

IRON OXIDES IN RELATION TO THE COLOUR OF MEDITERRANEAN SOILS

J. TORRENT AND V. BARRÓN*

ABSTRACT

Mediterranean soils contain relatively small amounts of iron oxides. These minerals, however, exert much influence on different soil properties, of which the most conspicuous is colour. Rubefaction, i.e. reddening due to pedogenic hematite formation, is common in Mediterranean soils and usually provides information on the soil environment. Colour can be measured by visual and spectrophotometric methods and used, when parameterised in different ways, to identify and quantify soil Fe oxides.

Keywords: Iron oxides, colour, goethite, hematite, ferrihydrite, lepidocrocite, maghemite. reflectance spectroscopy.

INTRODUCTION

The properties of iron (Fe) oxides in Mediterranean soils were cursory reviewed by Torrent (1994), who also examined the influence these minerals exert on various soil properties. Because of the lack of coincidence of warm temperatures and

* Departamento de Ciencias y Recursos Agrícolas y Forestales, Universidad de Córdoba, Apdo. 3048, 14080 Córdoba, Spain.

high moisture contents, the Mediterranean pedoenvironment does not favour intensive weathering. Consequently, the Fe oxides content rarely exceeds 50 g kg^{-1} in Mediterranean soils. Despite this, Fe oxides (a term used here to include oxides and oxihydroxides of Fe) determine soil colour and have a major influence on particle aggregation and specific ion adsorption. In this review we briefly examine the formation of Fe oxides in Mediterranean soils and the way these minerals influence soil colour. Attention is given to the measurement and parametrization of colour and to the use of colour as an indicator of various soil properties.

FORMATION OF FE OXIDES IN THE MEDITERRANEAN PEDOENVIRONMENT

In Mediterranean soils the weathering of Fe-bearing primary minerals generally results in the formation of crystalline Fe oxides. The crystallization of ferrihydrite (the poorly crystalline oxide that constitutes an initial product of weathering) is enhanced by the warm temperature and low organic carbon content typical of most Mediterranean soils (Schwertmann, 1985). Accordingly, the Fe_o/Fe_d ratio, i.e. the ratio between the poorly crystalline Fe oxides content, as measured by acid oxalate-extractable Fe (Fe_o), and the total content in Fe oxides, as measured by citrate/bicarbonate/dithionite-extractable Fe (Fe_d) is generally less than 0.1 (Torrent, 1994). Among the crystalline Fe oxides, goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are much more common than lepidocrocite ($\gamma\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and (lithogenic) magnetite (Fe_3O_4).

Pedogenic hematite formation, a process called *rubefaction* or *rubification* by pedologists, is quite common in Mediterranean soils. It follows decalcification because the presence of calcite in soil determines an alkaline pH, which hinders weathering of Fe-bearing primary minerals. The appropriate environmental conditions for hematite formation from ferrihydrite have been discussed at length by Schwertmann (1985). Hematite is formed (and favoured over goethite) at high temperatures, water activity below 1, low organic matter content, near neutral pH, and high concentrations of Ca^{2+} and Mg^{2+} . Many well-drained soils with moderate to severe summer drought meet these conditions. This is the case with *Terra Rossa*, a popular Italian term used to designate a red soil formed on hard, pure limestone, in which dissolution cracks ensure rapid drainage. In the absence of one or more of these conditions, goethite is the only pedogenic crystalline Fe oxide that forms in significant amounts. The term *braunification* (appearance of a yellowish brown colour) then applies (Buol *et al.*, 1997). It must be noted that rubefaction is accompanied by the production of substantial amounts of goethite, so that hematite rarely represents more than 70% of the crystalline Fe oxides present in rubefacted soils (Boero & Schwertmann, 1989).

In the process of soil formation, rubefaction seems to occur at a pace similar to that of clay translocation. Thus, hematite (and goethite), which tend to be associated with silicate clay particles, are transported to the illuvial (argillic) horizons.

This results in an increase in redness from the elluvial to the illuvial horizons, a feature characteristic of many Mediterranean soils.

There is neither field nor laboratory evidence that goethite can dehydrate to hematite under pedogenic conditions. That is, a «yellow» cannot be transformed into a «red» soil. The opposite, however, is likely to occur because hematite is more sensitive to reductive or acidic dissolution than goethite (Cornell & Schwertmann, 1996). The establishment of a perched water table (*pseudogleyization*) in old Mediterranean soils with a dense, slowly permeable argillic horizon results in the dissolution of hematite but not of coexisting goethite (Barrón & Torrent, 1987).

The contention that lepidocrocite and maghemite are relatively rare in Mediterranean soils has not been thoroughly tested because most mineralogical studies have been focused on the identification and characterization of hematite and goethite. Lepidocrocite results from the oxidation of Fe(II) compounds formed in reductomorphic conditions but it has occasionally been reported in well-drained Mediterranean soils (Stanjek, 1987). Maghemite, probably more common than lepidocrocite, forms by dehydroxilation of the latter, low-temperature oxidation of lithogenic maghemite, and heating of various Fe oxides in the presence of organic carbon (Schwertmann, 1985; Stanjek, 1987); the latter pathway is likely to be favoured by the high fire frequency typical of Mediterranean ecosystems. Recently, a direct pathway from ferrihydrite to maghemite has been proposed (Barrón & Torrent, 2002), which seems less dependent on *ad hoc* assumptions than the hypothesis of low-temperature oxidation of magnetite of bacterial or inorganic pedogenic origin (Maher, 1998).

COLOUR AND FE OXIDES IN MEDITERRANEAN SOILS

The strikingly red colour of some Mediterranean soils has caught the eye of not only soil scientist but also geographers, naturalists and travellers, as illustrated, for instance, by the detailed description of Terra Rossa in Goethe's «Italian travels» (Sticher, 1978). However, red or reddish brown hues are by no means universal in the soils of Mediterranean regions, the reason being that the impact of rubefaction depends, as discussed previously, on a number of pedoenvironmental factors (such as soil age, moisture regime, and carbonate content). In the absence of hematite, goethite, a ubiquitous crystalline Fe oxide in nature, plays a dominant role in soil hue. Occasionally, lepidocrocite (orange-yellow), ferrihydrite (reddish brown) or maghemite (dark reddish brown) exert some influence.

COLOUR CHARACTERIZATION

A brief introduction to soil colour notation and detailed measurement in the laboratory can be found in Torrent & Barrón (1993). Briefly, colour notation is based on the so-called *tristimulus values*, which are designated as X, Y, and Z,

and are a measure of the radiant energy that enters the eye and produces a sensation of colour. In practice, the different colour systems are based on more or less ingenious mathematical transformations of these values, so any colour can be represented by the three coordinates of a point in a three-dimensional *colour space*.

Pedologists have measured soil colour with the help of the Munsell Color Charts (Munsell Color Company, 1975) for more than fifty years. The Munsell system is based on: (i) hue (H), that is, the attribute of colour perception denoted as blue, red, yellow, and so on; (ii) value (V), that is, lightness, and (iii) chroma, that is, degree of difference from black-white or neutral colour. In recent years, the CIE 1976(L*a*b*) space has gained acceptance for some purposes because it provides a good way to visualize colour: the L* axis represents lightness, the a* axis is redness-greenness, and the b* axis is yellowness-blueness.

Visual evaluation of colour requires, among other factors, the control of the background and the spectral quality, intensity and angular size of the light source. Such control is rarely possible in the field but can be reasonably achieved in the laboratory. In practice, however, objective measurement of soil colour in the laboratory is based on the use of tristimulus colourimeters or spectrophotometers. Reflectance spectrophotometers, generally used to measure the colour of finely ground soil samples, provide a reflectance spectrum in the visible range (380–750 nm) that constitutes the basis for calculating colour notation in any of the common systems. In general, the *directional-hemispherical reflectance*, measured with an integrating sphere attachment, is considered to be the so-called *diffuse* or *diffusive reflectance*, a mathematical artifice with no direct physical meaning (Hapke, 1993).

Instrumental characterization of the appearance of soils in the field is based on remote sensors and spectroradiometers. In both cases the information includes not only colour *sensu strictu* but also the properties of the «surface state» (Escadafal, 1989).

QUANTITATIVE RELATIONSHIPS BETWEEN COLOUR AND FE OXIDES

The dominant effect of Fe oxides on the colour of Mediterranean soils is undisputable (Torrent *et al.*, 1980, 1983; Schwertmann, 1993; Torrent & Cabedo, 1986), even though these soils generally contain less than 50 g kg⁻¹ of Fe oxides (Torrent, 1994). Most Mediterranean soils have Munsell hues between 2.5Y (yellow) and 10R (red), with hues redder than 10YR suggesting the presence of hematite (Torrent *et al.*, 1983; Schwertmann *et al.*, 1982) or, less commonly, significant amounts of brown-coloured Fe oxides (ferrihydrite, maghemite). Hematite possesses a higher pigmenting power in Mediterranean than in tropical soils (Torrent *et al.*, 1983), probably because particles tend to be less aggregated in the former than in the latter.

Good relationships exist between colour and hematite content in Mediterranean soils. A redness rating (RR), defined as $(10 - H) \times C/V$ (where H is the number preceding YR in the Munsell hue, C is the chroma, and V the value) was found to be well correlated with the soil hematite content determined by differential X-ray diffraction (Torrent *et al.*, 1980, 1983). The predictive value of the RR was corroborated by different authors (Mirabella & Carnicelli, 1992; Peña & Torrent, 1984; Kemp, 1985; Torrent & Cabedo, 1986; Barrón & Torrent, 1987) and is illustrated in Fig. 1. It must be noted, however, that the optical properties of hematite can differ substantially from one specimen to another (Barrón & Torrent, 1984; Cornell & Schwertmann, 1996); such differences are then translated into differences in the soil RR or any other colour index.

Because the pigmenting power of hematite is higher than that of goethite, the latter mineral cannot be easily quantified from the RR or any other colour parameters. One way to quantify these two minerals is based on the Kubelka–Munk (K–M) theory, which was developed for pigment mixtures (Kubelka & Munk, 1931). This theory establishes that the response of a pigment mixture to incident light of wavelength λ can be characterized by two coefficients: K_λ (absorption) and S_λ (scattering). For thick mixture layers, the so called K–M or remission function $[F(R)]$ becomes: $F(R) = K/S = (1 - R)^2/2R$, where R is the diffuse reflectance

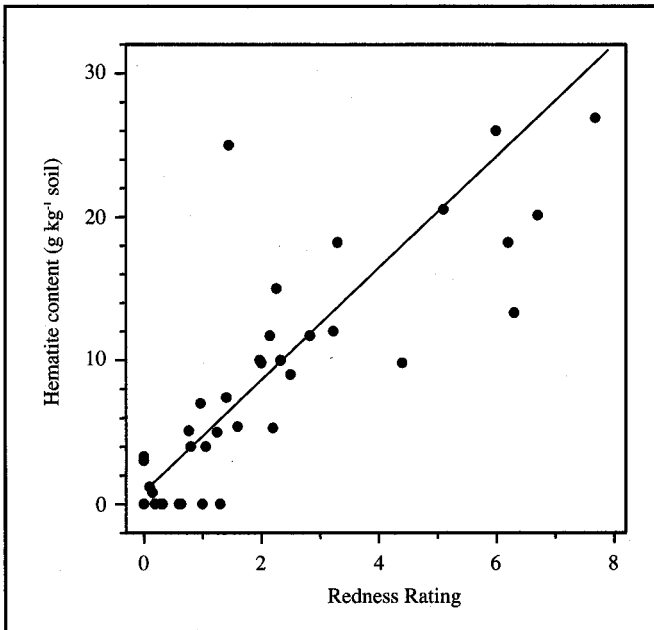


Fig. 1. Relationship between hematite content in soil (as measured by differential X-ray diffraction) and redness rating for a group of different Mediterranean soils from Spain, Italy and Portugal.

of the mixture. It was shown that *K* and *S* can be treated as linear combinations of the *K* and *S* values of the mixture pigments weighed according to their proportions (Duncan, 1940). Thus, the *K*-*M* theory can be used to estimate the concentrations of hematite and goethite in soil samples provided that these are the most important pigments (Barrón & Torrent, 1986; Fernandez & Schulze, 1992). To this end, one must assign *K* and *S* values to these oxides; this is done by acquiring the spectra of appropriate standards.

The Fe oxides exhibit different absorption bands in the near infrared to near ultraviolet range. These bands are produced by crystal-field transitions of Fe(III) in an octahedral ligand field (Sherman & Waite, 1985; Scheinost *et al.*, 1998). They appear in the diffuse reflectance (as well as in the remission function) spectrum of the soil or mineral mixture and their position and intensity can be mathematically enhanced by calculating the derivatives of the spectrum. Most of this work has been based on the second derivative of the absorption or remission function spectra (Kosmas *et al.*, 1984, 1986; Malengreau *et al.*, 1994; Scheinost *et al.*, 1998) because they show the absorption bands as strong minima (Fig. 2). Second-derivative diffuse reflectance spectroscopy allows quantification of hematite and goethite in a soil sample provided other Fe oxides are not present in significant amounts; this condition is generally fulfilled by Mediterranean soils. For this purpose, one must first calculate and smooth the first and second derivative curves of the remission function with appropriate algorithms (Scheinost *et al.*, 1998). Then, the amplitudes of the most typical hematite and goethite bands are measured and the amplitude ratio is used to predict the hematite/goethite ratio. This is based on the good correlation between this amplitude ratio and the soil hematite/goethite ratio as evaluated by X-ray diffraction (Fig. 3). From the hematite/goethite ratio one can then calculate the absolute contents of these two minerals by assigning the difference between citrate/bicarbonate/dithionite and oxalate-extractable Fe to the Fe contained in hematite and goethite. In contrast to other methods of quantification of Fe oxides, the second derivative spectrum is relatively insensitive to the organic matter content of the soil (Fernandes *et al.*, 1998).

COLOUR IN RELATION TO THE CLASSIFICATION OF MEDITERRANEAN SOILS

Colour terms have traditionally been used to denominate specific types of soils of the Mediterranean region. The traditional Italian terms «Terra Rossa» and «Terra Fusca» referred to soils developed on hard, pure limestones that owed their hue to hematite and goethite, respectively. These terms were incorporated in the classification of Kubišna (1953) and are still widely used by pedologists. The same applies to «Red Mediterranean Soils», which was adopted by several classifications with —unfortunately— somewhat different meanings. So, the term conveyed the concept of Terra Rossa *sensu stricto* to some pedologists but that of the brown-reddish Xerals of Soil Taxonomy (Soil Survey Staff, 1999) for others.

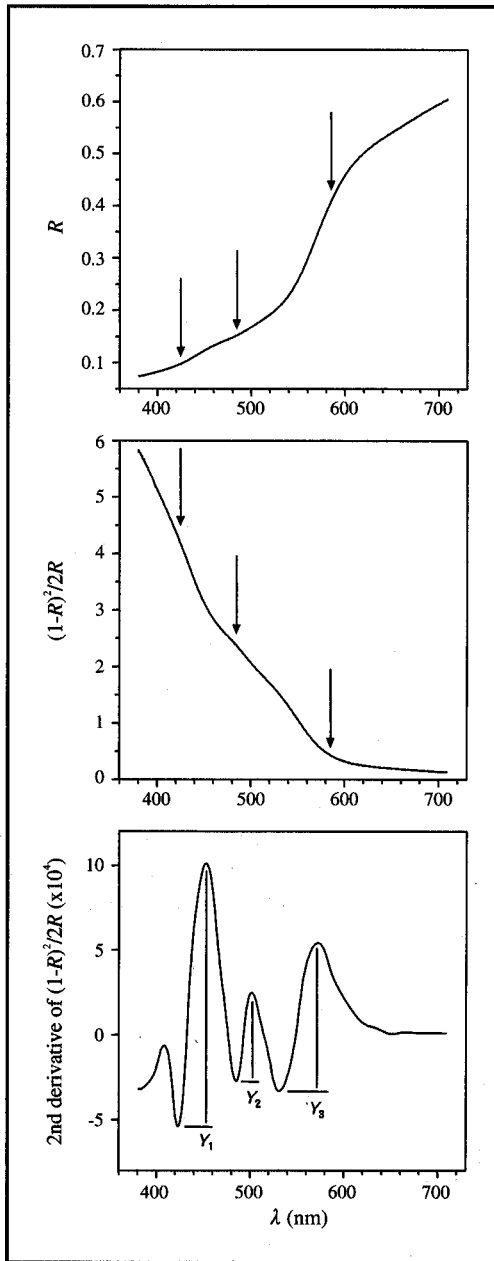


Fig. 2. From top to bottom: (a) Reflectance spectrum, (b) Kubelka-Munk function spectrum, and (c) Second derivative spectrum of the Kubelka-Munk function of a Mediterranean soil containing goethite and hematite. The weak absorption bands (arrows) of the reflectance and Kubelka-Munk function spectra are strongly enhanced in the second derivative spectrum. The Y_1 and Y_2 bands correspond to goethite and the Y_3 band to hematite.

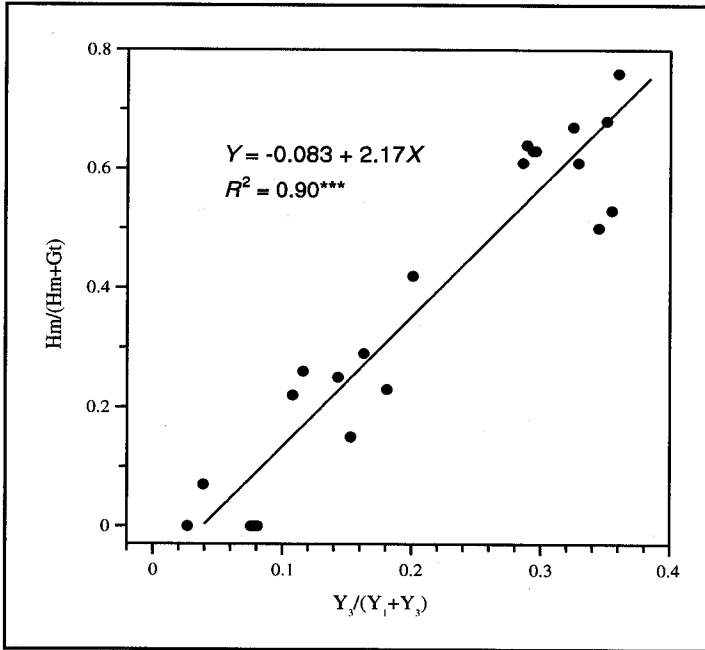


Fig. 3. Relationship between the hematite/(hematite+goethite) ratio (estimated by the differential X-ray diffraction method) and the $Y_3/(Y_1 + Y_3)$ ratio in the second derivative spectrum for a group of Mediterranean soils from Spain, Italy and Portugal.

The importance of red hues as indicative of specific pedoenviromental conditions is recognized in the two most used classification systems, viz. Soil Taxonomy and the FAO legend (currently, World Reference Base for Soil Resources; ISSS-ISRIC-FAO, 1998). For instance, the adjective or prefix «Rhodo» is used to designate the red Xeralfs (Rhodoxeralfs) of Soil Taxonomy and the adjective «Chromic» is used for the red Luvisols of the FAO legend.

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REFERENCES

- Barrón V. & Torrent J. (1984). Influence of aluminum substitution on the color of synthetic hematites. *Clays Clay Miner.* **32**, 157-158.
- Barrón V. & Torrent J. (1986). Use of the Kubelka-Munk theory to study the influence of iron oxides on soil colour. *J. Soil Sci.* **37**, 499-510.

- Barrón V. & Torrent J. (1987). Origin of red-yellow mottling in a ferric Acrisol of southern Spain. *Z. Pflanzenernähr. Bodenk.* **150**, 308-313.
- Barrón V. & Torrent J. (2002). Evidence for a simple pathway to maghemite in Earth and Mars soils. *Geochim. Cosmochim. Acta* (in press).
- Boero V. & Schwertmann U. (1989). Iron oxide mineralogy of Terra Rossa and its genetic implications. *Geoderma*, **44**, 319-327.
- Buol, S. W., Hole, F. D., McCracken, R. J. & Southard, R. J. (1997). *Soil Genesis and Classification*, 4th edn. Iowa State University Press, Ames, IA.
- Cornell, R. M. & Schwertmann, U. (1996). *The Iron Oxides*. VCH, Weinheim (Germany).
- Duncan, D. R. (1940). The colour of pigment mixtures. *Proc. Phys. Soc.* **52**, 390-401.
- Escadafal, R. (1989). *Caractérisation de la surface des sols arides par observations de terrain et par télédétection*. ORSTOM, Collection Etudes et Thèses, Paris
- Fernandes, R. B. A., Barrón, V. & Torrent, J. (1998). Effect of organic matter on the iron oxides. Identification and quantification from second derivative diffuse reflectance spectra of Brazilian Oxisols, p. 441 in: *Summaries, 16th World Congress of Soil Science*; Montpellier, France.
- Fernandez, R. N. & Schulze, D. G. (1992). Munsell colors of soils simulated by mixtures of goethite and hematite. *Z. Pflanzenernähr. Bodenk.* **155**, 473-478.
- Hapke, B. (1993). *Theory of Reflectance and Emittance Spectroscopy*. Cambridge University Press, Cambridge, UK.
- ISSS-ISRIC-FAO (1998). *World Reference Base for Soil Resources*. Acco Press, Leuven, Belgium.
- Kemp, R. A. (1985). The cause of redness in some buried and non-buried soils in eastern England. *J. Soil Sci.* **36**, 329-334.
- Kosmas, C. S., Franzmeier, D. P. & Schulze, D. G. (1986). Relationships among derivative spectroscopy, color, crystallite dimensions, and Al substitution of synthetic goethites and hematites. *Clays Clay Miner.* **34**, 625-634.
- Kosmas, C. S., Curi, N., Bryant, R. B. & Franzmeier, D. P. (1984). Characterization of iron oxide minerals by second-derivative visible spectroscopy. *Soil Sci. Soc. Am. J.* **48**, 401-405.
- Kubelka, P. & Munk, F. (1931). Ein Beitrag zur Optik der Farbanstriche. *Z. Technol. Phys.* **12**, 593-620.
- Kubišna, W. L. (1953). *The soils of Europe*. Thomas Murby, London.
- Maher, B. A. (1998). Magnetic properties of modern soils and Quaternary loessic paleosols: paleoclimatic implications. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* **137**, 25-54.
- Malengreau, N., Müller, J. P. & Calas, G. (1994). Fe-speciation in kaolins: a diffuse reflectance study. *Clays Clay Miner.* **42**, 137-147.
- Mirabella, A. & Carnicelli, S. (1992). Iron oxide mineralogy in red and brown soils developed on calcareous rocks in central Italy. *Geoderma*, **55**, 95-109.
- Munsell Color Company (1975). *Munsell soil color charts*. 1975 edn. Munsell Color Co., Baltimore, MD.
- Peña, F. & Torrent, J. (1984). Relationships between phosphate sorption and iron oxides in Alfisols from a river terrace sequence of Mediterranean Spain. *Geoderma*, **33**, 283-296.
- Scheinost, A. C., Chavernas, A., Barrón, V. & Torrent, J. (1998). Use and limitations of second-derivative diffuse reflectance spectroscopy in the visible to near-infrared range to identify and quantify Fe oxides in soils. *Clays Clay Miner.* **46**, 528-536.
- Schwertmann, U. (1985). The effect of pedogenic environments on iron oxide minerals. *Adv. Soil Sci.* **1**, 171-200.

- Schwertmann, U. (1993). Relationships between iron oxides, soil color and soil formation, pp. 51-69 in: *Soil Color* (J. M. Bigham & E. J. Ciolkosz, editors). Soil Science Society of America, Madison, WI.
- Schwertmann, U., Murad, E. & Schulze, D. G. (1982). Is there Holocene reddening (hematite formation) in soils of axeric temperate areas? *Geoderma*, **27**, 209-213.
- Sherman, D. M. & Waite, T. D. (1985). Electronic spectra of Fe³⁺ oxides and oxide hydroxides in the near IR to near UV. *Am. Mineral.* **70**, 1262-1269.
- Soil Survey Staff (1999). *Soil Taxonomy*. Agriculture Handbook 436, 2nd edn. United States Department of Agriculture, Washington DC.
- Sticher, H. (1978). Goethe und die Bodenkunde. *Bull. Bodenk. Gesellschaft Schweiz*, **2**, 3-14.
- Stanjek, H. (1987). The formation of maghemite and hematite from lepidocrocite and goethite in a Cambisol from Corsica, France. *Z. Pflanzenernähr. Bodenk.* **150**, 314-318.
- Torrent, J. (1994). Iron oxides in Mediterranean soils: properties and influence on soil behaviour. Vol 8a, pp. 2-14 in: *Transactions, 15th World Congress of Soil Science*. ISSS, The Mexican Society of Soil Science; Acapulco.
- Torrent, J & Barrón, V. (1993). Laboratory measurement of soil color: theory and practice, pp. 21-33 in: *Soil Color* (J. M. Bigham & E. J. Ciolkosz, editors). Soil Science Society of America, Madison, WI.
- Torrent, J. & Cabedo, A. (1986). Sources of iron oxides in reddish brown soil profiles from calcarenites in southern Spain. *Geoderma*, **37**, 57-66.
- Torrent, J., Schwertmann, U., Fechter, H. & Alférez, F. (1983). Quantitative relationships between color and hematite content. *Soil Sci.* **136**, 354-358.
- Torrent, J., Schwertmann, U. & Schulze, D. G. (1980). Iron oxide mineralogy of some soils of two river terrace sequences in Spain. *Geoderma*, **23**, 191-208.