Determination of organic carbon fractions of agricultural and forest soils on the basis of their degree of oxidation with permanganate

Z. Madinabeitia[1], I. Martínez de Arano[1], A. González Arias[1], M. Pinto[1], A. Aizpurua[1], M.A. Ortuzar[1], F. Macías[2], M. Camps Arbestain[1]

[1] NEIKER, Berreaga kalea, 1. 48160- Derio, Bizkaia, Spain

[2] Departamento de Edafoloxía e Química Agrícola, Facultade de Bioloxía, Universidade de Santiago de Compostela, 15782-Santiago de Compostela, Spain

OBJECTIVE

The aim of the present study was to determine the $KMnO_4$ reactivity of soil organic carbon (SOC) in soils developed from a wide variety of parent materials and under different land use (forest vs. agriculture) and type of forest (*Fagus sylvatica* L., *Pinus radiata* D. Don., *Quercus ilex* L.), all located in the Basque Country (N Spain).

MATERIALS AND METHODS

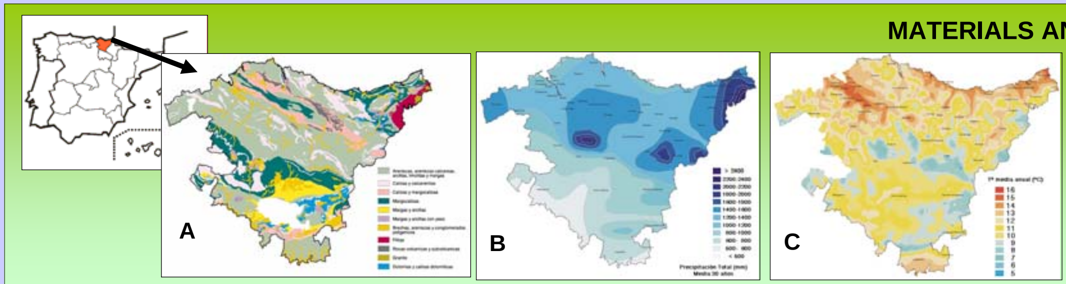


Fig. 1. Maps of (A) soil lithology, (B) total annual precipitation, and (C) mean annual air temperature of the Basque Country. On top, in an overhead, location of sampling sites (purple=beech; green=pine; blue=holm oak; black=agriculture).

Samples of the surface horizons of 44 soils under beech, 35 soils under pine, 20 soils under holm oak, and 12 agricultural soils (Fig. 1), were analyzed. The soils were air-dried and passed through a 2-mm sieve prior to analysis. The oxidability of SOC by $KMnO_4$ in the beech forest soils was determined with 33 mM $KMnO_4$ (POC) after different incubation times (1 h, 3 h, 6 h and 24 h), and that of the rest of the soils with the same reagent after 1 h incubation. General properties of all of the soils were determined (Table 1). Analysis of SOC was carried out with K_2CrO_7 with no external heat.

Table 1. Ranges of some physicochemical characteristics of the soils studied, grouped by land use and lithology.

Soil use	Lithology	n	pH-H_2O	SOC (g kg^{-1})	Total N (g kg^{-1})	C/N
Beech	Sandstones	9	4 – 6.4	9.8 – 67.8	0.7 – 4.5	12.9 – 24.8
	Argillites	5	4.3 – 4.9	18.9 – 54.6	1.2 – 3.8	11.9 – 22.8
	Limestones	20	4.3 – 8.2	14.1 – 103.9	0.7– 6.4	9.0 – 20.5
	Surface Detritus	2	5.7 – 7.6	28.0 - 96.7	1.8 – 5.8	15.9 – 16.8
	Marlstones	6	4.7 – 7.8	5.1 – 57.2	0.8 – 3.5	6.6 – 16.3
	Slates	1	4.1	29.5	2.5	11.8
	Volcanic materials	1	5.2	59.7	3.0	19.9
Pine	Sandstones	9	4.2 – 6.8	18.9 – 62.8	1.1 – 3.0	9.7 – 21.0
	Argillites	5	4.1 – 5.2	32.5 – 42.7	1.5 – 3.1	13.8 – 22.4
	Limestones	4	4.5 – 5.2	18.5 – 55.4	1.4 – 2.6	11.6 – 21.3
	Marlstones	10	4.0 – 7.5	21.7 – 52.8	1.7 – 3.5	6.2 – 18.6
	Slates	2	4.6 – 5.0	36.4 – 38.5	2.3 - 2.8	13.2 – 16.6
	Volcanic materials	5	4.5 – 5.9	11.7 – 54.5	0.5 – 3.8	12.9 – 25.8
Holm oak	Sandstones	3	4.6 – 8.5	6.6 – 60.3	0,5 – 3.3	14.4 – 18.3
	Limestones	14	4.3 – 7.8	16.0 – 71.6	2.1 – 5.6	4.1 – 21.7
	Surface Detritus	1	4.5	15.2	1.2	12.7
	Marlstones	2	5.3 – 7.1	29.7 – 32.8	1.2 – 1.7	19.5 – 24.5
Agriculture	Marlstones	6	8.2 – 8.4	7.1 – 8.8	0.9 – 1.5	5.8 – 7.9
	Limestones	1	7.6	13.8	1.6	8.6
	Surface detritus	3	7.6 – 8.0	10.9 – 13.0	1.4 – 1.6	7.7 – 8.1
	Marlstones	2	7.8 – 8.1	5.9 – 11.7	0.9 – 1.6	6.5 – 7.3

RESULTS AND DISCUSSION

1. Kinetics of POC of beech soils (0 – 24 h)

➢The cumulative amount of SOC oxidized by $KMnO_4$ increased with time, following a logarithmic trend (Fig. 2).

➢The slopes of the regression equations obtained for each soil were highly correlated with the SOC content (r=0.85) (not shown).

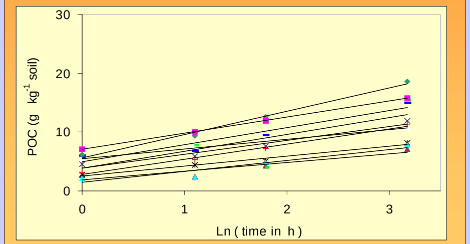


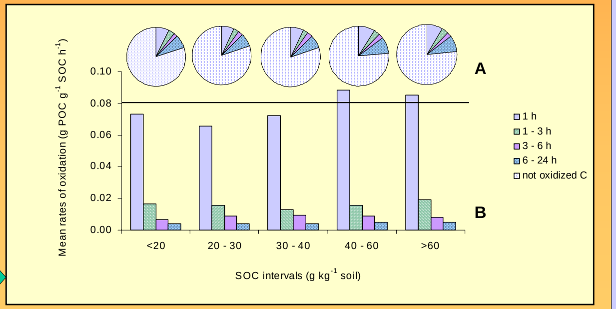
Fig. 2. Kinetics of SOC oxidation by 33 mM $KMnO_4$ at room temperature in some of the beech soils studied.

➢The cumulative POC as a fraction of SOC ranged from 3.7 to 12.5% after 1 h, from 3.9 to 17.5% after 3 h, from 6.7 to 22.5% after 6 h, and from 13.0 to 33.0% after 24 h. There was therefore a large fraction of SOC not oxidizable by $KMnO_4$ after 24 h (>65%) (Fig. 3 A).

➢In those beech soil samples with SOC contents > 40 g kg^{-1} soil, the mean ratio of POC/SOC after 1 h incubation was ≥ 8.5%, whereas that of soils with SOC contents < 40 g kg^{-1} was <7.3% (Fig. 3A).

➢The reaction rate was greater in the first hour of reaction (Fig. 3B), with a mean value of 0.077 g POC g^{-1} SOC h^{-1}, which was 4.8, 9.2, and 17.7 times greater than the rates of reaction of the 1-3 h, 3-6 h, and 6-24 h intervals.

Fig. 3 (A) The mean fractions and (B) the mean rates of SOC oxidation by $KMnO_4$, both at each time interval (0-1 h, 1-3 h, 3-6 h, 6-24 h), for each group of beech soils (grouped by SOC contents).



2. Comparison of POC-1h in agricultural and forest soils (under beech, pine, and holm oak stands) and also in different forest stands

➢POC of all soils was predominantly influenced by SOC (Fig. 4).

➢Agricultural soils had a significantly higher (P=0.08) $KMnO_4$ oxidability (%POC/SOC) compared with forest soils with the same range of SOC content (8.4 vs. 6.8%), probably attributable to the lower recalcitrance of crop residues (wheat) compared with those of forest stands.

➢When grouping all forest soils, two main groups were distinguished: A and B forest soils with <40 g kg^{-1} and >40 g kg^{-1} SOC, respectively. The A soils had a more regular pattern and a significantly lower (at P<0.05) POC/SOC ratio than B soils (7.5 vs. 8.8%) (Fig. 4).

➢Within the B type soils (Fig. 4), B1 and B2 type soils were distinguished: POC values above and below the regression line, respectively, with a mean POC/SOC ratio of 10.0 and 6.7%, respectively. In general, no clear relationship was found between the different SOC oxidability of these two soil groups (B1 and B2), and soil properties (soil pH, C/N ratios, and clay content), except for beech soils. Lithology had no clear effect.

➢More research is needed in order to discern whether this methodology is able to discriminate between labile and nonlabile C. We are currently investigating the organic matter composition of these soils by FTIR analysis.

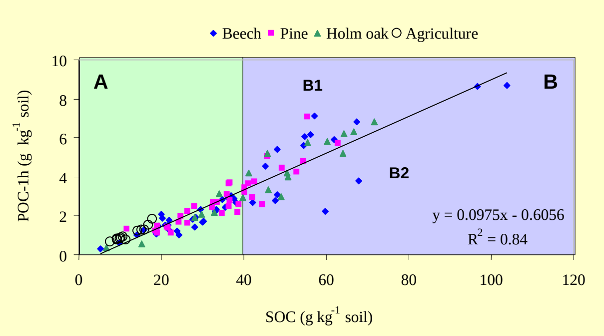


Fig. 4. POC-1h values of the forest and agricultural soils studied plotted against SOC.