Role of organic matter in obliterating the effects of iron on spectral reflectance and colour of Brazilian tropical soils

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Abstract. The relations between reflectance and soil constituents of groups, stratified according to the organic matter (OM) content, were quantitatively analysed in the 400–2500 nm spectral region. In order to demonstrate the OM spectral influence, a group of soil samples was submitted to the removal of this constituent by H_2O_2. Despite the relatively poor correlations obtained with reflectance, OM seems to be the main component responsible for lowering the reflectance in the 550–700 nm range. The presence of more than 1·7 per cent of OM effaces the iron spectral features and induces a reduction greater than 40 per cent in the negative correlation between total iron (Fe_2O_3) content and reflectance. The greater the amount of OM, the stronger is its effect in subduing the iron features, and in reducing the correlations between Fe_2O_3 and colour attributes (dominant wavelength, purity, and luminance). In the short-wavelength infrared, iron- and titanium-bearing minerals and clay minerals are accountable for lowering the reflectance. After the removal of OM by chemical treatment, the soils show slightly reddish shades, which are more saturated and especially brighter than those observed in untreated samples, as indicated by increases in the dominant wavelength, purity, and luminance values, respectively. The treated samples present a substantial reflectance increase (more than 100 per cent) and conspicuousness of iron related features in the 600–900 nm range. The general result of the OM removal is an increase in albedo and a change in the shape of the spectra. After the treatment, the increase in the values of the colour attributes and in the depth of the absorption band around 900 nm is less accentuated in soils with Fe_2O_3 content greater than 10 per cent because of the presence of other opaques.

1. Introduction

Several studies have shown that the presence of both, iron and organic matter (OM), tends to decrease the reflectance of soils (Bowers and Hanks 1965, Mathews et al. 1973, Schreier 1977, Stoner and Baumgardner 1980, 1981, Henderson et al. 1992), and generally affects the colour of the soils (Shields et al. 1968, Krishna Murti and Satyanarayana 1971, Karmanova 1982). Torrent et al. (1983) pointed out that secondary iron oxides in soils with low OM content are accountable for the colour variations, and Baumgardner et al. (1970) suggested that the effects of other constituents on the reflectance of the soils are repressed by OM contents greater than 2

and a simple but effective correlation analysis of the data. We estimate the amount of OM that interferes with the effect of total iron on spectral reflectance in the visible (VIS = 400–700 nm), very near-infrared (VNIR = 700–1000 nm) and short-wavelength infrared (SWIR = 1000–2500 nm) intervals, and on colour parameters of Brazilian soils.

2. Methodology

In this experiment, we have used reflectance spectra collected by Epiphanio et al. (1992) of 36 soil samples from the A horizon of 14 soil classes: *Latossolo Roxo (LR)*; *Latossolo Vermelho-Escuro (LE)*; *Latossolo Vermelho-Amarelo (LA)*; *Latossolo Variação Una (LU)*; *Latossolo Húmico (LH)*; *Podzólico Vermelho-Amarelo (PV)*; *Podzólico Vermelho-Escuro (PE)*; *Terra Roxa Estruturada Podzólica (PR)*; *Podzol (Pz)*; *Terra Roxa Estruturada (TE)*; *Brunizém Avermelhado (BV)*; *Areia Quartzosa (AQ)*; *Cambissolo (CB)*; and *Hidromórficos (Hi)*. The classification of these soils by the Soil Taxonomy System has been discussed in Valeriano et al. (1995). Their physico-chemical characteristics, provided by the Agronomy Institute of Campinas, can be seen in table 1. The concentrations of SiO_2, Fe_2O_3 (total iron), TiO_2, and

Table 1. Average and standard deviation (parentheses) data for some physico-chemical characteristics of the soils. N is the number of samples. Fe_2O_3 and OM indicate the contents of total iron and organic matter, respectively. The soil classes are identified in the text.

Soil class	Sand (%)	Silt (%)	Clay (%)	OM (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	TiO_2 (%)	N
LR	29	17	54	5·1	21·3	10·5	11·5	7·4	1
LE	52·8	7·0	37·3	2·4	7·5	11·8	10·4	2·5	6
	(27·9)	(8·8)	(15·5)	(1·1)	(3·2)	(5·5)	(7·3)	(1·2)	
LA	64·0	2·4	32·0	2·9	4·3	12·1	13·3	1·2	5
	(28·1)	(2·9)	(22·7)	(3·3)	(2·6)	(8·6)	(13·1)	(0·7)	
LU	55·0	8·0	37·0	3·3	10·1	10·6	11·6	3·5	3
	(22·9)	(4·3)	(18·5)	(1·7)	(7·8)	(4·5)	(9·9)	(1·0)	
LH	50·5	10·0	39·5	4·9	4·4	12·3	13·3	1·1	2
	(7·8)	(2·8)	(10·6)	(1·7)	(1·2)	(5·2)	(4·9)	(0·3)	
PV	75·3	12·5	13·0	1·7	2·0	4·2	4·7	0·6	6
	(16·3)	(12·5)	(7·0)	(1·2)	(1·5)	(1·5)	(2·8)	(0·6)	
PE	47·0	17·7	33·7	3·5	6·0	10·7	13·6	1·4	3
	(14·7)	(10·4)	(2·3)	(1·1)	(2·2)	(2·9)	(2·2)	(0·4)	
PR	58	14	28	2·2	17·4	7·5	7·9	11·3	1
PZ	88	2	10	2·0	0·5	2·8	4·2	0·2	1
TE	34·5	21·5	44·0	3·1	21·7	11·4	14·0	7·1	2
	(4·9)	(10·6)	(5·6)	(0·1)	(5·5)	(1·1)	(2·3)	(1·3)	
BV	23	45	35	4·8	23·6	7·7	18·5	6·6	1
AQ	92·0	0·5	7·5	0·7	1·1	1·6	1·6	0·2	2
	(2·8)	(0·7)	(2·1)	(0·1)	(0·0)	(0·7)	(0·6)	(0·1)	
CB	45·0	21·5	33·5	2·4	3·3	14·3	17·0	0·6	2
	(22·6)	(0·7)	(21·9)	(0·1)	(1·8)	(9·3)	(12·9)	(0·6)	
HI	66	11	23	3·9	1·3	8·9	8·0	0·9	1

Al_2O_3 were determined by treating the samples with H_2SO_4, whereas the contents of organic matter were obtained by the use of $K_2Cr_2O_7$, following procedures described in Camargo *et al.* (1986).

Bidirectional Reflectance Factors (BRF) were obtained for each sample, in laboratory, with an Infra-Red Intelligent Spectroradiometer (IRIS) positioned at 61 cm vertically above the target, which was illuminated by a tungsten lamp mounted at an angle of 15° off nadir. A spectralon plate was used as a reference. The samples were air-dried and then sieved through a 2 mm sieve. Each spectrum was collected by readings obtained at 2 nm intervals from 400–1000 nm, and at 4 nm from 1000–2500 nm.

Our analysis was initiated with the total set of 36 samples, which was subsequently stratified into three groups of 10 samples each, according to the content of OM: *A* (2·7–4·0 per cent), *B* (1·8–2·6 per cent), and *C* (0·1–1·7 per cent). The remaining six samples, with OM greater than 4 per cent, were not considered to constitute a homogeneous group. In fact, the criterion used to define these three ranges of OM was based on the identification of homogeneous groups derived from cluster analysis, using OM as a variable. The relations between reflectance and each soil constituent were then established, at 100 nm intervals, before and after the stratification, in the 400–2500 nm interval.

Reflectance studies with chemically subtractive experiments have been reported in investigations of OM in soils (Bowers and Hanks 1965, Mathews *et al.* 1973, Madeira Netto 1993), and of their components such as humic and fulvic acids (Obukhov and Orlov 1964, Henderson *et al.* 1992). In the present article, we selected the group A of samples with OM content of 2·7–4·0 per cent for the chemical removal of this constituent by the use of 10 per cent hydrogen peroxide, according to the procedures described in Camargo *et al.* (1986). The objective was to verify whether the correlations between Fe_2O_3 and the reflectances of samples from group *A* would present, after the OM removal, results that would be similar to those observed for the group *C* with low OM content (0·1–1·7 per cent). H_2O_2 is a substance generally used in spectral studies for the organic matter removal (e.g. Mathews *et al.* 1973, Henderson *et al.* 1992). The selected samples had their reflectances measured again, before and after the treatment, both under air-dried conditions.

Thus, the relations obtained between BRF and the total iron (Fe_2O_3) were compared for the untreated and treated samples. Similarly, we compared the relations between Fe_2O_3 and three colour attributes calculated from each spectrum: dominant wavelength (hue), purity (saturation), and luminance (intensity or brightness). Detailed discussions on the procedures for the calculations and implied meanings of these colour parameters are found in Bedidi *et al.* (1992).

Likewise, the relations between the depth of the 900 nm iron absorption band and Fe_2O_3 content were obtained before and after the OM removal. The depth of the band was estimated with the use of the straight-line continuum method, a common technique employed in the interpretation of reflectance spectra (e.g. Clark and Roush 1984, and references therein).
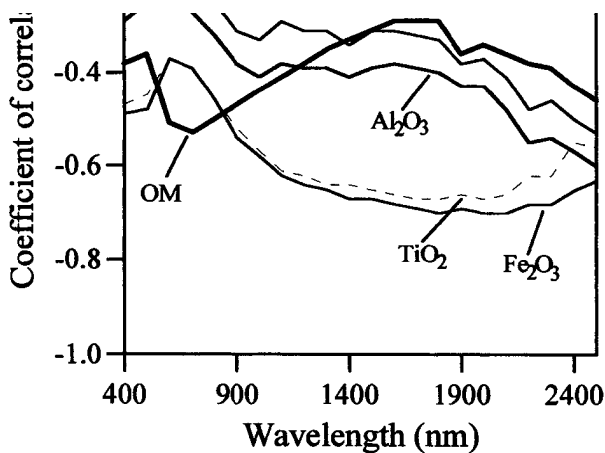
3. Results and discussion

Figure 1. Coefficients of correlation, determined at 100 nm intervals, between Bidirectional Reflectance Factors (BRF) and soil constituents of 36 samples. OM stands for organic matter and Fe_2O_3 expresses the total iron content.

soil components show negative correlations with reflectance, the behaviour of the OM correlation is strikingly unlike the others, in the VIS and VNIR intervals. The OM curve registers a prominent peak of negative correlation between 550–700 nm, the same interval in which the other constituents show an antagonistic decrease. A previous study by Henderson *et al.* (1992) indicated a correlation peak centred at 700 nm, when they analysed the effect of different soil sources on the relations of OM and reflectance. In the SWIR, there is an inversion in the behaviour of the correlation curves. Fe_2O_3 and TiO_2 present higher coefficients of correlations than OM in this interval. TiO_2 and Fe_2O_3 show a similar behaviour in figure 1 and have a positive inherent linear relations between them ($r = 0.87$), because tropical soils rich in iron oxi-hydroxides (e.g., hematite and goethite) tend to present also large amounts of titanium oxides (e.g. rutile, anatase, and ilmenite). The effect of argillaceous material is probably seen at wavelengths greater than 2000 nm because of the increase in the negative correlation of Al_2O_3, observed in figure 1. The SiO_2 pattern is similar to the Al_2O_3 because of their positive linear correlation ($r = 0.88$).

Despite the relatively poor correlations obtained with reflectance in figure 1, OM seems to be the major constituent responsible for the darkening (lowering of reflectance) of soils in the VIS interval, whereas iron- and titanium-bearing minerals and, secondarily, clay minerals, are accountable for the VNIR and SWIR ranges.

3.2. *Relations between total iron and reflectance: before and after chemical treatment*

Figure 2 shows the resulting variations in the coefficients of linear correlations between the reflectance (BRF) and Fe_2O_3, as a function of wavelength, for the three groups of samples stratified according to the different amounts of OM. It is clear, from figure 2, that the reduction in the negative relations between reflectance and iron is much more intense in the VIS interval for the groups that have OM greater
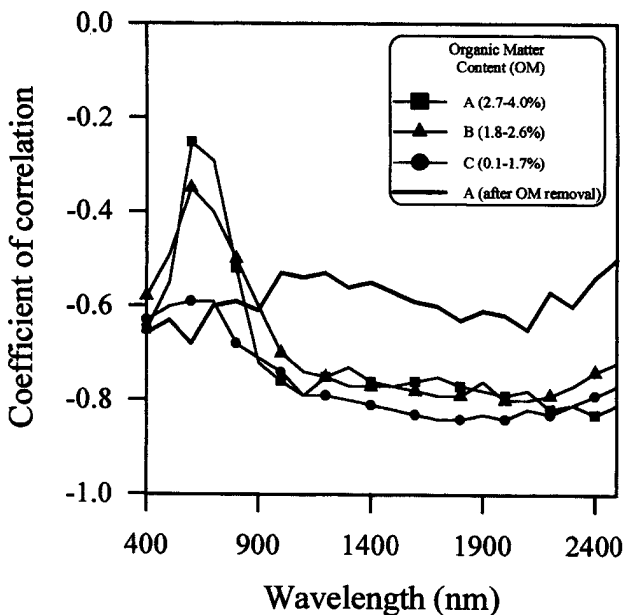
Figure 2.   Coefficients of correlation, determined at 100 nm intervals, between reflectance (BRF) and total iron (Fe_2O_3) for the three groups of ten samples each (*A*, *B*, and *C*) with different organic matter (OM) content. The line without symbols indicates the correlation curve for the group *A*, after the OM removal by chemical treatment.

than 1·7 per cent (groups *A* and *B*). The reduction in the coefficients, from group *C* to group *B*, at 650 nm, is about 42 per cent, and from *C* to *A* is about 58 per cent. In the VNIR and SWIR, there is no expressive change in the correlation curves of the three groups.

The coefficients of correlation of the chemically treated samples of group *A* are also shown in figure 2. Thus, after the OM removal, the curve, indicated by the line without symbols, shows that the linear correlations become much better in the VIS, in comparison with the untreated samples, but deteriorate in the VNIR and especially in the SWIR. To better illustrate how the removal of OM improved the correlation between Fe_2O_3 and reflectance, we show, in figure 3, the distribution of the reflectances at 600 nm of the untreated and treated samples. Linear regressions does not always offer the best fit through the points of our scatter diagrams. In figure 3, the coefficients of correlations are of $-0·33$ for the untreated samples and of $-0·80$ for the treated samples. Thus, the exponential decrease reveals that, after the OM removal, iron explains 64 per cent of the data variance (coefficient of determination of 0·64). As observed in this figure, the reflectance increase due to the OM removal is stronger (more than 100 per cent) in soil samples with Fe_2O_3 less than 10 per cent.

The reflectance changes introduced by the OM removal are seen in figures 4 (*a*) and (*b*) for four samples. Comparison of the spectra of untreated (solid line) and treated (dashed line) samples shows the remarkable reflectance increase in the VIS
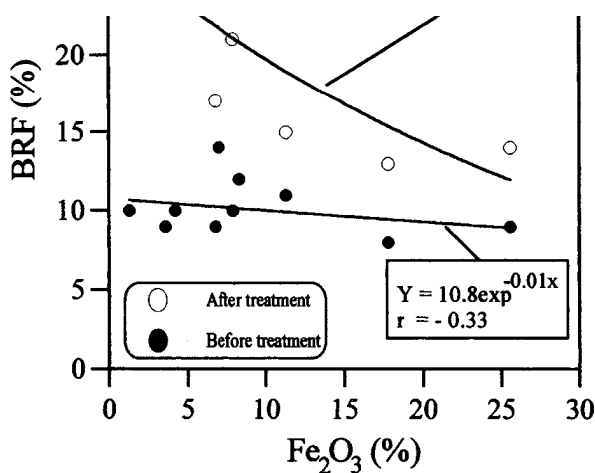
Figure 3. Relations between reflectance (BRF) at 600 nm and total iron (Fe_2O_3) for the untreated (dots) and the treated (open circles) soil samples of group A with 2·7–4·0 per cent of organic matter.
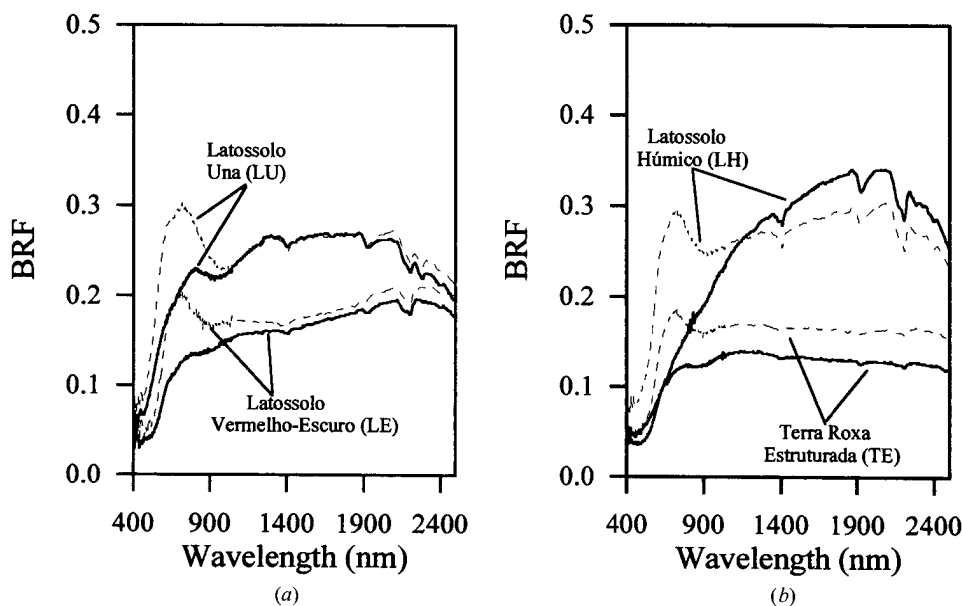

Figure 4. Changes observed in the spectra of the untreated soil samples (solid line) after chemical treatment (dashed line) are shown for LE and LU curves in (a), and for TE and LH curves in (b).

unchanged or with a small increase (figure 4(a)), a result which is similar to the one described by Bowers and Hanks (1965). However, 40 per cent of the samples presented a substantial reflectance increase in the SWIR (figure 4(b), spectrum of TE) in agreement with the results obtained by Henderson *et al.* (1992). Only one sample presented a reflectance decrease in the SWIR (figure 4(b), spectrum of LH), which is like the result found by Mathews *et al.* (1973). According to Madeira Netto (1993), the origin of the different patterns of spectral response in Brazilian soils, brought by the OM removal with H_2O_2, is associated with mineralogically distinct soil types. In other words, the variations in the contents of iron oxides (e.g., hematite and goethite) and opaque minerals (e.g., magnetite and ilmenite) are probably responsible for the variable reflectance response obtained after the chemical treatment.

In our study, the causes of the divergences in the SWIR response of the treated samples remain to be investigated because of the lack of additional determinations of the concentrations of these minerals. Anyway, such diverging results explain the decrease in the SWIR correlation between Fe_2O_3 and reflectance in figure 2 (line without symbols), observed after the removal of OM. Otherwise, if all the treated samples had presented a spectral pattern in the SWIR interval like the one depicted in figure 4(a), the curve of correlation between Fe_2O_3 and reflectance would show similar behavior to that observed in the curves obtained in the same interval for the non-treated samples (lines representing groups *A*, *B*, and *C* in figure 2).

In figures 4(a) and (b), the steep decrease in reflectance, from the red to the blue wavelengths, accentuated by the OM removal, is ascribed to the iron-oxygen charge transfer process (Hunt 1980). The other well-defined absorption band around 900 nm is the result of electronic transitions involving iron ions (Hunt and Salisbury 1970).

In figure 5, we have plotted the relations between the depth of the 900 nm band and the total iron content of the samples, before (dots) and after (open circles) the
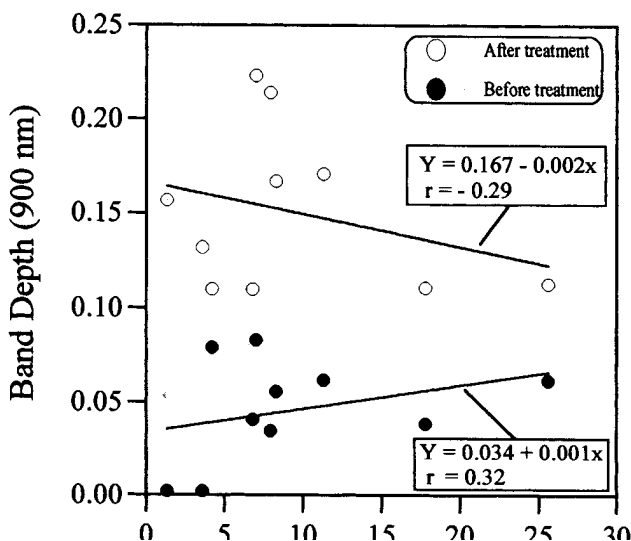
900 nm which are observed in all spectra obtained after the OM removal. However, after the treatment, the deepest features occur predominantly in spectra of soils with less than 10 per cent of Fe_2O_3 (e.g., spectrum of LU in figure 4(a)), and the shallowest features occur associated with samples with more opaque minerals, such as magnetite and ilmenite, that is, in samples with a higher content of Fe_2O_3 and TiO_2 (e.g., spectrum of TE in figure 4(b)). Thus, variations in the OM content can have an indirect influence on the depth of the 900 nm iron absorption band, and can affect the estimates of the iron content from the band depths.

In general, the transition from the surface to the subsurface horizons of tropical soils produces an effect in the VIS that is similar to the spectral changes resulting from the chemical treatment for OM removal. According to Galvão et al. (1997), from the A to the B horizons, the reflectance tends to increase in the VIS because of the decrease in the OM content and the consequent enhancement of the iron spectral features. In the SWIR, the reflectance tends to decrease because of the increase in the clay fraction with depth.

3.3. *Relations between total iron and colour attributes*

Figure 6 summarizes the relations between total iron and the colour parameters for the three groups of samples with different OM content. As the OM content decreases from group A to C, the correlations between Fe_2O_3 and the three colour parameters become stronger, especially for the relations between Fe_2O_3 and luminance. Because of the positive correlation with the dominant wavelength and purity,
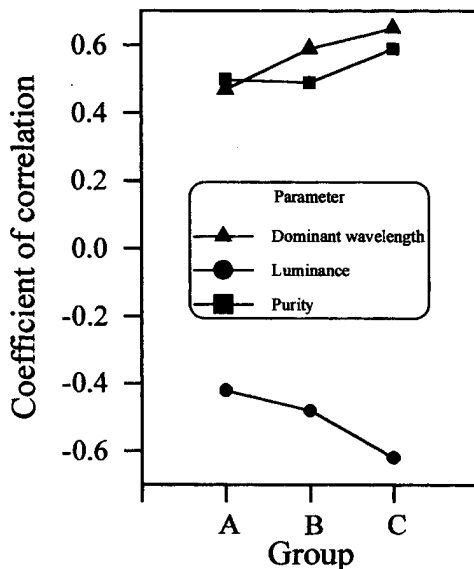

Figure 6. Coefficients of correlation between total iron (Fe_2O_3) and the colour attributes (dominant wavelength, purity, and luminance) for the soil groups A (2·7–4·0 per cent of OM), B (1·8–2·6 per cent of OM), and C (0·1–1·7 per cent of OM).

an increase in Fe_2O_3 content produces a shift in the dominant wavelength towards longer wavelengths, and also towards greater saturation, respectively. On the other hand, because of the negative correlation with luminance, there is a decrease in intensity or brightness for any increase in Fe_2O_3. These relations tend to be stronger for samples with low OM content.

The chemical removal of OM also shows that this constituent interferes with the relations between Fe_2O_3 and colour. After the treatment, the soils show slightly reddish colours documented by small displacements in the dominant wavelength towards longer wavelengths. The resulting colours are more saturated and especially brighter than those observed in the untreated samples, because of the increase in purity and luminance values, respectively.

In figure 7, the luminance values of treated and untreated samples are compared as a function of the Fe_2O_3 content. The coefficient of correlation changes from -0.57 (before treatment) to -0.79 (after treatment). After the OM removal, increments in luminance values of more than 100 per cent are observed in samples with Fe_2O_3 content of less than 10 per cent. The exponential decrease of the curve shows that iron explains 63 per cent of the data variance (coefficient of determination of 0.63) after the OM removal. The smaller changes observed in samples with more than 10 per cent of Fe_2O_3 are probably related to the presence of a greater content of opaque minerals (magnetite, ilmenite). The spectral effects of opaques on the reflectance of laterites have been discussed in Galvão *et al.* (1995) through the binary mixtures of Fe_2O_3 and carbon.

4. Conclusions

In the present article, we have demonstrated that OM obliterates the effects of total iron on reflectance and colour, especially when the content of OM is greater
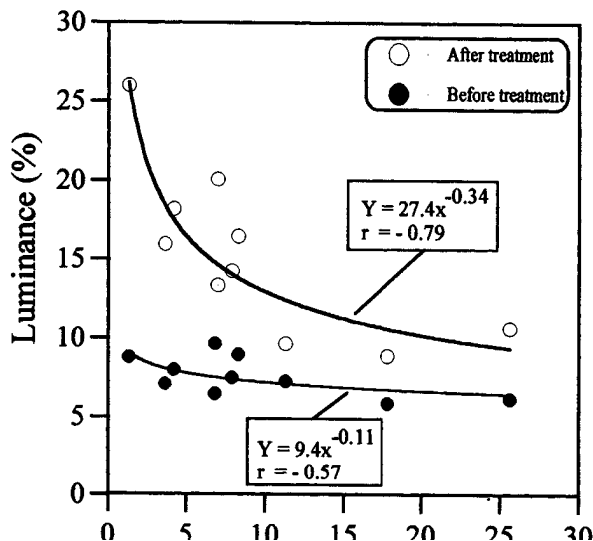
stronger relations between reflectance and total iron in the VIS, and of a more well-defined iron absorption band around 900 nm in the soil spectra. However, the depth of this feature varies according to the content of other opaques in the soils. Despite the presence of a greater amount of total iron, low albedo soils tend to exhibit spectra with shallower 900 nm absorption bands than those observed in spectra of soils with higher albedo, which are poor in iron and other opaque minerals such as magnetite. The removal of OM has produced soil materials that have slightly saturated and reddish colours and, especially, brighter shade, than the original soil.

In the literature, some indexes have been proposed as quantitative links between redness and iron oxide content in soils, especially of hematite (e.g., Torrent *et al.* 1983, Madeira Netto 1993). The next step in our investigation involves the determination of the content of distinct iron oxides, and of the implications of the present results on the performance of these indexes for soils rich in organic matter.

Acknowledgments

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