Sorption (kinetic and capacity) and desorption of trace elements in volcanic soils of Italy and the Azores

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Introduction. Andosols have a high binding capacity for heavy metals which may be naturally accumulated or anthropogenically derived. These metals are bound in mineral structures, on mineral surfaces, and complexed by organic matter. Some trace elements may be so strongly bound that they become unavailable to plants. But in this respect, information is very scarce, but extremely important for improved environmental protection (COST Report 2000). Beside the formation of organic complexes, "many trace metals form surface complexes with aluminol and silanol groups as evidenced by extensive studies on silica and Al-oxides; however, few studies have been performed on allophane and imogolite" (Clark & Mc Bride 1984). The dominance of variable charge sites in Andosols has driven us to study the pH-depended sorption and desorption of trace elements.

Materials. Horizons of COST- profiles of Italy and the Azores have been selected in order of distinct differences of contents in organic matter and short range ordered minerals (see Tab. 1). For comparison an Ap-horizon without short range ordered minerals of a Chernozem (Germany) is also included in the study.

Tab. 1: Selected data of the investigated soil samples (COST-data)

Soil	Depth cm	Hor.	Clay %	Silt %	Sand %	pH KCl	Corg %	CEC $cmol_c/kg$	Fe_d %	Al_o %	Fe_o %	Si_o %
N1 Italy	0-16	Ap	10	63	27	4,7	2,7	27,3	0,5	0,3	0,2	0,1
N1 Italy	54-95	Bw2	9	62	29	5,2	0,7	21,8	0,6	0,3	0,2	0,1
N3 Italy	0-22	A1	16	58	26	4,9	6,7	33,5	1,0	2,9	0,6	1,1
N3 Italy	48-70	AB	14	66	20	5,4	2,1	20,9	1,3	4,1	0,6	1,9
N3 Italy	98-125	Bw2	12	56	32	5,5	0,6	13,5	0,8	3,1	0,4	1,9
N6 Azores	0-20	Ah	39	61	0	4,6	19,1	73,7	0,0	6,0	2,9	0,9
N6 Azores	40-60	2AB	32	68	0	5,4	11,0	67,0	0,0	9,3	4,2	2,1
N6 Azores	100-120	2Bw3	29	71	0	5,7	4,5	59,4	0,0	10,8	3,3	3,6
Chernozem	0-24	Ap	21	68	11	7,5	2,0	21,5	0,6	0,0	0,1	0,0

Methods. Batch experiments (according to OECD-Guideline 106) have been carried out to establish sorption- and desorption-isothermes of the trace elements Cu, Cd, Pb, Cr and Ni at pH-levels relevant to Andosols (pH 4 to 7). (1) Time-Dependence of trace element sorption: Field-moist samples equivalent to 2 g dry (105°C) soil were shaken (2 days; room temperature and ambient pH) in 50 mL of [5 mmol $TE(NO_3)$ + 10 mmol $Ca(NO_3)_2$] L^{-1} solution. After 10, 20, 40, 80, 160, 320 minutes and 10, 22, 48 hours shaking, the samples were centrifuged and 0.5 mL of the supernatant removed to measure the trace elements.
(2) pH-Dependence of trace element sorption-isotherms: Field-moist samples equivalent to 2 g dry (105°C) soil were prepared in three treatments (i) equilibrated to pH 4 (with HNO_3 and NaOH), (ii) ambient pH, (iii) equilibrated to pH 7 (with HNO_3 and NaOH). Each treatment was shaken (2 days) in 10 mL of [1, 5, 10, 100, 300, 1000, 2000 mg elements$\cdot L^{-1}$ $TE(NO_3)$ +

10 mmol $Ca(NO_3)_2$] L^{-1} solution (room temperature). For the pH 4-treatment, additionally the solution was adjusted to pH 4. Elements were measured after centrifuging and filtering.
(3) pH-Dependence of trace element desorption-isotherms: Loaded samples from (2) were shaken 10 consecutive time in 20 mL 10 mmol $Ca(NO_3)_2$] L^{-1} for 2 days each . elements were measured after centrifuging and filtering.
The elements have been measured by means of AAS and ICP

Results. From the sorption kinetics it can be concluded that in all samples the sorption of trace elements is governed by ion association, ion exchange and rapid sorption (Sparks, 2000) within a few hours. All samples have a very high sorption capacity. Without any exception no clear maximum of sorption was reached up to a maximum concentration of 2000 mg L^{-1} in the solution. The pH-depence of sorption is most prominent for Cd and Ni. It is to notice that especially the allophane rich subsoils from N6 Azores and N3 Italy have around pH 4 sorption isothermes for Cd and Ni at distinct lower levels than at soil pH or around pH 7. The sorption of Cr and Pb are only less affected by pH changes.

Literature Cited.

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