

KINETICS OF ORGANIC MATTER IN SOILS

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INTRODUCTION

Mohr & van Baren (1954) indicated that organic matter accumulation in soils is balanced by decay due to oxidation and microbial attack. Usually, organic matter increases with altitude where it is cooler (Birch & Friend 1956). In most soil profiles the content of total organic carbon is at a maximum at the surface and decreases log normally with depth. The decay of organic matter is often a first order reaction (Jenkinson & Rayner 1977). Original resistates of high molecular weight (e.g., lignin) degrade to simple molecules that form the building blocks for highly polymerised products called collectively humus (Figure 1). In the top few centimetres of the soil turnover times of organic matter are very rapid; as little as 0.165 years at Rothamsted (Jenkinson & Rayner 1977). It is here that low molecular weight carbon compounds polymerise up towards humus (Thomas *et al.* 1978) so that residence times of macromolecular associations (Hayes 1998) can become several thousand years in lower topsoils (Allison 1973). This paper examines the chemical kinetics mainly of andisols under tropical rainforest. Temperate and cold region examples are given for comparison. Toposequences in pristine environments of crestral sites provide the best data but are rare.

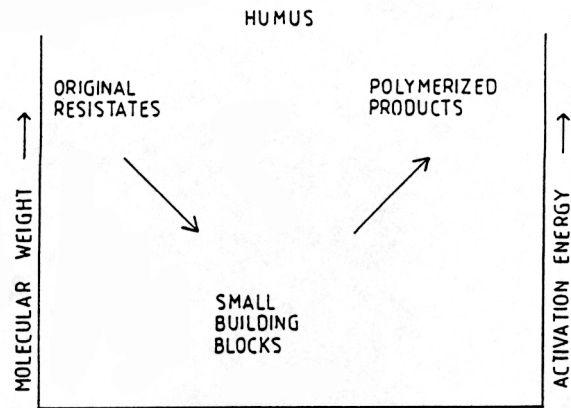


Figure 1: The breakdown and condensation of organic matter.

TROPICAL ANDISOLS

The type examples come from Papua New Guinea (PNG) at altitudes of 500 m to 2,800 m where temperature varies from 25°C to 12°C. Annual rainfall is from 1,500 mm lower down rising up to 4,000 mm. Soils are andisols and humic andisols with A/C profiles. The 10 to 30 cm depth was sampled in the 4,000 year old andesitic (silimbu) volcanic ash (Ruxton 1988). The fresh sand size ash has 56% micropumice, 27% plagioclase, 15% horn-blende, and 2% biotite. After 4,000 years of weathering the ash soil has 34% glass, 34% plagioclase and hornblende, 17% allophane and 15% organic carbon. Thus 32% is allophane-humus resistant complex. Cellular lignin, wax, resin and humates are refractory components. The exchange capacity of this soil is 110 m eq. 100 g decreasing at depth. The pH varies from 4 to 6. There is no sooty wax or corundum so the area has probably been fire free. The glass weathers to allophane gel, allophane and imogolite. Biotite weathers to vermiculite. The glass and the organic matter have half-lives of around 1,650 years. In a typical soil profile weathering goes in steps. In the first stage in the top 2-3 cm iron stained organic gel encases highly reactive micropumice dust. In the second stage between 10 and 30 cm, pumice decreases and wax, lignin and resin are common. In the third stage at 30 to 75 cm, and 6,800 years, humates and charred wood are left with slightly etched plagioclase and hornblende (Figure 2). The sites in Costa Rica were also in primary rainforest.

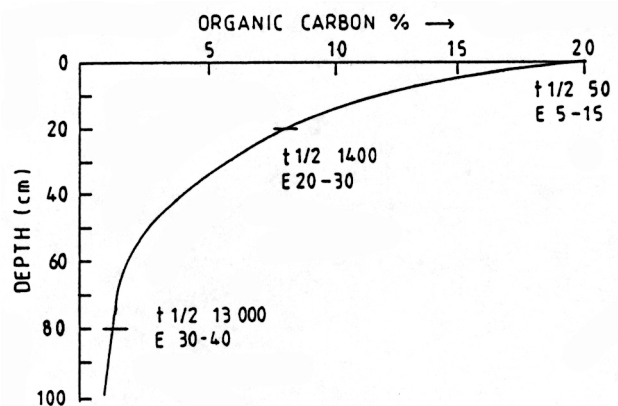


Figure 2: The half-lives ($t_{1/2}$) and activation energies (E) of organic matter in a volcanic soil.

ACTIVATION ENERGY

If the macromolecules of humus are the same going up slope in this andesitic ash soil, getting more abundant as the altitude increases, then the percentage of organic carbon should increase, being related to the

temperature through the Arrhenius relationship. In other words, the net excess of organic carbon is related to the rate of growth compared with its decay. Thus the logarithm of organic carbon content plotted against the inverse of the absolute temperature should give a straight line (Table 1) (Figure 3). It does in five instances with correlation coefficients being 0.99 in each case (Ruxton 2000, 2002; Table 2). There is a very small error as the aromaticity increases with decreasing altitude. Twice the slope of the lines on the graph give a pseudo-activation energy in kcal/mol. The values seem to be too high. If allowance is made for aggressive microbes they may be scaled down by a third to give more realistic values (Table 1). The scaling is done so as to be in line with values of 20 kcal/mol for oxidised lignin and podzols. Corroboration comes from a pit on a summit at 1,830 masl altitude in andesitic ash where there is a shortfall of weathering in a sample dated as 17,500 years B.P. due to colder conditions in the last glacial maximum at 18,000 years B.P. (Ruxton 2000, 2002). Using the scaled down activation energy of 20 kcal/mol and the Arrhenius equation there was a temperature drop of $5.5 \pm 1^\circ\text{C}$, similar to coral and other evidence.

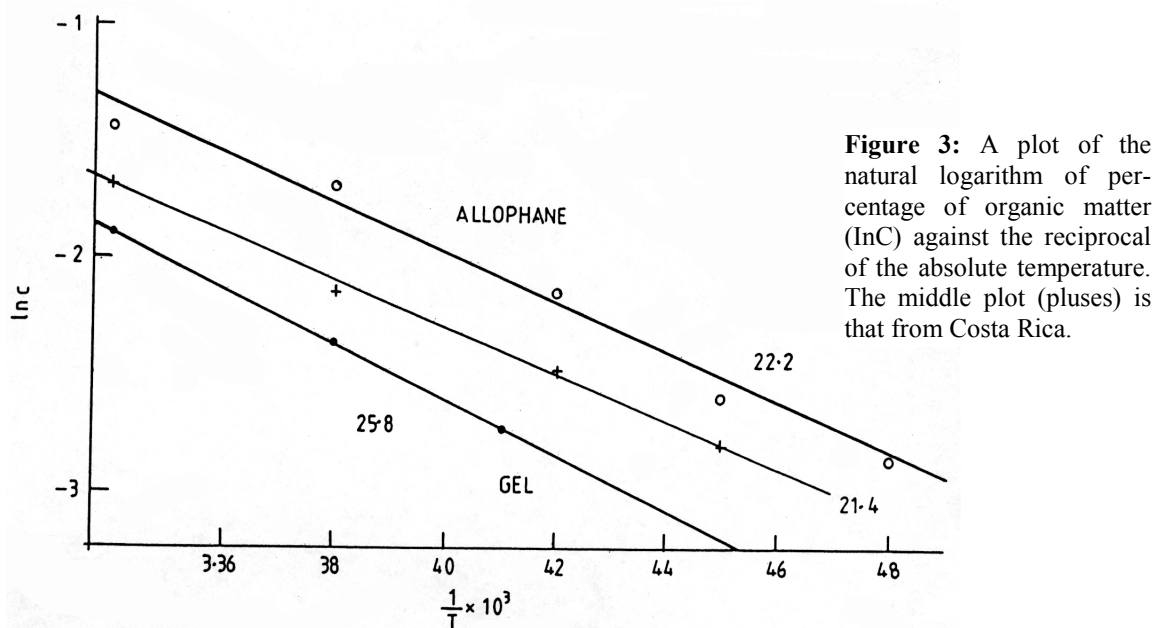


Table 1: some values of organic carbon, altitude and temperature

| Organic Carbon | lnC | Altitude metres | T°K | 1/Tx10 ³ | Comment |
|-------------------|------|-----------------|-------|---------------------|--------------------|
| 15.5 | 2.74 | 1355 | 283.4 | 3.41 | Allophane gel, PNG |
| 10.7 | 2.37 | 975 | 295.8 | 3.38 | " |
| 6.7 | 1.90 | 520 | 298.4 | 3.35 | " |
| 17.4 ¹ | 2.86 | 2240 | 287.0 | 2.48 | Allophane, PNG |
| 13.4 | 2.60 | 2000 | 289.5 | 3.45 | " |
| 8.7 | 2.16 | 1525 | 292.5 | 3.42 | " |
| 5.5 | 1.70 | 980 | 295.8 | 3.38 | " |
| 4.2 | 1.44 | 500 | 298.2 | 3.35 | " |
| 17.6 ¹ | 2.87 | 1060 | 277.2 | 3.61 | NE Japan |
| 9.7 | 2.27 | 790 | 280.2 | 3.57 | " |
| 6.5 | 1.87 | 410 | 282.2 | 3.54 | " |
| 16.5 ¹ | 2.80 | 2000 | 289.5 | 3.45 | Costa Rica |
| 12.0 | 2.48 | 1500 | 292.5 | 3.42 | " |
| 8.6 | 2.15 | 1000 | 295.8 | 3.38 | " |
| 5.5 | 1.70 | 500 | 299.0 | 3.34 | " |

¹ The three top altitude topsoils have $17 \pm 0.5\%$ organic carbon

The single values given for activation energy are the mean of a range of values that, in the tropics, encompass lowland, lower montane and montane forests. The two profiles from northeast Japan in the temperate zone are also on andesitic volcanic ash. The Caucasian mountain site is on granite with phosphorus being proxy for carbon in a cool temperate zone.

Activation energy increases as pH decreases. It may also vary with seasons and in drought. On drying suction pressures at wilting point can be up to 1.5 mPa (Miller & Gardiner 1998). On wetting again polymerised water at least to (H₂O)₁₆ will revert to the dimer giving out heat (Xanthus 1995). Energy is then available to polymerise the polycondensation.

Table 2: some activation energies of organic matter in soils

| Locality | Kcal/mol | Scaled | Age | Remarks |
|---|----------|--------|------|-----------------|
| Papua | 25.8 | 16.5 | 4000 | Allophane gel |
| Papua | 22.2 | 14.2 | 4000 | Allophane |
| NE Japan ¹ | 31.2 | 20 | 5000 | Lower ash |
| NE Japan | 14.8 | 9.5 | 1000 | Upper ash |
| Costa Rica ² | 21.5 | 13.8 | - | Volcanic rock |
| Indonesia | 20 | 12.8 | - | Andesite ash |
| Caucasus ³ | 25 | 16.3 | - | Soil on granite |
| Other reference values kcal/mol: Cellulose 46, Lignin 28, Oxidised Lignin 20, Bhorizon podsol 20. Typical silicate minerals 16.7 ⁴ | | | | |

¹ Shoji et al. 1988, ² Grieve et al. 1990, ³ Makarov et al. 1996, ⁴ Kowalewski and Rimstidt, 2003.

DISCUSSION

With six plots in five different regions, with exact unusual formula fits, some underlying unity of humus nuclei structure is suspected. The uniformity of the result in the cold (-1.2°C), wet and acid soils with low bacterial activity of the northern Caucasus would suggest a physiologically inert high molecular size fraction (Makarov *et al.* 1996). The binding of allophane and silica with humus can give a cohesion from 1 to 2.3 kg cm². Thus andisols have a high humus content of intermediate molecular weight and can stand stable on 55° slopes.

Other soils under forest (in Poland) have profiles with uniform contents of organic matter throughout. The first exothermic reaction of the humus is between 4.3 and 6.1 kcal/mol representing the functional groups. The second exothermal reaction of 12.3 to 14.3 kcal/mol breaks down the nuclei. Total values of energy are 16.6 to 20.4 kcal/mol which are comparable with values of andesitic volcanic ash (Debska 1997). The functional groups vary very widely but there may be some commonality in the nuclei.

Podzols have two organic matter peaks, one near the surface (A_o) and one in the B horizon. Activation energies of a typical profile are 6.4 and 18.4 kcal/mol respectively (Turner & Schnitzer 1962).

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