



Soils and Organic Sediments

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Introduction

The organic component of soils is basically made up of substances of an individual nature (fats, waxes, resins, proteins, tannic substances, and many others), and humic substances (Kononova, 1966). These are complex polymers formed from breakdown products of the chemical and biological degradation of plant and animal residues. They are dark coloured, acidic, predominantly aromatic compounds ranging in molecular weight from less than one thousand to tens of thousands (Schnitzer, 1977). They can be partitioned into three main fractions:

- (i) Humic acid - soluble in dilute alkaline solution, but can be precipitated by acidification of the alkaline extract.
- (ii) Fulvic acid - soluble in alkaline solution, but is also soluble on acidification.
- (iii) Humin - cannot be extracted from the soil or sediment by dilute acid or alkaline solutions.

It has mostly been assumed that the humic and fulvic acid components of the soil are part of the mobile, or “active” component, and the humin component is part of the “passive” component.

Other types of organic sediments are likely to contain chemical breakdown products of plant material, plant fragments and material brought in from outside sources. The outside material can be contemporaneous with sediment deposition, can be older material, or younger material incorporated into the sediment long after deposition. Recognition of “foreign” material is essential for dating, but is mostly extremely difficult.

Problems

The overriding problem for absolute dating of soils is that an exact numerical soil age may be impossible. Absolute ages can be linked only to the ^{14}C measurement of buried palaeosols, to charcoal, wood fragments, or plant remains. All other ^{14}C measurements yield model age levels, expressed as Apparent Mean Residence Time of the dated organic carbon fraction (Scharpenseel and Becker - Heidmann, 1992). Geyh et al. (1971, 1983) indicated that age determinations of the organic component of soils originating in calcareous parent materials could be affected by an unknown amount of fossil CO_2 formed by the decomposition of soil carbonates, resulting in a ^{14}C age older than the true age. Alternatively, with non calcareous soils, the ^{14}C age would be younger than the true age because of continuous incorporation of younger organic material coming from continuous surface decomposition of plant material. Scharpenseel and Schiffmann (1977) came to the same conclusion.

Radiocarbon dating of the organic component of soils, lake sediments and other organic deposits, is often complicated by inclusion of “foreign” organic matter. Most classic pretreatment techniques commonly used for removing “foreign” organic material from samples of charcoal or wood have been shown to be inadequate for completely eliminating contamination. Occasionally, charcoal or plant fragments may be found in the sediments, and these may provide a useful dating

medium. However, material that was originally collected as charcoal has often been found to consist of a thin black organic layer covering a small rock fragment or clay aggregate. This phenomenon has been shown to be common in meadow soils or swampy sediments, where aeration may have been restricted, and degraded plant material has been reduced to a "charcoal" like component (Kononova, 1966). Similarly, Skjemstad et al., (1994) have examined layers of fine grained charcoal fragments that have most probably moved down relatively loose textured sandy soil profiles, and have become concentrated at a specific level within the profile. These fragments, when examined using electron microscopy, indicate a woody origin, yet ^{13}C CP MAS nuclear magnetic resonance spectrometry indicates that this material basically contains a condensed aromatic structure.

Soil component modelling

Soils have been considered as consisting of a complex mix of organic molecules whose turnover times range from a few years to thousands of years. Harrison (1996) estimated the passive soil turnover time from soil ^{14}C measurements made at depths where little or no active soil carbon was present. He found that the average value for a series of sites was 4700 yr. He also estimated the active soil carbon turnover time using the postbomb increase in soil ^{14}C concentrations, and found that a 25 yr turnover time produced the best fit to the available data. He then used a time-step one-box model containing atmospheric ^{14}C values and CO_2 concentrations for every year from AD 1800 to the present, together with bulk soil ^{14}C measurements. The model was arranged so that the user could select the carbon inventory divided by the exchange flux, which is added to the box (photosynthesis) or is lost from the box (respiration). The model could be run in either a steady state or a nonsteady state mode. Extensive modelling experiments using ^{14}C measurements have also been carried out by Wang et al., (1996), Chichagova and Cherkinsky (1993), Cherkinsky and Brovkin (1993), and many others, but space limitations do not allow them to be considered here.

Pretreatment techniques

Olson and Broecker (1958) considered that the most useful technique to remove organic contamination from soils was to separate soil humic acids from the more inert chemical component of soil organic matter. Humic acids were considered to be the most mobile component within the soil. They outlined a technique where the soil sample was treated with boiling 2% NaOH solution, the black NaOH soluble material was then filtered off and acidified to a pH of < 1. The humic component formed a precipitate, and could be separated by filtration or centrifugation, rinsed and dried. The NaOH insoluble residue, or non - humic component of the sample, was treated with a boiling solution of 5% HCl, then was filtered, rinsed and dried. This was assumed to be the most likely fraction to produce a reliable ^{14}C age. This basic technique continues to be used in the preparation of chemical fractions even though many of the concepts used in setting up the technique have been found not to apply. There is a distinct likelihood of introduction of atmospheric CO_2 into the fraction to be dated thus providing ages that are younger than they should be.

Head et al., (1989) and Zhou et al., (1990) used a solvent extraction technique similar to that used in the pretreatment of wood (Head, 1979), after decalcification of sediment samples before using the normal (Olsen and Broecker) alkali leaching technique for separation of humic acid and

humic acid fractions from swamp sediment and palaeosol samples at Bei Zhuang Cun, China. The humic acid fractions of swamp sediment samples from the bottom of the profile gave ^{14}C ages that were not significantly different from ^{14}C ages of wood fragments found in the sediment samples, but gave significantly older ages than the corresponding humin fractions. For palaeosol samples in the upper part of the profile, the humin fractions gave older ages, but even these were younger than the ages of corresponding materials and historically dated pottery. Palaeosols from the Baxie loess / palaeosol sequence at Baxie and other sites in China (Zhou et al., 1992, 1994) gave similar results in that the humin fractions were older, but were still significantly younger than corresponding thermoluminescence ages. In these cases most of the organic material was very tightly bonded with the considerable clay component, which meant that the chemical fractionation techniques could not work efficiently.

A comparison of ^{14}C measurements from soil organic matter fractionated using different physical and chemical separation methods was made by Trumbore and Zheng (1996). All samples are sieved to remove components >2 mm. Density separation procedures used involve flotation in Na-polytungstate (2.0-2.1 g/cc). Low density material consists of plant matter and charcoal. The more dense fractions consist of mineral associated organic matter, and some microbial cell debris. In general, the low density material has higher ^{14}C values and turns over more rapidly than much of the soil organic matter. Chemical fractionation procedures often rely on extraction using acids and bases. More labile components are assumed to be soluble, leaving behind more refractory (and therefore more ^{14}C depleted) constituents. These procedures will also affect soil mineral content and can cause changes in soil organic matter chemistry and structure. Extraction with Na-pyrophosphate and 6M HCl will dissolve sesquioxide minerals and remove organic matter complexed with Fe and Al. heating SOM in strong acid can cause condensation reactions

Recently, a further evaluation of separation techniques for humic and non humic components has been carried out following a technique suggested by Tan, (1996). The method used is as follows:-

- i) The sample (100 g to 1 kg, depending on C content) is washed with hot dilute HCl to remove carbonates, and to remove calcium from the soil, then is rinsed and air dried. The acid treatment needs to be thorough to ensure all calcium salts are removed. Sometimes, further treatment with dilute H_2SO_4 may be deemed necessary.
- ii) 0.1M NaOH solution is added and the slurry is shaken for 24 hr in a nitrogen atmosphere.
- iii) The dark coloured supernatant solution is collected by centrifugation, and the soil is rinsed with distilled water. The residue is acidified, rinsed and dried as the NaOH insoluble (humic) fraction.
- iv) The black liquid is then acidified to pH 2, and the resulting precipitate (humic acid) is separated and rinsed by centrifugation.
- v) The humic acid precipitate is redissolved with 0.1 M NaOH under nitrogen, and is centrifuged to separate any undissolved fraction, which is discarded. The dissolved humic acid is then reacidified to pH 2, and centrifuged. The supernatant liquid is discarded.
- vi) The humic acid precipitate is then shaken with a HCl/HF mixture to make sure no colloidal clays have managed to stay with the sample. The humic acid is

- washed with distilled water and centrifuged, then is dried at a low temperature (30°C).
- vii) The solvent extraction procedure mentioned previously (Head 1979) is carried out at this stage, and the humic acid sample is dried at a low temperature.
 - viii) The humic acid is again redissolved using 0.1 M NaOH solution under nitrogen and is centrifuged. Any solid material is discarded.
 - ix) The humic acid solution is purified further by passing it through a H – saturated cation exchange column (Dowex 50 - X8), then is freeze – dried. The interesting result of the ion exchange step is that the pure acid form of the humic acid is produced, which is soluble at acid pH, as against the sodium salt, which is insoluble at acid pH. Preliminary analyses indicate this humic fraction may represent a much purer form of humic acid and may be a potentially useful dating fraction, as against the acid and alkali insoluble humin fraction which is still tightly bound within the soil clay fraction.
 - x) The humic acid, after freeze-drying or drying at a low temperature, is subjected to a decarboxylation procedure, where the sample is heated in O₂ (about 1/3 atmospheric pressure) at about 150°C for one hour. This step is very necessary and should not be disregarded.

Many other pretreatment procedures have been used (Gillespie et al., 1992), but space does not allow me to go into any detail.

Conclusions

The whole concept of soil and sediment dating is still somewhat tenuous, and depends on the information required by the sample submitter. Each sample must be regarded as a research project in its own right. In most cases, detailed examination, analysis, and preliminary separation of soil components is needed before a pretreatment strategy can be decided upon. Hence, the ¹⁴C dating of soils cannot be regarded as a routine operation, as useful results may not be forthcoming, even after much work has been carried out on the samples.

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