

Isotopic Composition of Organic Carbon in Some Soils of Semiarid Africa

G.P. Warren and J.A. Meredith

*Department of Soil Science, University of Reading,
Whiteknights, PO Box 233, Reading RG6 6DW, UK*

Introduction

Unique information concerning the stability and sources of the humified soil organic matter (SOM) can be obtained from the isotopic composition of its carbon (C). It is now understood that SOM is formed by microbial processing of plant and animal residues occurring in the soil. Therefore, the isotopic composition of SOM should reflect the C isotopic composition of the plant ecosystem above the soil. Three isotopes of C exist in natural ecosystems (Table 3.1). Radioactive ^{14}C originates in the upper atmosphere and moves into biological materials via photosynthetic fixation. Its use for the dating of archaeological materials is well known and the half-life of 5568 years means that results are most reliable for materials with an age in the range 200–40,000 years (Goh, 1991). However, it can also be used to indicate the apparent mean age of soil C (Jenkinson, 1966). Dating of soil C indicates that some fractions of SOM are remarkably resistant, with ages of the order of 9000 years (Stout *et al.*, 1981). Carbon-13 is a stable isotope and, again, it is ultimately derived from the atmosphere. Its concentration in SOM depends on both atmospheric concentration at the time of photosynthetic fixation and the photosynthetic pathway. Thus, at the ecosystem level, ^{13}C measurements are useful in following the flow of C through food chains and identifying the sources of C in soil and sediments (Boutton, 1991). For example, by changing the cover vegetation from a C_3 to a C_4 species, or vice versa, an estimate of the mineralization rate of the older C (Martin *et al.*, 1990), or the effects of land management on C mineralization (Balesdent *et al.*, 1990), can be obtained.

Table 3.1. Isotopes of atmospheric carbon.

Parameter	Atomic weight		
	12	13	14
Half-life (years)	∞	∞	5568
Natural abundance (%)	98.89	1.11	1×10^{-16}

The cost of making isotopic analyses is high - normally over \$US400 per sample at commercial rates - so it is imperative that samples are selected carefully and the objectives defined before embarking on such work. Additional value may be obtained by cooperation between different projects. Thus, the work reported here draws on preliminary results of two different projects, in order to make comparisons across soil types from four uncultivated sites in semi-arid eastern Africa. As far as we know, no such analysis has been undertaken previously for soils of these ecosystems.

Sites and Organizations

The location and general environmental characteristics of the four sites are given (Table 3.2). Machanga and Mutuobare are experimental agriculture sites, operated by the Kenya Agricultural Research Institute (KARI). The other pair of sites provides representative natural ecosystems on contrasting soils, for a separate project. The Nairobi site is maintained by the Department of Botany, University of Nairobi. Misamfu site is located at the Misamfu Research Station, Kasama, of the Ministry of Agriculture, Zambia. The two projects mentioned have different objectives, so there were some differences in the sampling horizons used and locations of the analyses for

Table 3.2. Environmental information about the sites.

Parameter	Machanga	Mutuobare	Nairobi	Misamfu
Country	Kenya	Kenya	Kenya	Zambia
Latitude and longitude	1°S, 37°E	1°S, 37°E	1°S, 37°E	10°S, 31°E
Altitude (m)	1050	900	1500	1300
Rainfall (mm year ⁻¹)	740	809	762	1275
Peak rainfall	November, April	November, April	November, April	January
Mean temperature (°C)	23	25	19	26

each pair of sites. This should be borne in mind, but we believe that these differences do not affect the conclusions drawn.

None of the experimental areas sampled for this work has experienced arable cultivation in recorded times. They are considered to represent stable ecosystems, in which the only impact by humans has been the traditional long-term, low-intensity uses of grazing and wood harvesting.

Machanga and Mutuobare

This pair of sites is located in lower Embu district, Kenya, on shallow chromic cambisols (35-70 cm deep) overlying granitoid gneiss (van de Weg and Mbuvi, 1975) and supporting *Acacia-Commiphora* bush. The major soil clay minerals are kaolinite and illite. Many properties of the two soils (e.g. pH, mineralogy) are very similar (Table 3.3). The sites differ because Mutuobare is believed to lie on a minor outcrop of phosphate-bearing rock, indicated by an anomalously high concentration (30 mg kg^{-1}) of phosphorus (P) extractable by the Olsen method (0.5 mol l^{-1} sodium bicarbonate, NaHCO_3). Consequently, plant growth is vigorous in comparison with that at Machanga. At Machanga, trees provide an incomplete canopy cover, and a diverse range of grasses maintain ground cover throughout the year. The site is influenced by grazing, by domestic goats and cattle in recent decades and by wild herbivores before. Mutuobare site has a similar history, except that human settlement in the vicinity is more recent. The tree density is greater than at Machanga, in line with its higher soil fertility, and the number of grass species lower.

At Machanga, 48 soil-sampling pits were dug for the 0-20 cm horizon, representing an experimental area $100 \text{ m} \times 40 \text{ m}$. Of these, 26 pits were deepened to sample the 20-35 cm horizon. At Mutuobare, 19 soil-sampling pits were dug for the 0-20 cm horizon, representing an area $120 \text{ m} \times 15 \text{ m}$. Of these, 12 pits were deepened to sample the 20-35 cm horizon. The

Table 3.3. Selected properties of the surface horizons.

Parameter	Machanga	Mutuobare	Nairobi	Misamfu
pH (water)	6.5	6.5	6.9	4.6
Clay (%)	24	20	47	8
Olsen-P (mg kg^{-1})	0.9	30.0	—	—
C/N ratio	11.2	11.3	14.1	15.6

Dashes indicate that no values were available.

N, nitrogen.

maximum practical sampling depth by this method was 35 cm, because of the increasing concentration of stones.

Nairobi

The site is located on a calcareous vertisol within the Nairobi National Park. The major soil clay mineral is an interstratified material with a major swelling (smectitic) component. Vegetation is open grassland with a few scattered trees, because of constant grazing by wild herbivores. There has been no direct influence of humans in the 40 years since the park was established. Sixteen soil-sampling pits were dug for the 0-15 cm horizon, representing an area about 100 m × 20 m. All the pits were deepened to sample the 15-30 cm and 30-45 cm horizons.

Misamfu

The soil here is a sandy oxisol with little SOM, especially in the subsoil. The main clay mineral is kaolinite, with micas as secondary components. It supports a *miombo* woodland with a single-storey canopy. Soil sampling was performed to the same horizons as at Nairobi (0-15, 15-30, 30-45 cm) to represent an area about 60 m × 10 m. Eight sampling pits were dug, taking care to avoid termite mounds and bare patches.

Field-sampling and Laboratory Methods

The soils were sampled in February or March 1994. The top horizon of each sampling pit was excavated by hand from an area 50 cm × 50 cm, utilizing a square steel ring to shore up the sides of the pit and prevent topsoil from falling into samples from the lower horizons. The lower horizons were excavated in a similar way, using smaller steel rings nested inside. The soil was sieved through a coarse mesh (12 or 17 mm aperture) to remove most plant roots, mixed, and a sample of about 1 kg taken. The sample was air dried and ground to pass a 2 mm mesh, excluding gravel.

Chemical analyses were performed at Reading. The soil was finely ground (< 0.2 mm) in a 'Tema' puck mill. Total organic C was measured on all replicate samples individually, by the method of Kalembasa and Jenkinson (1973), in which wet oxidation by sulphuric acid (H₂SO₄) and dichromate (K₂CrO₇) is used, followed by back-titration with ammonium ferrous sulphate, (NH₄)₂SO₄·FeSO₄.

For isotopic analysis, composite samples were prepared from < 2 mm sieved soil. For Machanga and Mutuobare, each site/horizon combination

was represented, using an equal amount of soil from each sampling pit. This soil was mixed and finely ground (< 0.2 mm). Isotopic analysis was carried out by dry combustion to release C as carbon dioxide (CO₂), followed by accelerator mass spectrometry to determine the proportions of ¹²C, ¹³C and ¹⁴C. Isotopic analysis was carried out by the Research Laboratory for Archaeology and the History of Art, University of Oxford, UK. For the Nairobi and Misamfu soils, replicate composite samples were made up by combining soil from alternate pits; results given are the horizon means. Isotopic analysis was carried out through the National Environmental Research Council (NERC) Radiocarbon Laboratory, East Kilbride, UK, in association with the University of Arizona. For the Nairobi soil, it was necessary to remove carbonate-C with cold dilute hydrochloric acid (HCl) prior to combustion of the SOM organic C (SOM-C).

Composition of Organic Carbon in Soil

Total organic carbon

The highest concentration of SOM-C was in the clay-rich Nairobi soil (Table 3.4). This is as expected, since clay stabilizes organic matter in physically protected humus-clay complexes.

The Mutuobare surface horizon has a greater concentration of SOM-C compared with the otherwise similar soil at Machanga. This is ascribed to the visibly greater standing plant biomass at Mutuobare, caused by the generous soil P supply, and leading to larger C inputs at the surface. Below 20 cm, the concentration of SOM-C was the same in these two soils.

With little clay, stabilization of SOM at Misamfu should be poor and, as expected, SOM-C was lowest of the four soils, except for the top horizon, where it appeared a little more than in Machanga. Since Machanga has bimodal rainfall, but Misamfu only unimodal, it might be that the higher rate of wetting-drying cycles at Machanga gives more vigorous decomposition

Table 3.4. Organic C (mg g⁻¹) in each horizon (depths given in the text).

Horizon	Machanga	Mutuobare	Nairobi	Misamfu
Top	8.8	10.9	23.6	9.3
Middle	6.1	6.1	12.9	3.0
Bottom	–	–	11.5	1.7

Dashes indicate that no samples were available.

of SOM-C. The decline of SOM-C concentration with depth was especially marked at Misamfu.

Carbon-14 concentration

The reporting and understanding of ^{14}C results for soil and its components present some serious problems; here, they are touched upon only lightly. This arises because of: (i) the complexity and diversity of SOM; and (ii) the wide variations in atmospheric ^{14}C after the mid-1950s, caused by atmospheric testing of nuclear weapons. The latter events caused inputs of highly labelled C, the activity of which tends to swamp the signals from the low-activity old materials. The present reporting convention is the '% modern' basis, which measures the ratio of sample ^{14}C concentration to the concentration in a standard material (National Bureau of Standards (NBS) oxalic acid) as at 1950. This is appropriate for comparisons between materials, as here.

In the topsoils, SOM-C was always greater than 100% modern, meaning that the average age is more recent than 1950. For pre-1950 material, approximate ages can be ascribed. The 20-35 cm horizons at Machanga and Mutuobare were dated at 835 and 415 years before the present (BP), respectively, and the Nairobi 15-30 cm horizon at 320 years BP. Thus it is clear that SOM-C of the subsurface horizons is rich in resistant fractions of humic matter. However, it must be remembered that SOM-C is in a state of turnover. Some must be very new and there is a continuum of different fractions, each of unknown amount and concentration of labelling, giving the overall mean age observed.

The radiocarbon (^{14}C) age of SOM-C consistently increased down the profile (Table 3.5), accompanying the decrease in SOM-C concentration, the main inputs of C being from surface roots and litter. Therefore, SOM in lower horizons both is lower in concentration and has a higher age and slower mean turnover. Topsoil SOM-C was younger at Mutuobare than at Machanga, suggesting that the additional SOM-C formed by vigorous plant growth is added to a fast-turnover pool and the resistant, organomineral-

Table 3.5. Carbon-14 concentration of organic C in each sampled horizon: radiocarbon age (% modern relative to 1950).

Horizon	Machanga	Mutuobare	Nairobi	Misamfu
Top	103.4	110.2	103.0	117.0
Middle	90.1	94.9	95.6	107.3
Bottom	--	--	87.1	101.6

Dashes indicate that no samples were available.

protected core SOM fraction may be of similar size in both soils. Thus different biomass inputs give different ratios of decomposable to recalcitrant SOM.

For each horizon, the youngest SOM was at Misamfu, where there is relatively little clay to stabilize SOM. Even the bottom horizon was 101.6% modern (Table 3.5), suggesting poorer stabilization of SOM in this soil compared with the others and also explaining the sharp decline in SOM-C with depth (see Table 3.4).

The results for Nairobi soil in comparison with the other soils were not quite as expected. It was thought that the high clay content would stabilize much SOM-C and give a greater age than at the other sites. In comparison with Machanga, topsoil SOM-C age was about the same, while middle horizon SOM-C was younger (Table 3.5). However, there are several complicating factors in making this comparison. First is the different depth of sampling. The deeper top horizon sampled at Machanga (0-20 cm) means that older, subsurface SOM contributes more at Machanga than at Nairobi (0-15 cm). In a comparison of topsoils to the same depth, Machanga would probably be newer than Nairobi. The second problem is that Nairobi is a vertisol; deep cracks form during the dry season and some topsoil falls in. Thus the lower horizons are 'contaminated' with topsoil C, reducing differences between horizons. The trends down the profile are less marked in Nairobi than in the other soils, for both ^{14}C (Table 3.5) and ^{13}C measurements (Table 3.6).

Carbon-13 concentration

Results for ^{13}C measurements are customarily expressed relative to ^{13}C in a standard fossil carbonate (PD belemnite). At the four sites, the concentrations of ^{13}C in SOM-C were clearly associated with vegetation type. The higher plants, utilizing the C_4 photosynthetic route, have $\delta^{13}\text{C}$ in the range -19‰ to -6‰ (Smith and Epstein, 1971) and these are largely tropical grasses, including crops such as maize and sorghum. At Nairobi, the dominant vegetation is grass, and SOM-C here contained $\delta^{13}\text{C}$ of -11.7‰ in the surface

Table 3.6. Carbon-13 concentration ($\delta^{13}\text{C}\text{‰}$) of organic C in each horizon.

Horizon	Machanga	Mutuobare	Nairobi	Misamfu
Top	-19.4	-22.4	-11.7	-24.2
Middle	-17.8	-19.2	-11.1	-22.1
Bottom	-	-	-10.9	-21.6

Dashes indicate that no samples were available.

horizon (Table 3.6), which agrees well with the general mean around -13‰ for C₄ plants in the present environment (Boutton, 1991).

Most other species use the C₃ photosynthetic pathway, giving δ¹³C in the range -34‰ to -24‰ (Smith and Epstein, 1971), with a general mean of -27‰ at present (Boutton, 1991). At Misamfu, topsoil δ¹³C of -24.2‰ was near the mean value for C₃ species. This suggested that the grass cover underneath the tree canopy made relatively little contribution to SOM-C. At Machanga, δ¹³C was approximately intermediate between the mean C₃ and C₄ values, in line with the observed mixture of grass and tree species. At Mutuobare, the dense bush largely excludes grass, but δ¹³C = -22.4‰ for topsoil SOM-C seemed high in the expected range for a C₃-dominated ecosystem. However, the relative positions of Machanga and Mutuobare are as anticipated. Plants with Crassulacean acid metabolism, notably the *Cactaceae* and *Euphorbiaceae*, are able to switch between the two photosynthetic processes and their δ¹³C typically varies from -20‰ to -10‰. The presence of these plants might explain the Mutuobare result, but no members of these families are found there or at the other sites.

The δ¹³C increased down the soil profile (Table 3.6). Three mechanisms are at work here (Balesdent *et al.*, 1987): (i) discrimination against ¹³C in decomposition of plant material, giving resistant residues enriched with ¹³C; (ii) discrimination against ¹³C in mineralization of the SOM, leaving SOM further enriched in ¹³C; and (iii) the change in atmospheric CO₂ composition. However, at least in temperate soils, the third process can account for most of the differences between plant C and SOM-C in δ¹³C (Balesdent *et al.*, 1990). The mean δ¹³C value of atmospheric CO₂, currently -7.8‰ in rural areas, has decreased by about 1.2 over the last 130 years (Boutton, 1991), a consequence of anthropogenic CO₂ release from fossil fuels, which have δ¹³C of about -26‰. The higher δ¹³C in the older, subsurface SOM-C probably reflects the higher atmospheric δ¹³C at the time of its formation. Mutuobare and Misamfu sites have faster SOM-C turnover rates than Nairobi and Machanga, as indicated by ¹⁴C measurement (Table 3.5), so the influence of changes in atmospheric ¹³C should be greater in the former two soils. This can be seen by comparing the differences in δ¹³C between the middle (older) and top (younger) horizons (Table 3.6). Faster turnover at Mutuobare and Misamfu means that the δ¹³C difference between upper and lower horizons is more than at Nairobi and Machanga, where older, resistant fractions have more influence on the δ¹³C.

If it is accepted that the middle horizons of Machanga, Mutuobare and Nairobi have mean ages in the 300-800-year range, then it seems that the vegetation mix has probably changed little over several centuries. This is because the between-horizon difference in δ¹³C is obviously associated with atmospheric ¹³C change, and so there have been no large shifts between C₃ and C₄ plant populations. It is implied that the present ecosystems are reasonably close to a steady state.

Conclusions

By and large, the results presented here give strong qualitative support for present theories of SOM formation and turnover and their applicability to the natural East African ecosystem. The measurements show differences in the mean age of the SOM between sites and horizons and characteristic trends down the profile. The results are consistent with the concept of SOM comprising several pools of material, which have different turnover rates and hence different mean ages. It appears that the ratio of labile to resistant pools can vary between soils. This has implications for the rates of change in SOM under different land-use strategies.

Results obtained from the four sites of the two projects generally reinforced each other in this, necessarily qualitative, comparison. Given the high costs of sampling and analysis involved, it is a valuable conclusion, because this outcome increases confidence in further stages of the work. The results suggest that the sites are reasonably typical of the ecosystems.

To obtain full value from the numerical results, a modelling approach is indicated, since the net balance of SOM formation and destruction depends on many interacting processes. In the present projects, the current Rothamsted model of SOM (Jenkinson, 1990) has been adopted as the interpretative tool. At Machanga and Mutuobare, new bare fallow and cropped treatments (sorghum) have been imposed on some of the land. The changes in both total organic C and isotopic composition are being monitored to test and, if necessary, tune the model for this ecosystem. Funds permitting, the sites will be maintained for about 10 years. Soil from the Nairobi and Misamfu sites is being fractionated with a view to investigating components of different ages. Eventually, reliable model descriptions of SOM turnover will enable better prediction of the consequences of land management options and, hopefully, a better quality of land management.

Acknowledgements

In planning and carrying out the soil sampling in Kenya, we thank Dr J.I. Kinyamario, University of Nairobi, and Mr P.I. Mutwiri, KARI Machanga station. For sampling the Zambian soil, we thank Mr B. Mwakalombe (Misamfu) and Dr M.T.F. Wong (Reading). Botanical information was supplied by Dr Kinyamario (Nairobi) and clay mineralogical analysis was carried out by Dr B. Singh (Reading). We gratefully acknowledge the financial support of the Overseas Development Administration, UK (G.P.W. and M.T.F. Wong), and NERC, UK (J.A.M.). Soil samples were imported to the UK under licence from the Ministry of Agriculture, Fisheries and Food.

References

- Balesdent, J., Mariotti, A. and Guillet, B. (1987) Natural ^{13}C abundance as a tracer for soil organic matter dynamics studies. *Soil Biology and Biochemistry* 19, 25-30.
- Balesdent, J., Mariotti, A. and Boisgontier, D. (1990) Effect of tillage on soil organic carbon mineralization estimated from ^{13}C abundance in maize fields. *Journal of Soil Science* 41, 587-596.
- Boutton, T.W. (1991) Stable carbon isotope ratios of natural materials: II. Atmospheric, terrestrial, marine and freshwater environments. In: Coleman, D.C. and Fry, B. (eds) *Carbon Isotope Techniques*. Academic Press, San Diego, USA, pp. 173-185.
- Goh, K.M. (1991) Carbon dating. In: Coleman, D.C. and Fry, B. (eds) *Carbon Isotope Techniques*. Academic Press, San Diego, USA, pp. 125-151.
- Jenkinson, D.S. (1966) The turnover of organic matter in soil. In: *FAO/IAEA Technical Meeting Report. The Use of Isotopes in Soil Organic Matter Studies*. Pergamon Press, Oxford, UK, pp. 187-197.
- Jenkinson, D.S. (1990) The turnover of organic carbon and nitrogen in soil. *Philosophical Transactions of the Royal Society, B* 329, 361-368.
- Kalembasa, S.J. and Jenkinson, D.S. (1973) A comparative study of titrimetric and gravimetric methods for the determination of organic carbon in soil. *Journal of the Science of Food and Agriculture* 24, 1085-1090.
- Martin, A., Mariotti, A., Balesdent, J., Lavelle, P. and Vuattoux, R. (1990) Estimates of the organic matter turnover rate in a savanna soil by the ^{13}C natural abundance. *Soil Biology and Biochemistry* 22, 517-523.
- Smith, B.N. and Epstein, S. (1971) Two categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher plants. *Plant Physiology* 47, 380-384.
- Stout, J.D., Goh, K.M. and Rafter, T.A. (1981) Chemistry and turnover of naturally occurring resistant organic compounds in soil. In: Paul, E.A. (ed.) *Soil Biochemistry*. Marcel Dekker, New York, USA, pp. 1-73.
- Van de Weg, R.F. and Mbuvi, J.P. (1975) *Soils of the Kindaruma Area*. Reconnaissance Soil Survey Report No. R1, Kenya Soil Survey, PO Box 14733, Nairobi, 135 pp.