

Società Italiana della Scienza del Suolo

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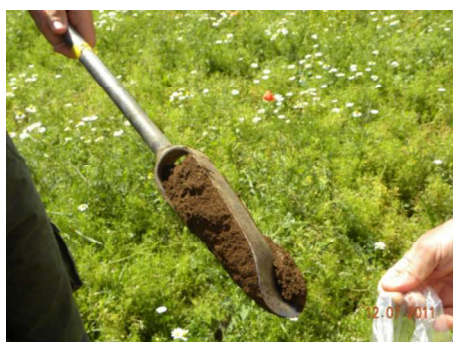
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LIBRO DEI RIASSUNTI



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THE INFLUENCE OF CRYSTALLINE AND POORLY CRYSTALLINE IRON OXIDES ON THE SURFACE AREA OF PODZOL AND LUVISOL B HORIZONS

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Iron oxides, oxyhydroxides, and hydroxides (hereafter oxides) have profound influence on soil physical and chemical properties, and greatly contribute to the specific surface area (SA) of the soils. Crystallinity and particle size determine the SA, and strongly depend on formation conditions. As in natural soil environment such conditions are extremely variable, the SA of Fe oxides covers wide ranges (ferrihydrite: 100-700 m² g⁻¹; goethite: 20-200 m² g⁻¹; hematite: 2-90 m² g⁻¹). However, the association of Fe oxides with other soil components may significantly affect their relative contribution to the bulk SA.

To evaluate the influence of different Fe oxides on soil SA, we selected and characterized spodic and argic horizons from three Podzols (5 samples) and three Luvisols (7 samples). The samples were expected to differ in amounts and crystallinity of Fe oxides as result of differing pedogenic processes. The samples were treated with NaClO to remove organic matter, and with DCB-NaClO to dissolve both organics and pedogenic Fe oxides; the residue of the latter treatment represented the silicate phase. The SA was measured on untreated and treated samples, by applying the BET theory to N₂ adsorption data. The difference between the SA of NaClO and DCB-NaClO treated samples gives an estimate of the Fe oxide SA.

In Podzols, the mineral SA was affected by the oxalate-extractable Fe (Fe_o), representing poorly crystalline oxides (r²=0.65), in Luvisols Fe from crystalline oxides explained most of the variability (r²=0.99). This is in agreement with pedogenesis, resulting in a preferential formation of poorly crystalline oxides in Podzols (Fe_o/Fe_{DCB}=0.66±0.06) and crystalline oxides in Luvisols (Fe_o/Fe_{DCB}=0.11±0.03). Oxide phases contributed 80±17% to the mineral SA of Podzols, while for Luvisols the contribution of oxide and silicate fractions was comparable. Considering that the amount of Fe_{DCB} never exceeded 4% w/w, oxide phases had always larger SA than silicates. Unexpectedly, the SA of the oxide fraction did not significantly differ between soils with only slightly smaller values in Luvisols (158±20 m² g⁻¹ oxides) than in Podzols (182±34 m² g⁻¹ oxides). This indicates for Podzols a SA close to the lower limit of ferrihydrite, while for Luvisols suggests the occurrence of small microcrystalline goethite or/and hematite. Another explanation could be that the effects of both the larger SA of poorly crystalline oxides and the translocation of Fe and its recrystallization promote strong interactions of organic matter and oxides, e.g. due to co-precipitation in illuvial horizons, preventing complete removal of organics by NaOCl and causing underestimation of the SA.

Our results suggest that in different natural environments, despite the Fe oxide types and contents, the SA of Fe oxide phases shows no major differences. That points at other effects than just crystallinity to influence the SA of Fe oxides, such as interactions during pedogenic processes.

Keywords: N₂ adsorption, spodic and argic horizons, specific surface area, soil iron oxides.



THE INFLUENCE OF CRYSTALLINE AND POORLY CRYSTALLINE IRON OXIDES ON THE SURFACE AREA OF PODZOL AND LUVISOL B HORIZONS

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Iron oxides, oxyhydroxides, and hydroxides (hereafter Fe oxides) have a large influence on soil physical and chemical properties, and greatly contribute to the **specific surface area (SA)** of the soils. Crystallinity and particle size determine the SA, and strongly depend on formation conditions. However, the association of Fe oxides with other mineral or organic components may significantly affect their relative contribution to the soil SA.

Podzols and Luvisols are expected to differ in type of organo-mineral interaction and in amounts and crystallinity of Fe oxides as a result of differing pedogenesis.

The downward translocation of organo-Fe complexes into the **spodic horizons (Bs or Bhs)** of Podzols and their crystallization promote the formation of co-precipitates formed by organic matter and ferrihydrite (SA: 100-700 m² g⁻¹).



Goethite (20-200 m² g⁻¹) and hematite (2-90 m² g⁻¹) are the most common oxides in **argic horizons (Bt)** of Luvisols due to their thermodynamic stability. Organic matter may interact by coating the oxide surfaces.



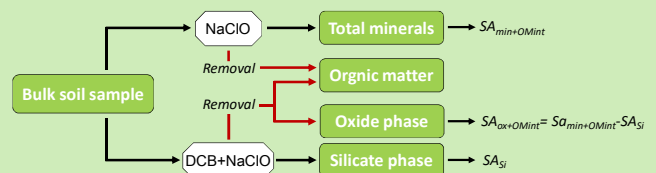
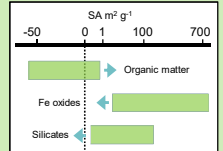
We evaluated if the differences in Fe oxide features and type of organo-mineral associations influence soil surface properties by comparing the SA of separated soil phases of spodic and argic B horizons.

We selected and characterized *spodic and argic horizons* from three Podzols (P, 5 samples) and three Luvisols (L, 7 samples).

The samples were **treated with NaClO to remove the poorly mineral-associated organic matter**, and with **DCB+NaClO to dissolve both organics** (poorly and strongly mineral-associated) **and pedogenic Fe oxides**.

The SA was measured on untreated and treated samples by applying the **BET theory to N₂ adsorption data**.

Contribution to bulk SA of soil phases



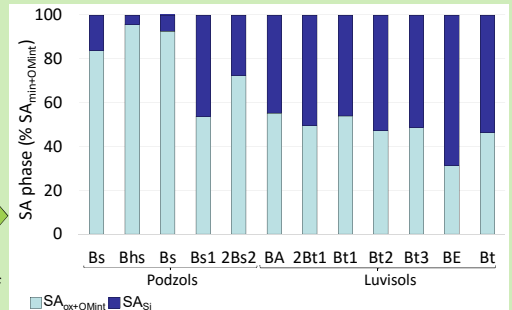
Main chemical properties (Fe_{DCB} and Fe_O : dithionite-citrate-bicarbonate and oxalate extractable Fe; OC: total organic carbon; OC_{NaClO} : OC removed by NaClO treatment; OC_{DCB} : OC removed by NaClO+DCB treatment minus OC_{NaClO}) of Podzol (P) and Luvisol (L) horizons.

Profile	Horizon	Fe_{DCB} g kg ⁻¹	Fe_O g kg ⁻¹	Fe_O/Fe_{DCB}	OC g kg ⁻¹	OC_{NaClO} % OC	OC_{DCB} % OC
P1	Bs	9.1	5.3	0.58	16.6	48	21
	Bhs	35.9	23.4	0.65	37.1	67	26
P2	Bs	23.0	14.3	0.62	22.5	65	29
	Bs1	4.3	3.1	0.72	8.8	74	12
P3	2Bs2	10.6	7.8	0.73	9.6	60	21
	BA	19.6	2.8	0.14	10.1	84	4
L1	2Bt1	12.6	1.1	0.09	2.3	50	23
	Bt1	31.6	3.2	0.10	5.7	67	13
L2	Bt2	31.7	2.7	0.08	4.5	68	11
	Bt3	35.1	3.7	0.10	6.2	69	13
L3	BE	8.4	1.3	0.15	9.7	78	4
	Bt	9.9	1.2	0.12	6.0	74	4

In Podzols the amounts of poorly crystalline oxides (Fe_O) affect the $SA_{min+OMint}$ ($r^2=0.65$). In Luvisols the crystalline oxides are more abundant ($Fe_{CY}=Fe_{DCB}-Fe_O$) and explain most of the $SA_{min+OMint}$ variability ($r^2=0.99$).

The proportion of OC released upon NaClO treatment (OC_{NaClO}) is larger in Luvisols, while in Podzols the proportions of OC removed by pedogenic oxides dissolution (OC_{DCB}) show higher values.

Specific surface area of the mineral phase ($SA_{min+OMint}$) of Podzol and Luvisol horizons and the relative contribution of oxide ($SA_{ox+OMint}$) and silicate (SA_{Si}) phases.



Oxide phases contribute 80±17% to the $SA_{min+OMint}$ of Podzols, while for Luvisols the contribution of oxide and silicate phases is comparable.

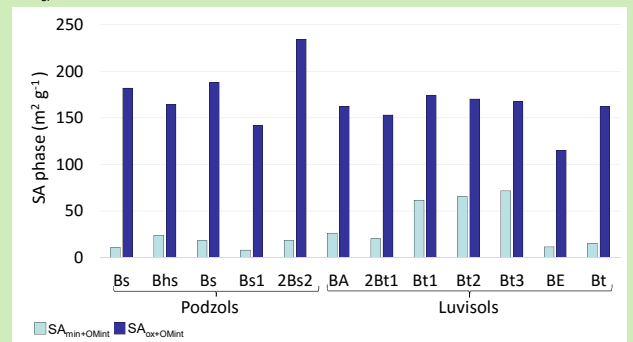
The SA of the oxide ($SA_{ox+OMint}$) phase do not significantly differ between soils with only slightly smaller values in Luvisols (158±20 m² g⁻¹) than in Podzols (182±34 m² g⁻¹).

This is indicative of the different association between oxides and organics in the two soil types, which possibly influences the estimated SA of the oxide phase.

Podzols → the effects of both the larger SA of poorly crystalline oxides, the translocation of Fe and its crystallization promote strong interactions between the co-precipitated organic matter and oxides, preventing the complete removal of organics by NaOCl and probably causing underestimation of the $SA_{ox+OMint}$.

Luvisols → the NaClO treatment removes the OM coating more efficiently resulting in an estimation of $SA_{ox+OMint}$ less influenced by the negative effect of OM. The calculated $SA_{ox+OMint}$ is close to the higher limit of goethite suggesting the occurrence of small microcrystalline goethite or/and hematite.

Specific surface area of mineral ($SA_{min+OMint}$), oxide ($SA_{ox+OMint}$) and silicate (SA_{Si}) phases.



Our results suggest that in soil environments, despite the diverse crystallinity and amount of Fe oxides, the SA of oxide phase calculated by selective organic and oxide removal shows no major differences. That points at the formation of diverse organo-mineral interactions during pedogenesis and at their influence on the structure and reactivity of natural soil Fe oxides.

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