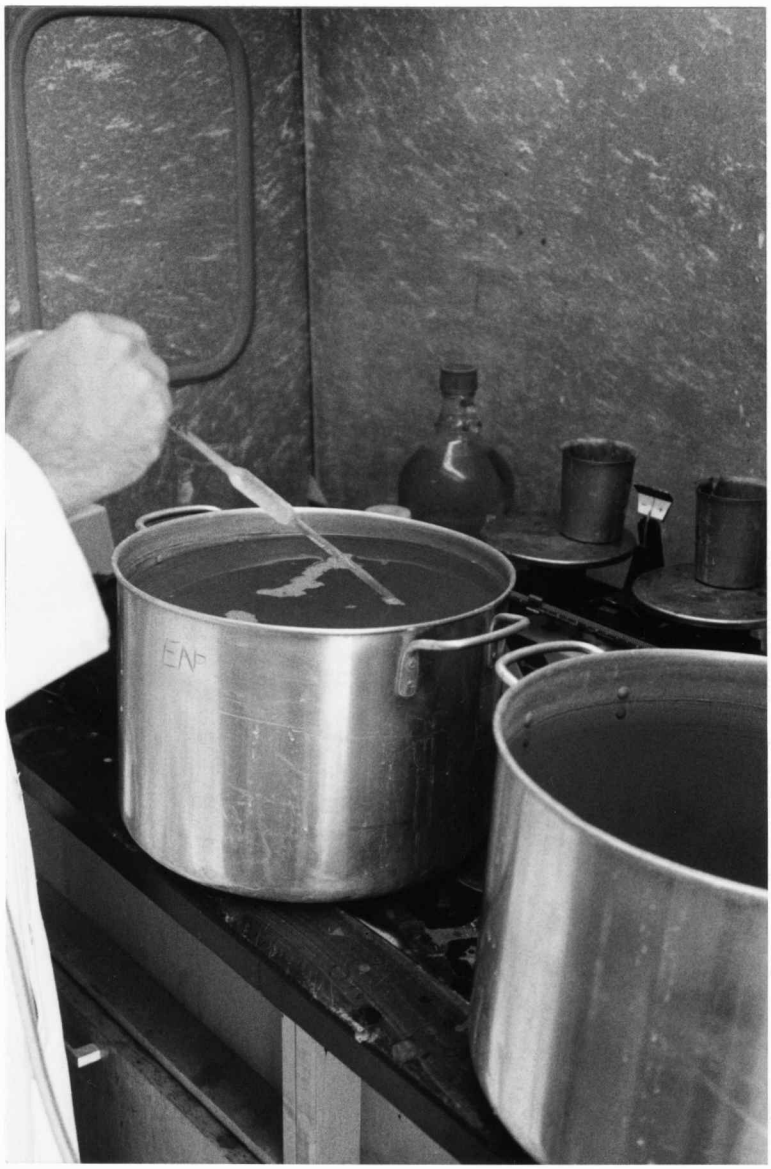

Figure 1. Siphoning distilled water from the 20-quart pots prior to transfer of sample to 4-liter beakers.

Figure 2. Four-liter beakers containing the acidified sample settling in the fume hood.

Figure 3. A sample drying in the mechanical convection oven.

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