

Effect of soil manganese oxides on redox capacity in various soils, Korea

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1. Introduction

According to previous work (McKenzie, 1989), Mn oxides have a strong oxidation potential and have a high adsorption capacity for weakly hydrated cations such as copper (Cu), cobalt (Co), nickel (Ni) and zinc (Zn) and anions of acids such as molybdate, phosphate and selenate. Mn oxides increases the mobility and toxicity of Cr by the oxidation of Cr(III) to Cr(VI) in soil and aquifer (Kim *et al.*, 2002). However, they detoxify arsenic (As) by oxidizing more toxic and mobile form (arsenate) to less toxic and mobile form (arsenite) (Driehaus *et al.*, 1995). Iron oxides have revealed the high adsorption capacity for both cationic and anionic contaminants depending on pH (Borggaard *et al.*, 2004; Illes and Tombacz, 2004; Liu and Huang, 2003). Fine particles of Mn and Fe oxides are also known important colloidal media for the migration of contaminants in soil and aquifer (Ryan *et al.*, 1998; Swartz and Gschwend, 1998).

The objectives of this study is to characterize the redox capacity (reactivity) of the various soils. In addition, the relationship of the redox activity, Mn oxides, Fe oxides and other soil properties, were assessed.

2. Materials and methods

25 moist/dry soil samples were collected from 7 soil profiles in Korea. The four Mn extraction methods and physical/chemical/mineralogical details of the soil samples were showed in Table 1. Cu, Cd, Pb and Zn in the soil samples were extracted using aquaregia extraction. The concentrations of Cu, Cd, Pb and Zn in the solutions were determined by ICP-AES. Standard chromium net oxidation test was (Barlett and James, 1996) was performed without modification. Briefly, 2.5 g soil or 2 mL moist soil were shaken with 25 mL of 0.001M CrCl₃ for 15 min or 24 hour, a phosphate buffer was added to remove adsorbed Cr(VI), the sample was centrifuged, and Cr(VI) determined in the supernatant using s-diphenyl carbazide. The suitability of two sample conditions (dry and wet samples) were evaluated after 15 minute and 24 hour of reaction time. The relationship between the

net Cr oxidation, soil parameters such as Mn and Fe oxide content, pH, CEC, and moisture content, and the extractable heavy metals was determined using a multivariate statistical analysis (PCA, Principal Component Analysis).

Table 1. Physical, chemical and mineralogical characteristics of the soil samples.

ID	Soil	Horizon	Depth (cm)	Mn ^a (mg/kg)	Mn ^d (mg/kg)	Mn ^h (mg/kg)	Mn ^r (mg/kg)	Fe ₂ O ₃ ^a (%)	Fe ₂ O ₃ ^d (%)	Moisture (%)	I.L.(%)	CEC (cmolc/kg)	pH	BC (µs/m)	Mineralogy
DJ-A1	DJ	A1	2-7	380	73.6	74.4	4.09	1.07	0.180	10.82	0.80	6.5	4.52	32.9	Q, F, M, K
DJ-A2		A2	7-37	420	51.2	61.2	0.33	1.28	0.146	11.04	0.43	5.7	6.07	25.0	Q, F, M, K
DJ-A3		A3	37-54	509	82.0	89.2	0.28	1.38	0.150	10.64	0.38	7.0	4.96	9.5	Q, F, M, K
DJ-C1		C1	54-114	364	71.2	76.8	0.24	1.23	0.157	13.42	0.46	8.1	5.62	7.2	Q, F, M, K, V
DJ-C2		C2	114-	475	82.4	116.0	0.21	1.45	0.102	13.07	0.21	8.8	5.45	6.6	Q, F, M, K, V
SH-A1	SH	A1	2-12	610	81.6	64.8	2.70	10.71	1.847	17.56	1.58	7.1	4.74	27.5	Q, K, M, F, V
SH-A2		A2	12-74	912	173.6	162.4	7.94	10.91	2.121	16.03	1.06	7.6	4.93	31.0	Q, K, M, F, V
SH-A3		A3	74-122	941	211.2	144.4	1.18	11.60	2.029	18.43	1.10	7.7	6.41	20.2	Q, K, M, F, V
SH-C		C	122-	1334	215.2	191.6	0.69	10.47	1.747	16.66	0.84	6.9	6.58	11.9	Q, K, M, F, V
TG-1	TG	¹ OB1	0-30	552	152.8	156.0	1.56	3.57	0.768	15.69	0.49	8.5 ¹	5.70	29.8	Q, F, M, K
TG-2		OB2	30-60	768	170.4	230.0	7.68	3.71	0.529	15.52	0.86	7.6	4.89	25.1	Q, F, M, K, C
TG-3		¹ PS	60-75	518	173.6	187.2	4.28	4.08	0.806	20.24	0.86	11.0	5.06	38.5	Q, F, M, K
TG-4		C	75-80	2414	928.0	910.4	12.32	2.17	0.445	22.73	0.41	8.1	4.76	34.4	Q, F, M, K
TG-5		R	80-	2011	788.0	673.6	4.71	3.57	0.474	0.80	0.30	10.3	5.62	22.7	Q, F, I, K
US-A	US	A	1-10	4152	272.0	651.2	3.85	23.78	2.937	18.98	1.17	10.6	6.18	29.9	Q, K, H
US-B		B	10-20	4848	147.4	660.8	1.38	22.38	3.518	21.64	0.85	11.5	5.59	7.3	Q, K, H
US-C		C	20-	1978	108.4	58.8	0.06	19.39	3.345	20.84	0.84	11.5	5.90	6.2	Q, K, H
US-SA	US1	SA	0-20	3178	131.4	737.6	1.58	18.40	1.983	25.20	0.85	41.9	5.75	10.5	A, T, V, E, Mh, Ch, S
US-SC		SC	20-	3216	24.0	545.6	0.63	18.40	1.529	26.26	0.92	43.2	5.90	16.7	A, T, V, E, Mh, Ch, S
YS1-A	YS1	A	1-14	706	22.8	0.4	0.21	8.00	1.713	11.44	0.61	8.6	4.67	32.1	Q, M
YS1-C		C	14-29	701	26.8	1.6	0.37	9.37	1.586	13.30	0.62	8.6	4.67	36.7	Q, M
YS1-R1		R1	29-45	116	23.6	2.0	0.92	7.62	3.104	7.42	3.84	12.6	2.56	746.0	Q, M, P
YS-A	YS	A	2-38	422	92.0	84.8	0.88	16.20	1.443	16.36	1.05	7.6	5.76	10.3	Q, M, K, V
YS-C		C	38-64	<24	99.6	72.4	0.63	3.81	2.219	18.45	0.88	8.7	5.63	20.9	Q, M, K, V
YS-RA		R	64-	1349	121.6	193.2	0.37	5.70	0.615	28.65	0.48	9.5	6.34	21.4	Q, M, K, V

Fe₂O₃^a: iron oxide content extracted with aquaregia (3 ml of 12M HCl + 1 ml of 15M HNO₃), Fe₂O₃^d: iron oxide content extracted with DCB (dithionite-citrate-bicarbonate), Mn^a: total Mn extracted with aquaregia, Mn^d: Mn extracted with DCB, Mn^h: Mn extracted with 0.1M NH₂OH HCl in 0.01M HNO₃, Mn^r: reactive Mn extracted with 0.002 M hydroquinone, Moisture: 60°C overnight, I.L.: loss on ignition, CEC: cation exchange capacity, pH and EC: 1 soil : 10 water method.

¹OB: the overburden soil, ¹PS: the old paddy soil.

Mineral abbreviations: Q: quartz, F: feldspar, M: mica, K: kaolin, V: vermiculite, A: amphibole, T: Talc, E: epsomite, Mh: maghemite, Ch: chlorite, S: serpentine, P: pyrite.

3. Results and discussion

The amount of total oxidized Cr(VI) in the soil samples (the net Cr oxidation) were showed in Fig. 1. The soils used in this study provided a medium to extremely high range of Cr oxidation capacity and Mn content (Table 1).

Manganese and Fe oxides in the black coating material found in the conducting fractures had high surface area and low crystallinity. The properties indicate their high reactivity with conducting solute and contaminant. Standard chromium net oxidation test can be useful for estimating the potential of a soil either to oxidize reduced substances or, alternatively, to reduce oxidized substances (Bartlett and James, 1996). We studied soil redox using the net Cr oxidation as a redox tool and characterizing behavior in soils of other redox substances and parameters, especially various extractable Fe and Mn oxides. The several Mn-extraction methods were used for the understanding of the stability of Mn oxides in various soils. The soils showed extremely high and low range of Mn^a and Mn^r content, respectively. However, Mn^d and Mn^h content had a similar medium concentration range except for US and YS1 soils.

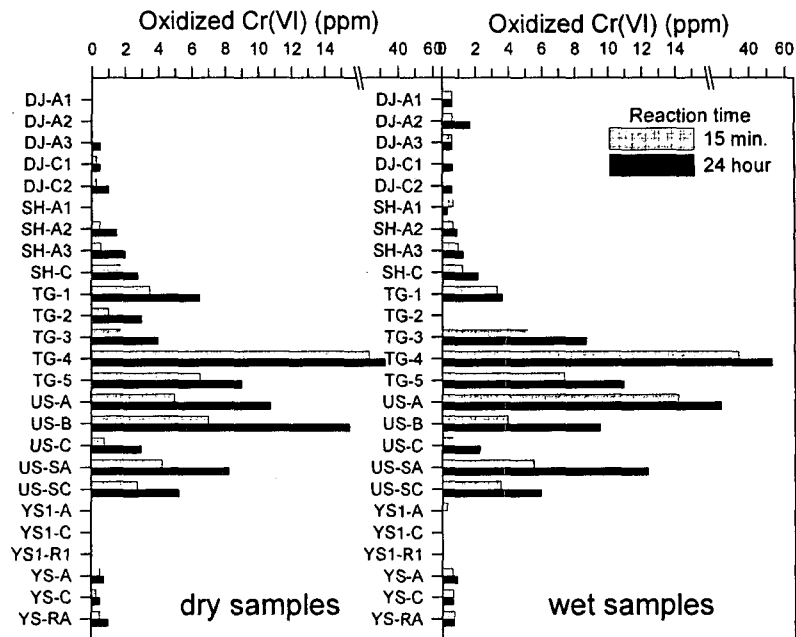


Fig. 1. The standard Cr net oxidation test on dry/wet soil samples.

Table 2. Rotated Component Matrix for the soil data.

Element	Component			
	1	2	3	4
Mn ^a	0.466	0.702	-0.208	0.371
Mn ^d	0.889	-0.114	-0.098	-0.138
Mn ^h	0.798	0.288	-0.164	0.408
Mn ^f	0.785	-0.127	0.087	-0.140
Fe ₂ O ₃ ^a	-0.033	0.927	-0.013	0.294
Fe ₂ O ₃ ^d	-0.101	0.878	0.357	0.000
Cr(VI) wet 15min.	0.964	0.048	-0.026	0.045
Cr(VI) wet 24hour	0.958	0.116	-0.037	0.083
Cr(VI) dry 15min.	0.972	0.045	-0.041	0.065
Cr(VI) dry 24hour	0.950	0.191	-0.075	0.090
Moisture content	0.138	0.429	-0.319	0.454
Loss on ignition	-0.155	0.262	0.914	0.022
CEC	0.023	0.192	0.034	0.970
pH	-0.066	0.242	-0.845	0.118
EC	-0.058	-0.020	0.952	-0.008
Zn	0.092	0.821	-0.221	0.338
Pb	-0.010	0.134	-0.037	0.978
Cd	-0.126	0.909	0.060	0.120
Cu	0.339	0.880	-0.102	-0.122
% of explained variance	37.7	25.7	14.6	9.7

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

Component loadings > 0.7 are shown with bold numbers.

Fe₂O₃^a; iron oxide content extracted with aquaregia (3 ml of 12M HCl + 1 ml of 15M HNO₃), Fe₂O₃^d; iron oxide content extracted with DCB (dithionite-citrate-bicarbonate), Mn^a; total Mn extracted with aquaregia, Mn^d; Mn extracted with extracted with DCB, Mn^h; Mn extracted with 0.1M NH₂OH HCl in 0.01M HNO₃, Mn^f; reactive Mn extracted with 0.002 M hydroquinone.

The PCA was used to determine the variation of the net Cr oxidation as a redox tool and various Mn extraction method in different soil samples. Also, the soil data was analysed using the multivariate method to investigate the relationship between the oxidation capacity, soil parameters and heavy metals. PCA is a multivariate statistical analysis converting the variables (analytes concentrations) in the so-called factors for principal components. The results of the PCA for the soil data are reported in Table 2. The PCA produced four components that explained 87.7% of the total variance in the data. The component 1 was composed of Mn^d, Mn^h, Mn^f and the net Cr oxidation, and it explained 37.7% of the data variance. These elements had loadings of >0.95 for the net Cr oxidation and ~0.80 for Mn content, respectively. The component 2 extracted explained 25.7% of the variance, and it was made up of Mn^a, Fe₂O₃^a, Fe₂O₃^d, Zn, Cd and Cu, with respective loadings of 0.702, 0.927, 0.878, 0.821, 0.909 and 0.880.

There was no significant differences of the oxidized Cr(VI) concentration depending on storage treatments (dry/wet) and the reaction time in the soil sample. However, the magnitude of the Cr net concentration for the wet samples and 24 hour was higher than for the dry samples and 15 min, respectively. These results appears to be due to reduction of the reactive Mn in soils because of sample drying. In addition, the chromium oxidation rate in the soils must have not reached a steady state within 15 minute. Ross *et al.* (2001) confirmed previous findings that studies on the reactivity of soil Mn oxides need to avoid sample drying. Base on the statistical analysis, the content of Mn oxides, except for aquaregia extractable total Mn oxides (Mn^a), were main factors controlling the net Cr oxidation in the soils (component 1). Iron oxides in soils showed a significant relationship with the total manganese oxide, and then related with heavy metal concentration except for Pb (component 2). However, the other soil parameter such as LOI, pH, CEC and EC were not statistically significant in relation to the net Cr oxidation.

4. Conclusions

The magnitude of the Cr net concentration for the wet samples and 24 hour was higher than for the dry samples and 15 min, respectively. These results appears to be due to reduction of the reactive Mn in soils because of sample drying and insufficient reaction time. The reactive Mn oxides were main factors controlling the net Cr oxidation in the soils. However, iron oxides in soils showed a significant relationship with the total manganese oxide, and then related with heavy metal concentration except for Pb.

5. Acknowledgements

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6. References

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