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EVALUATION OF ^{14}C AGES OF ORGANIC FRACTIONS OF PALEOSOLS FROM LOESS-PALEOSOL SEQUENCES NEAR XIAN, CHINA

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ABSTRACT. The ^{14}C dating of organic fractions from paleosol layers containing <2% carbon in loess-paleosol sequences from the loess plateau in China has yielded results that are quite often much younger than the true age of the sediments. Percolation of modern organic materials from agricultural activities, and binding of these materials within the weathered clays of the paleosols has meant that conventional pretreatment techniques for ^{14}C dating would not isolate a reliable chemical fraction. The total sequence from Bei Zhuang Cun, in Shaanxi Province, reflects the climatic history of the area for ca 30,000 years, ranging from the interstadial of the last glacial period to the postglacial period. Analysis of solvent extracts of organic material from this site indicates that they are mainly composed of carbohydrate residues originating from the relatively recent agricultural activity. Validity of the humic components for dating will be discussed.

INTRODUCTION

The ^{14}C dating of loess-paleosol sequences from the loess plateau in China has been constrained by the lack of suitable dating material and by the possible presence of younger organic or inorganic carbon-containing material in most of the samples collected and dated. Previously dated materials, mainly by the Radiocarbon Laboratory, Guiyang Institute of Geochemistry, Academia Sinica, Guiyang, China, include cultural remains (eg, wood, bone), organic matter in soil, carbonate in loess and soil, and snail shells (Qiao *et al*, 1985).

Studies of the geochemistry of loess-paleosol sequences indicate pH values varying between 7.5 and 8.5 (Wen, Diao & Sun, 1985). Gilet-Blein, Marien and Evin (1980), showed that for basic soils, alkaline extraction techniques would probably provide a humic acid fraction with an older ^{14}C age than the corresponding humin fraction. Scharpenseel (1977) indicated that for hydromorphic soils, humic matter fractions followed the age sequence fulvic acid < humin < humic acid, since younger, non-humic materials would be preserved under hydromorphic conditions, and would appear as younger contamination in the humin fraction. A similar conclusion was made from the ^{14}C dating of organic matter fractions of a dark chestnut soil profile from Inner Mongolia, in China (Becker-Heidmann, Liu & Scharpenseel, 1988). They also found that humins from the lower depths seemed to be different in composition from the humins of the upper horizons, as indicated by both ^{14}C age and δ^{13}C measurements.

Goh, Molloy and Rafter (1977) studied Quaternary loess-paleosol sequences from the Banks Peninsula, Canterbury, New Zealand, and indicated that whole loess dates were as old or older than clay-humus dates. Humic-acid fractions separated using a solution mixture of 0.1M NaOH and 0.1M $Na_4P_2O_7$ gave older ^{14}C ages than residue or humin fractions, though the situation was reversed when humic acids were separated from colluvial gravels.

According to Stevenson (1985), soil humic materials are formed by a multi-stage process that includes decomposition of all plant components into simple monomers, metabolism of monomers with an accompanying increase in soil biomass, repeated recycling of biomass carbon with synthesis of new cells and concurrent polymerization of reactive monomers into high molecular weight polymers. Stevenson also suggests the two main mechanisms for binding chemical compounds with humic material are direct chemical attachment of residues to reactive sites on colloidal organic surfaces, and incorporation into structures of newly formed humic and fulvic acids during humification. On this basis, a soil profile could be a natural chromatographic column, in which downward translocation of soluble organic matter occurs, which can be complexed with weathering clays or older humic material.

Kigoshi, Suzuki and Shiraki (1980) separated successive humic acid fractions from clayey soil samples belonging to one profile and found strong evidence of contamination from very young organic components that had been obviously washed down the profile. The degree of contamination seemed to correlate with the following: 1) most of the young contaminants were extracted in the second humic acid fraction for samples taken from a layer above the nonpermeable layer; 2) young carbon contaminants were mainly extracted in the first fraction of the humic acid for samples from the upper layer. The largest concentration of young contaminants directly overlay the non-permeable layer.

Thus, we expected that the humic acid fraction of organic material from the loess-paleosol sequences would provide the must useful ^{14}C ages, provided it was free of possible organic components that had leached down the profile to become incorporated (by physical adsorption or chemical combination) into the humic acid structure. The pretreatment techniques used for the organic material were determined by the factors mentioned above, and involved potential removal and categorization of likely younger contaminants physically adsorbed to the original humic components.

SITE DESCRIPTION

The Qin Shui River to the east, originating from Jian Yu Ling in the Qin Ling Mountains at an altitude of 2449m joins the Zhuo Shui River to the west, originating from Wang Wang Shan in the Qin Ling Mountains at an altitude of 1553m, to form the You River, which in turn flows into the Wei River (Fig 1). Materials washed from the Qin Ling Mountains are usually deposited in the You River area. Bei Zhuang Cun (34°30′N, 109°E), is in Weinan County, Shaanxi Province, 500m southeast of Yang Guo township, east of Xian.

During the Pleistocene, the You River area was tectonically forced downwards with respect to the Qin Ling Mountains, and this resulted in the deposition of thick fluvial sediments. The Qing Shui and Zhuo Shui Rivers, two tributaries upstream of the You River, cut through the loess "yuan" (platform) at different altitudes from north to south. Modern fluvial and plu-

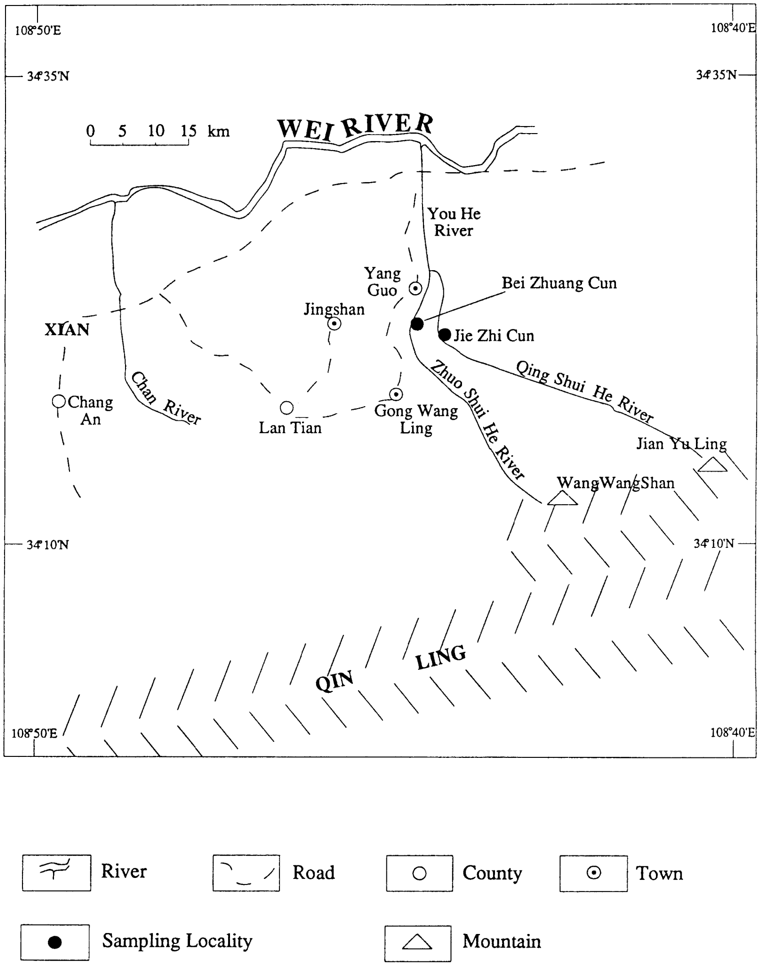

Fig 1. Sketch map showing profile locality

vial sediments were deposited in the Zhuo Shui River valley, and two terraces have developed on both sides. The younger terrace consists of Holocene secondary loess, and the Bei Zhuang Cun profile is developed on the second terrace, which started forming around Malan Loess (~30,000 BP), producing a facies change. The profile (Fig 2) is 16.5m deep and is also described elsewhere (Cao, 1966; Inst Botany, 1966).

The lowest unit, 1650–1350cm, consists of yellowish brown gravel containing a thin layer of greenish brown to grayish green subclay, indicating alternating periods of energetic and less energetic flows. A 2m pit was dug at the northern end of the profile in order to further define the geological setting within this unit (Fig 2). The top 30cm of the pit consists of brown gravel, and from 30–100cm depth, the sediment consists of dark grayish mud containing plant residues. From 100–130cm, the sediment consists of another layer of grayish green mud, underlain by brown gravels down to 2m depth.

From 1350–900cm, the soil consists of dark grayish to grayish green muds at the bottom. These muds contain a large quantity of plant residue, which mainly consists of reed roots. The upper part of the unit consists of pale grayish brown and light gray sandy muds. From 920–900cm, a very distinctive thin layer of yellowish brown sand is present.

The next unit, 900–600cm, consists of light brown secondary loess containing sand lenses and gastropods.

The upper unit, 600–200cm, contains 3 paleosol layers, which are cinnamon-soil-type swamp sediments, interspersed with 2 layers of loess containing obvious evidence of bioturbation. At the base of the lowest paleosol is a thin horizon of broad bean-size carbonate nodules. The lower loess layer, 475–425cm, contains reddish pottery fragments belonging to the Yang Shao culture (5000–6000 BP). The upper loess layer (300–200cm) contains gray potsherds, dating to ca 3000 BP. The top 200cm consists of sediment mainly modified by farming activities.

The variation of sediment layers in the Bei Zhuang Cun profile suggests three major environmental and climatic changes. The mud overlying gravel represents a change from a relatively warm and wet climate with periodic flooding along the river to cooler, drier conditions allowing the deposition of 4.3m of mud from relatively slow flowing water. The upper portions of the mud horizon gradually become sandy, grading into a thin (20cm) layer of yellowish brown sand, reflecting a change to a cold, dry, climate. The mud and sand horizons are overlain by 3m of reworked loess, indicating a much more extreme colder and drier climate. The loess-paleosol sequence in the top unit indicates a series of climatic fluctuations within the Late Holocene.

SAMPLE COLLECTION

We collected fossil plant material or wood fragments, carbonate nodules, organic paleosol and organic river mud. Wood fragments were from the top 30cm of the pit at Bei Zhuang Cun (86-C-18), with organic mud (86-C-20) from 130cm below the pit surface (Fig 2). We also collected wood fragments from the lowest unit at Jie Zhi Cun (86-C-16C), to cross-correlate with the lowest section of the dark grayish-green muds of Bei Zhuang Cun (ca 1350–900cm depth), from which fossil plant residue (86-C-16A) in dark gray mud (86-C-16) was collected (Fig 2). Another wood sample (86-C-16B) was collected by Sun Jian Zhong, Xian Geology College, from the Bei Zhuang Cun profile during the 1970s, which also correlates with the base of this section at ca 1350cm depth. Five samples of sandy mud (86-C-21, 86-C-15, 86-C-23, 86-C-24 and 86-C-25) were collected from the middle and top of the section, 1260–950cm below surface.

The section from 900–600cm below surface, secondary loess, was devoid of dating material, leaving a gap of ca 300cm in the chronological sequence. Four samples were collected from the upper unit, starting with the broad bean-size carbonate nodules from the lowest paleosol (86-C-11). Sample 86-C-12 was taken from the top of the lowest paleosol. Samples 86-C-13 and 86-C-27, were taken from the top of the middle paleosol, and 86-C-28 was taken from the top of the upper paleosol (Fig 2).

EXPERIMENTAL

Chemical Fractionation of Paleosols

The paleosol samples were wet sieved using a 0.5mm sieve, treated with hot 1M HCl, rinsed with distilled water, then dried and crushed to <0.5mm. Successive solvent extractions were carried out in an ultrasonic bath for 30 min at a time (McIver, 1962), using redistilled solvents. Benzene/ethanol (2:1) was followed by ethanol, then multiple extractions with water until no solvent could be detected within the samples. After each extraction, the solvent was separated as rapidly as possible by vacuum filtration, and the residue was air dried. We decided that the extraction process could possibly be improved by replacing benzene with chloroform, which did not seem to alter the efficiency of the extractions, and if anything, the chloroform/ethanol mixture seemed to be more efficient than the benzene/ethanol mixture. The above sequence of solvents was used both to provide a progressive increase in polarity and to facilitate removal of the organic solvents from the samples (Head, 1979).

After solvent extraction, NaOH soluble and insoluble fractions were prepared by adding hot 0.5M NaOH solution, which was then removed (after stirring periodically for at least an hour) by filtration. The resulting dark-colored NaOH solutions were acidified and the dark brown precipitates formed were rinsed by decantation, then dried at low temperature. The sodium-hydroxide-insoluble residues were acidified, rinsed and dried. Where possible, ^{14}C and $\delta^{13}C$ determinations were carried out on both fractions. On some occasions, the NaOH soluble fraction was either not obtainable or was not large enough for dating.

Treatment of Wood and Plant Material

The wood and plant material samples were chopped into small pieces and dried. The material was then placed in ca 800ml distilled water containing 3ml concentrated HCl to achieve a pH of ~3. The samples were heated on a steam bath to ca 75°C, and sodium chlorite ($NaClO_2$) was added at a concentration of ca 7.5g/25g sample. The reaction was allowed to proceed at 75°C for ca 2 hr, then the pH was checked and more HCl was added when necessary to bring the pH back to 3. If the wood had not become light yellow, a second portion of $NaClO_2$was added. Three of the four samples treated did not turn light yellow, and we decided not to add more $NaClO_2$, since the degree of degradation of the wood was such that further pretreatment may not have left enough material for dating. On completion of this treatment, the samples were filtered, thoroughly rinsed and dried.

Treatment of Soil Carbonates

The small carbonate nodules found at the base of the lowest paleosol, ca 600cm below the surface (86-C-11),were separated from the matrix sediment and any soft material adhering to the surface of the nodules was removed with a dentist's drill. The nodules were then washed in distilled water and dried. A thin section cut from the largest nodule showed that the matrix of the nodules consisted of paleosol sediment with at least three possibly different forms of calcium carbonate. Microcrystalline carbonate had precipitated within voids and cracks, formed halos around the cracks and could also be found as a microcrystalline cement. We decided to test the proposition that not all of the carbonate inclusions were contemporaneous and that they could be successively hydrolyzed using acid solutions of different strengths. The nodules were hence crushed to <0.5mm and treated with 50% acetic acid solution at room temperature to evolve CO_2 for benzene synthesis. The reaction was allowed to run at close to atmospheric pressure, and as soon as most effervescence had ceased, CO_2 collection was stopped. The reaction was then allowed to proceed at reduced pressure until all effervescence had ceased. The residue was then filtered, rinsed and treated with 1M HCl solution. The reaction was allowed to proceed at room temperature and reduced pressure until all effervescence had ceased and the evolved CO_2 was also taken for benzene synthesis. Consequently, three carbonate fractions were separated for dating. The paleosol matrix left as a residue after the acid treatment was rinsed, dried and given the same treatment of solvent extraction and leaching with 0.5M NaOH solution as the other paleosol samples.

Fractionation of Solvent Extracts

The distilled-water-soluble fractions contained negligible amounts of organic material, so these fractions were discarded. The benzene/ethanol (chloroform/ethanol) and ethanol solvents were removed by distillation, and the residues were dried on a hot water bath. Chromatographic columns were set up using chromatographic grade silica gel, which had been previously heated to 130°C in an oven for ca 3 hr. The organic extracts were dissolved in hexane/benzene (90:10 v/v), then passed through the columns using the following solvent eluents: a) hexane/benzene (90:10 v/v), b) benzene, c) benzene/ethanol, (90:10 v/v), d) ethanol (Hodgson *et al*, 1968). In this step also, the benzene was replaced by chloroform. The organic fractions eluted by these solvents were then collected by distillation of the solvents, the residues were taken almost to dryness on a hot water bath, then dried with a vacuum desiccator.

Analytical Procedures

For chemical analyses, each available humic acid sample was redissolved in 0.5M NaOH solution in a nitrogen atmosphere, the solutions were filtered and the humic acids were reprecipitated by acidification using 1M HCl solution. The humic acid precipitates were then rinsed with distilled water, freeze-dried and stored in a dry nitrogen atmosphere. C, H, N and ash content analyses were done on these humic acid samples and the oven dry, ash free C, H and N concentrations were calculated, with the concentration of O being obtained by subtraction.

Optical density measurements were taken on solutions of humic acid fractions using the technique described by Kononova (1966). Portions of the humic acids were taken up in 0.05M $NaHCO_3$ solution and were stored without exposure to light for ca 4 days. The measurements were carried out using a Pye Unicam Spectrophotometer at wave lengths of 465 and 665nm. Extinction ratios (E4:E6) could then be calculated from the data.

RESULTS AND DISCUSSION

Solvent Extracts

The organic fractions obtained from the solvent extraction procedures have not as yet been thoroughly analyzed. Further initial chromatographic separation using silica gel columns, together with preliminary qualitative analysis has indicated that there may only be a trace of neutral organic compounds present in the extracts. The predominant organic compounds seem to be carbohydrate residues, with possibly some phospholipids (Christie, 1984). This conclusion is in agreement with the data obtained by Jia Liu and Yuan (1987). They stated that the organic components found in paleosols from the Luochuan Section, Shaanxi Province, indicated that the source material was most probably bacterial residue.

Solvent extracts from the organic mud and paleosol samples are more prevalent in the lowermost sediments of the Bei Zhuang Cun profile than in the upper sediments, indicating that extensive leaching has occurred down the profile. It is also an indicator of the significantly decreased degree of porosity within the lower muds. The general organic composition of the extracts from the benzene (chloroform)/ethanol extractions, and the ethanol extractions seems to be very similar. Hence, the grouping of organic components is most probably quite narrow, indicating either a relatively narrow range of input sources for the organic material, or intensive leaching down the profile with selective adsorption of a narrow range of compounds. This latter interpretation could explain the relatively low concentration of organic carbon in all of the sediments from this profile (<2% C).

Elemental Analysis

Table 1 indicates H/C, O/C, and C/N atom ratios for a series of humic acid fractions from the Bei Zhuang Cun profile. Steelink (1985) states that H/C, O/C, and C/N (or N/C) ratios can prove quite useful to 1) identify types of humic substances, 2) monitor structural changes of humates in soils and sediments, 3) devise structural formulae for humates, and 4) eliminate the role of ash content. According to Steelink, the O/C ratio is the clearest indicator of humic types, and that normal humic acid ratios' cluster around a value of ca 0.50, with H/C ratios above 1.3 normally indicating that the material may be a non humic substance. H/C ratios were plotted against O/C ratios for the seven fractions listed in Table 1, together with values obtained from Steelink (1985), Head (1987), and Calderoni and Schnitzer (1984). Only three of the fractions listed in Table 1 could be considered to fit the cluster of soil humic acid values.

In Table 1, sample 86-C-15 and 86-C-23 (Fig 2) give every indication of being soil humic acids, since their H/C and O/C ratios are very similar to what would be expected (Steelink, 1985). Samples 86-C-28 (1–3) were collected by successive treatments with hot 1M HCl and hot 0.5M NaOH solutions, similar to the treatments carried out by Kigoshi, Suzuki and Shiraki

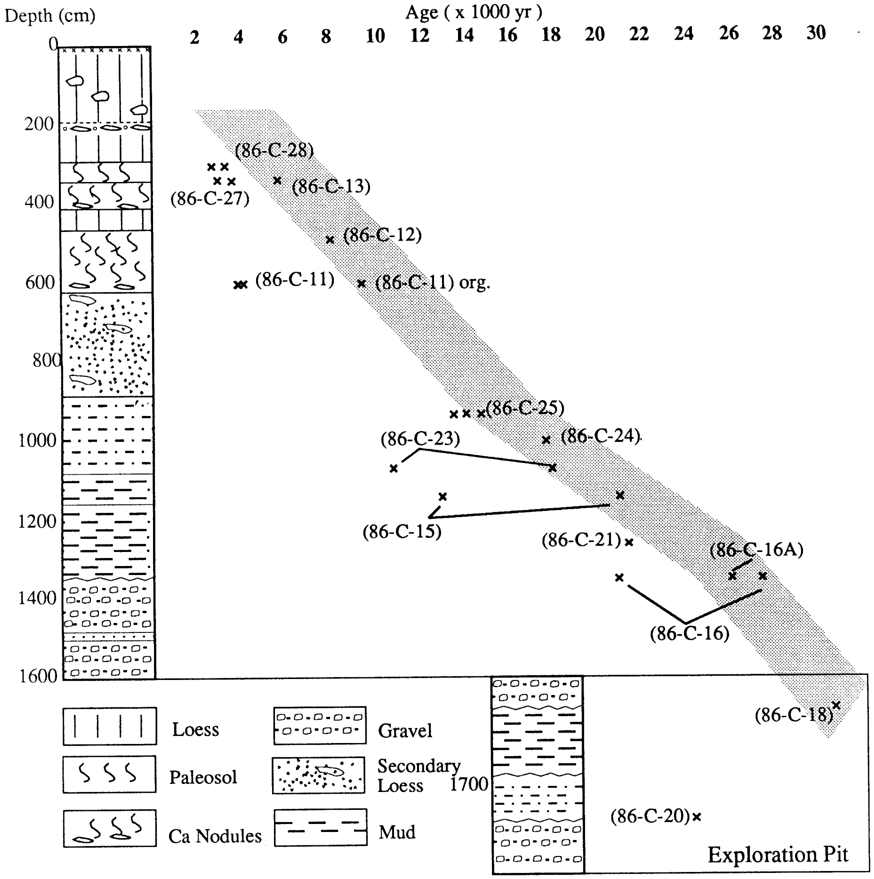

Fig 2. Age-depth curve for Bei Zhuang Cun profile. Sample numbers are marked on the diagram. Radiocarbon ages are given in Table 2. (Stratigraphic column is after An Zhi Sheng, pers commun). Shaded area indicates region in which the most reliable ages fit.

(1980). Fraction 86-C-28(1) has a very low H/C ratio (0.56), but quite a high O/C ratio (0.90), possibly indicating a polyphenolic structure. If this is the case, the fraction could contain lignin breakdown products that have not undergone biological conversion to humic acids. Fraction 86-C-28(2) also has a high O/C ratio (0.76). Apart from this, it could fit the soil humic acid values quite well. Hence, this fraction could contain an abundance of polyphenolic groups within the humic acid structure. With fraction 86-C-28(3), the same explanation could apply for its high O/C ratio (1.19). Fractions 86-C-27(1) and 86-C-27(3) were also collected by successive treatments with hot 1M HCl and hot 0.5M NaOH solutions (the 2nd fraction was not analyzed). Fraction 87-C-27(1) could be considered to be structurally similar to normal soil humic acids, but fraction 86-C-27(3) does not fit the criteria listed above, and hence is non-humic in structure. The H/C and O/C ratio values could be indicative of a carbohydrate residue composition. The C/N value, however, strongly suggests the presence of a relatively large number of amino acid functional groups. C/N ratios for the other fractions in Table 1 do not indicate any specific pattern.

TABLE 1

Analysis of humic acids on an oven-dry ash-free basis with H/C, O/C and C/N ratios

Sample	%C	%H	%O	%N	H/C	O/C	C/N
86-C-15	56.96	4.57	34.36	4.11	0.96	0.45	16.2
86-C-23	53.23	4.85	39.99	1.93	1.09	0.56	32.2
86-C-28(1)	43.26	2.05	52.02	2.67	0.56	0.90	18.9
86-C-28(2)	46.54	2.91	47.22	3.33	0.75	0.76	16.3
86-C-28(3)	36.53	3.17	58.13	2.17	1.03	1.19	19.6
86-C-27(1)	55.44	2.75	39.15	2.66	0.59	0.53	24.3
86-C-27(3)	26.29	2.97	57.98	12.76	1.35	1.65	2.4

Optical Density Measurements

Optical density measurements were carried out at wave lengths 465 and 665 nm, and E4:E6 ratios for the humic acid fractions listed in Table 1 are plotted against H/C ratios in Figure 4. Ertel and Hedges (1983) have indicated that this type of plot should show a direct correlation for terrestrial humic acids. Figure 3 indicates a linear correlation between samples 86-C-15, 86-C-23, and 86-C-27(3), and a different linear correlation between samples 86-C-27(1), 86-C-28(2), and 86-C-28(3). Sample 86-C-28(1) does not correlate with any of the others.

Thurman (1985) stated that in groundwater humic acids, there is an inverse relationship between E4:E6 ratios and mean residence time. There is also an inverse relationship between E4:E6 ratios and the molecular weight of humic acids (Steelink, 1985). The values of the E4:E6 ratios in Figure 3 vary between 3.70 and 5.11, and there is no correlation between those samples having H/C and O/C ratios indicating humic acid, and non-humic structure. In fact, the samples having the lowest E4:E6 ratios (and hence supposedly the highest molecular weight), are those which do not fit the humic acid structural guidelines mentioned above.

^{14}C Determinations

Results of ^{14}C determinations carried out on the various chemical fractions of wood, mud, carbonate nodules and paleosol are reported in Table 2 as conventional ages (Stuiver & Polach, 1977), and the ^{14}C ages are plotted against the Bei Zhuang Cun stratigraphy in Figure 2. Samples labeled with the Laboratory Code XLLQ were pretreated, and age determinations were carried out, in the Radiocarbon Laboratory of the Xian Laboratory of Loess and Quaternary Geology, Academia Sinica. The remaining samples were treated in the ANU Laboratory.

The lowest unit in the Bei Zhuang Cun profile (1650–1350cm), contains mostly gravel, and no material was found for dating. However, in the pit dug below this unit, which exposed a further 2m of sediment, a layer of dark grayish-green mud (30–100cm) was found containing plant fragments. Reed root fragments were separated from these, at the top of the horizon, and the holocellulose fraction gave an age of 30,930±320 BP (86-C-18).

Further below this sample, at the bottom of a grayish-green mud layer (100–130cm), a sample of the mud was taken for dating (86-C-20), and an age of 24,470±320 BP was obtained from the NaOH insoluble fraction only, since no NaOH soluble fraction could be separated. The age for sample 86-C-20 is significantly younger than that for the reed roots (86-C-18), yet the reed root result must be considered to be more reliable. Hence, deposition of these fluvial sediments would have commenced well before 31,000 BP.

TABLE 2

^{14}C ages of fractions of samples collected from the Bei Zhuang, Cun area

Sample no.	Lab code	Depth (cm)	Type of material	Age × 10^3 yr BP
86-C-28	ANU-6201	300	Organic soil*	3.27±0.20
86-C-28	ANU-6201	300	Organic soil**	2.54±0.25
86-C-27	ANU-6202	360	Organic soil*	3.42±0.36
86-C-27	ANU-6202	360	Organic soil**	3.01±0.36
86-C-13	XLLQ-111	360	Organic soil*	5.72±0.10
86-C-12	XLLQ-37	490	Organic soil*	8.00±0.08
86-C-11	XLLQ-30	600	Inorg CO_2(1)†	3.86±0.16
86-C-11	XLLQ-33	600	Inorg CO_2(2)†	3.75±0.09
86-C-11	XLLQ-35	600	Inorg CO_2(3)†	4.09±0.14
86-C-11	XLLQ-104	600	Nodule organics*	9.60±0.17
86-C-25	XLLQ-106	950	Organic soil*	14.65±0.19
86-C-25	ANU-6393	950	Organic soil*	13.46±0.78
86-C-25	ANU-6393	950	Organic soil**	14.00±1.70
86-C-24	XLLQ-105	1000	Organic soil*	17.71±0.40
86-C-23	XLLQ-109	1070	Organic soil*	10.83±0.38
86-C-23	XLLQ-101	1070	Organic soil**	18.38±0.52
86-C-15	XLLQ-46	1140	Organic soil*	12.97±0.31
86-C-15	XLLQ-44	1140	Organic soil**	21.03±0.44
86-C-21	XLLQ-107	1260	Organic soil*	21.42±0.26
86-C-16	XLLQ-48	1350	Organic soil*	21.00±0.50
86-C-16	XLLQ-45	1350	Organic soil**	27.44±0.32
86-C-16A	XLLQ-26	1350	Holocellulose	26.08±0.27
86-C-16B	XLLQ-28		Holocellulose	28.44±0.34
86-C-16B	XLLQ-28(2)		Whole wood	24.30±0.30
86-C-18	XLLQ-58	Pit,30cm	Holocellulose	30.93±0.32
86-C-20	XLLQ-112	Pit,100cm	Organic soil*	24.47±0.32
86-C-16C	XLLQ-29	Jie Zhi Cun	Holocellulose	27.09±0.42

* NaOH insoluble fraction from soil or mud

** NaOH soluble fraction from soil or mud

† Inorganic C from carbonate nodules

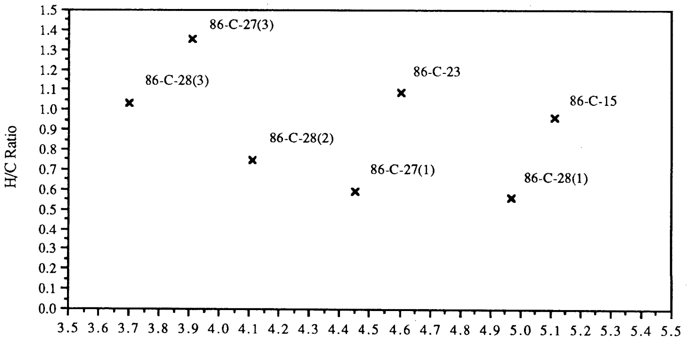

Fig 3. Plot of E4/E6 ratios against H/C ratios for humic acid fractions listed in Tables 1 and 2. There is a linear correlation between samples 86-C-28(3), 86-C-28(2) and 86-C-27(1), all of which contain a non-humic component. There is also a linear correlation between 86-C-27(3), 86-C-23 and 86-C-15, yet 86-C-27(3) contains a non-humic component.

The next unit (1350–900cm) can be considered to be dated at the bottom by a sample of the dark grayish-green mud containing reed root fragments. NaOH soluble and insoluble fractions of the mud (86-C-16) were dated, with the NaOH soluble fraction providing the most acceptable age (27,440±320 BP). The holocellulose fraction of the reed root fragments contained in the mud (86-C-16A), provided an age of 26,080±270 BP, which is consistent with the concept of the reed roots growing into the mud. Both the holocellulose fraction and untreated wood fragments (86-C-16B), which were collected in the 1970s by Sun Jiang Zhong, Xian Geology College, from the bottom of the unit, provide ages of 28,440±340 and 24,300±300 BP, respectively. Hence, the untreated wood contained younger foreign material. The holocellulose ages correlate well with the age obtained from the holocellulose fraction of wood fragments collected within mud from Jie Zhi Cun (86-C-16C), 27,090±420 BP.

Dark greenish mud (86-C-21) was collected 1260cm below surface, and the NaOH insoluble fraction (no NaOH soluble fraction could be recovered), dated to 21,420±260 BP, which seems too young. Green mud from the top of the horizon, 1140cm below surface (86-C-15), yielded 21,030±440 BP for the NaOH soluble fraction and 12,970±310 BP for the NaOH insoluble fraction. The pattern of young NaOH insoluble ages is followed with this sample, and the age for the NaOH soluble fraction is consistent with the most reliable results from the lower sediments. The H/C and O/C ratios obtained for this humic fraction, together with the E4:E6 ratio, indicate that it could be considered to be a normal, terrestrial humic acid. If a uniform rate of sedimentation is postulated for this mud layer, then ca 24,700 BP is more feasible for 86-C-21.

Sample 86-C-23 was collected 1050cm below surface, at the top of a dark mud horizon (Fig 2). The NaOH soluble fraction was 18,380±520 BP, while the NaOH insoluble fraction was 10,830±380 BP. H/C and O/C ratios, together with the E4:E6 ratio, indicate that this fraction is a terrestrial humic acid. Hence, the result for the NaOH soluble fraction is considered to be the most reliable. Sample 86-C-24 was collected from the center of a transitional horizon of mud and secondary loess, 1000cm below surface. The NaOH insoluble fraction (no NaOH soluble fraction could be recovered) was 17,710±400 BP, which is not significantly different from the result obtained for 86-C-23 (NaOH soluble). This result does not seem to be in keeping with the results obtained from NaOH insoluble fractions further down the profile, and could be interpreted as being reliable.

A series of successive acid/alkali leaches were done on sample 86-C-25, collected from the mud and secondary loess horizon, 950cm below surface. So far only the second humic acid fraction and the NaOH insoluble fraction were dated. NaOH insoluble fractions were separated from this sample at both the Xian Laboratory of Loess and Quaternary Geology and ANU (Table 2). Regrettably, the fractions separated at ANU were very small, resulting in a large error figure for the NaOH insoluble fraction (13,460±780 BP). Within the error limits obtained, there is no significant difference in age between the three determinations. This possibly provides a justification for accepting the ^{14}C age obtained from the NaOH insoluble fraction of 86-C-24. The transitional layer of mud and secondary loess from 950–900cm, where there is a thin dark sandy layer, contained no datable material. Directly above this (900–600cm), is a layer of secondary loess which also does not contain any datable material.

The upper unit (600–200cm) consists of 3 paleosols separated by 2 thin layers of loess. The lowest paleosol (600–475cm) contains a layer of small, broad bean-size carbonate nodules (86-C-11) at the base. Three fractions were separated and dated: 3860±160 BP (fraction 1), 3759±90 BP (fraction 2), and 4090±140 BP (fraction 3). These results are not significantly different, and could be considered to cover the same age range. The NaOH insoluble fraction (no NaOH soluble material was recovered) of the paleosol matrix within the nodules, yielded 9700±250 BP, which seems to fit the sedimentary profile, while the ages obtained from the inorganic fractions do not. Sample 86-C-12 (490cm below surface, near the top of the paleosol layer), dated to 8000±80 BP from the NaOH insoluble fraction, with no NaOH soluble fraction present. This fits in with the general trend of ages within the profile.

Two samples were taken from the middle paleosol layer (425–350cm), 86-C-13, from 400cm, and 86-C-27, from 360cm below surface. The NaOH insoluble fraction of 86-C-13 (no NaOH soluble fraction was recovered) dated to 5700±100 BP. However, NaOH soluble and insoluble fractions of 86-C-27 gave ^{14}C ages of 3010±360 and 3420±360 BP, respectively. The ages for both of these fractions are not significantly different and are substantially younger than that for 86-C-13. The loess layer below this paleosol (475–425cm) contains reddish potsherds belonging to the Yang Shao culture, which has an age range of 5000–6000 BP. Hence, the age obtained for 86-C-13 (NaOH insoluble) fits the sequence. In Table 1, humic acid fractions from 86-C-27 indicate, from H/C, O/C and C/N ratios, the possible presence of both humic and non-humic components. Since the NaOH soluble fraction of 86-C-27 was a composite, the presence of younger contaminants would be likely. Hence, the NaOH insoluble fraction is also likely to contain younger material. Obviously, the pretreatment techniques have not been successful with this sample.

Sample 86-C-28 was collected from the top of the upper paleosol (350–300cm), and both NaOH soluble and insoluble fractions were separated, giving ^{14}C ages of 2540±250 BP and 3270±200 BP, respectively. In this case, the NaOH insoluble fraction age is closer to the true age since the loess layer above (300–200cm) contains gray potsherds of ca 3000 BP. From Table 1, H/C, O/C and C/N ratios from humic acid fractions 2 and 3 of 86-C-28 indicate the possible presence of non-humic components. Hence, the NaOH soluble fraction of 86-C-28 contains a younger, non-humic component.

CONCLUSIONS

The Bei Zhuang Cun section is situated well above the present water table. With extensive farming in the area, relatively large amounts of water-soluble organic residues would percolate down through the sediments and possibly be adsorbed by both fossil humus substances and the weathered clay component of the sediments. The pretreatment techniques used in this study have enabled us to obtain reliable ^{14}C ages from the organic sediments that fit built-in controls such as the wood and plant material samples from the base of the profile, and historical evidence from the top of the profile.

A general picture of environmental and climatic changes can be obtained from the ^{14}C ages considered to be reliable in this study (shaded area in Fig 2). From at least 31,000 to ca 28,000 BP, the sediments below 1350cm formed, indicating a change from a relatively warm and wet climate with periodic flooding to cooler, drier conditions allowing the deposition of mud from relatively slow flowing water. From ca 28,000–18,000 BP similar conditions dominated. From ca 18,000–14,000 BP there was a gradual change to a cold, dry climate. From ca 14,000–10,000 BP much more extreme cold and dry conditions dominated and from ca 10,000–8000 BP, conditions became warmer and wetter. Colder, drier conditions occurred between ca 8000–6000 BP and a warmer, wetter period then continued from ca 6000–3000 BP. Extensive agricultural use of the valley has modified the upper sediments to such an extent that any interpretation of climatic changes from 3000 BP is difficult.

Relatively simple analytical techniques, such as the calculation of H/C, O/C, and C/N atom ratios, together with the measurement of E4:E6 ratios can provide useful selection criteria for estimating the humic/non-humic component of soil humic acids, and hence the potential reliability of ^{14}C ages from humic acid fractions. More widespread use of these techniques may clarify problems found by Kigoshi, Suzuki and Shiraki (1980) and Goh, Molloy and Rafter (1977).

In this study, we have concentrated mainly on NaOH soluble and insoluble fractions of organic sediments, and have found that for the basal section at Bei Zhuang Cun (>900cm), after solvent extraction, the NaOH soluble humic components offer the most reliable dating fraction. In the top section, it has been much more difficult to isolate humic acids from the non-humic components, and more work needs to be carried out to identify the processes.

The most logical explanation for younger NaOH insoluble fractions is that continuing weathering processes in the clay component of the sediments is providing active sites for adsorption of, or chemical combination with, soluble organic material being washed down the profile. By separating soil samples into size components from 0.25–20μ, Scharpenseel *et al* (1986) have found a relationship between carbon content and age (the largest fractions have the highest carbon content), and the middle size fractions usually are the oldest. This type of approach should shed more light on interpretation of ages from organic sediments.

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