

Changes in Elemental Composition with Andosolization

著者	NANZYO Masami, TAKAHASHI Tadashi
journal or publication title	Journal of Integrated Field Science
volume	2
page range	83-87
year	2005-03
URL	http://hdl.handle.net/10097/30945

Changes in Elemental Composition with Andosolization

Masami NANZYO and Tadashi TAKAHASHI

Graduate School of Agricultural Science, Tohoku University
1-1 Tsutsumidori-Amamiyamachi, Aobaku, Sendai, 981-8555, Japan

Key words : volcanic ash soil, weathering, trace element, ultratrace element, Andisol

Abstract

A total of 57 elements in volcanic ash soils from 18 pedons distributed in Japan were analyzed and the relationships between noncrystalline material content and that of individual elements were examined. The content of the noncrystalline materials was estimated by using acid-oxalate extraction. Oxalate-extractable Fe (Fe_o) and Al (Al_o) corresponds to Fe in ferrihydrite and Al in allophane-imogolite plus Al complexed with humus, respectively. Silicon and alkaline or alkaline-earth elements such as Na, K, Ca, and Sr tended to decrease during the process of volcanic ash soil formation, i.e., andosolization. In contrast, the contents of Al, Y and the first transition metals tended to increase with the increasing content of noncrystalline materials. The first transition metals showed a high correlation with Fe_o suggesting their similarity in chemical behavior during andosolization. The lanthanoid elements tended to increase with the increasing Al_o and Fe_o content.

Introduction

A characteristic process of Andosolization is preferential formation of noncrystalline materials such as allophane, imogolite, opaline silica, ferrihydrite, and Al-humus complexes (Kato, 1983; Shoji et al., 1993; Soil Survey Staff, 1999). The Al and Fe in these noncrystalline materials are extractable with acid-oxalate solution (Parfitt and Henmi, 1982; Childs et al., 1990). No significant translocation of Al, Fe and dissolved organic carbon take place. These soil components are Al- or Fe-rich materials except the opaline silica that is found in the A horizon of young Andisols. (Shoji et al., 1993) The Si/Al atomic ratio of imogolite is 0.5 and that of allophane in Andisols is mostly around 0.5 according to selective dissolution analyses (Parfitt and Kimble, 1989; Shoji et al., 1993).

In contrast, the Si/Al ratio of pyroclastic materials and volcanic glasses, major parent materials of Andisols, are 4.8–2.4 and 5.2–2.3, respectively. These materials are rich in Si compared with those of the Al-rich noncrystalline materials mentioned above. Thus, a large amount of Si is removed during Andosolization, and Al and Fe is concentrated in Andisols (Ugolini et al., 1988). It is easily deduced that contents of other elements are also affected during Andosolization.

Although biologically essential or beneficial nutrients and some contaminated elements in soils (Aubert and Pinta, 1977; Kitagishi and Yamane, 1981; Mortvedt et al., 1991; Gobran et al., 2001) were studied previously, researches covering a wide range of elements are in the introductory stage in soil science (Goody et al., 1995; Yamasaki, 1996, 2000a,b; Yamasaki et al., 2001). The primary objective of this paper is to examine the relationships between their contents and formation of active Al and Fe. Allophane, imogolite and Al-humus are the major forms of active Al and ferrihydrite is the major form of active Fe in the volcanic ash soils used in the present study. Detailed definition of the active Al and Fe was described by Wada (1980).

Materials and Methods

Soil samples

Ninety-five soil samples from 18 pedons in the Hokkaido, Tohoku, Kanto, Chubu and Kyushu districts were used and the locations of the pedons are shown in Figure 1. Soil profile descriptions and the chemical, mineralogical and physical properties of these samples (H5, I1, I4, T1, T2, Ib1, Ib2, S2, S3, S5, S6, S7, K1, K3, K4, M3, M5 and M6) were given elsewhere (Wada, 1986). All the 18 pedons used in the present study were selected from allophanic areas determined by Saigusa and Matsuyama (1998) to minimize the mixing of aeolian dusts (Inoue and

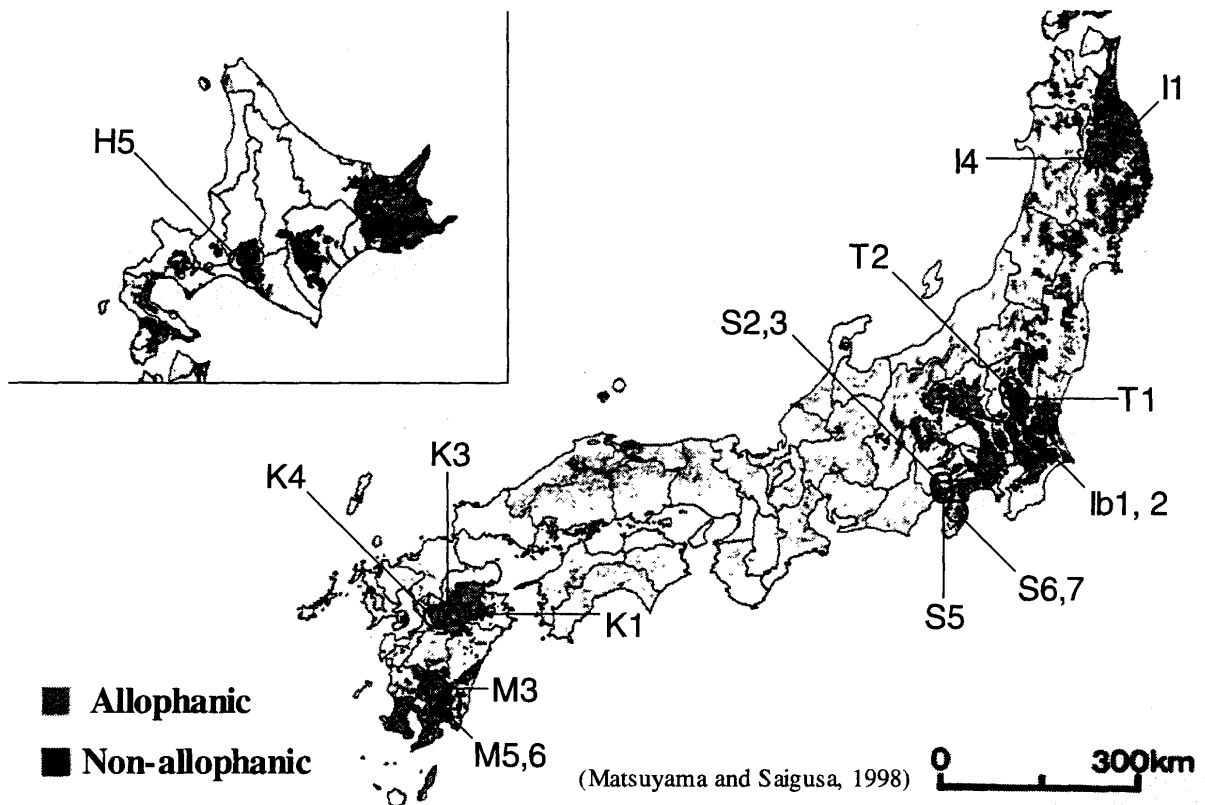


Figure 1. Locations of 18 pedons.

Mizota, 1988) although some humus-rich horizons are dominated by Al-humus. These samples contain both young and highly weathered volcanic ash soils. The active Al and Fe content of these soil samples were described by nanzyo et al. (2002).

Analytical methods

Air-dried fine earth fractions of the soil samples were finely powdered using an agate mortar. The C and N contents were determined by using the dry combustion method. The Al, Si, K, Ca, Fe, P and Ti contents were analyzed by using a glass-bead X-ray fluorescence spectrometer. The Na, Mg, Mn, Zn and Cu contents were analyzed by using an atomic absorption spectrometer after $\text{HNO}_3\text{-HClO}_4\text{-HF}$ digestion. These analytical results were cited from Wada (1986). After digesting 1 g of the air-dried and finely powdered fine earth fraction with $\text{HNO}_3\text{-HClO}_4\text{-HF}$, the dried residue was dissolved in 1 : 20 (v/v) HNO_3 and the trace and ultratrace elements were determined by the induced coupled plasma-mass spectrometric method (Nanzyo et al., 2002). Acid-oxalate extractable Al, Si and Fe of the fine earth fraction were obtained by using the method of Blakemore et al. (1981).

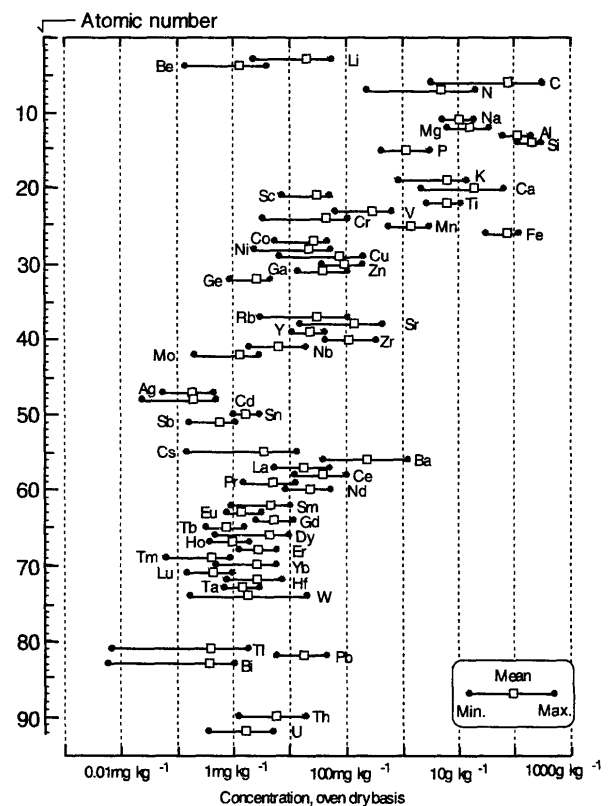


Figure 2. Concentration ranges of major, trace and ultratrace elements in volcanic ash soils of Japan.

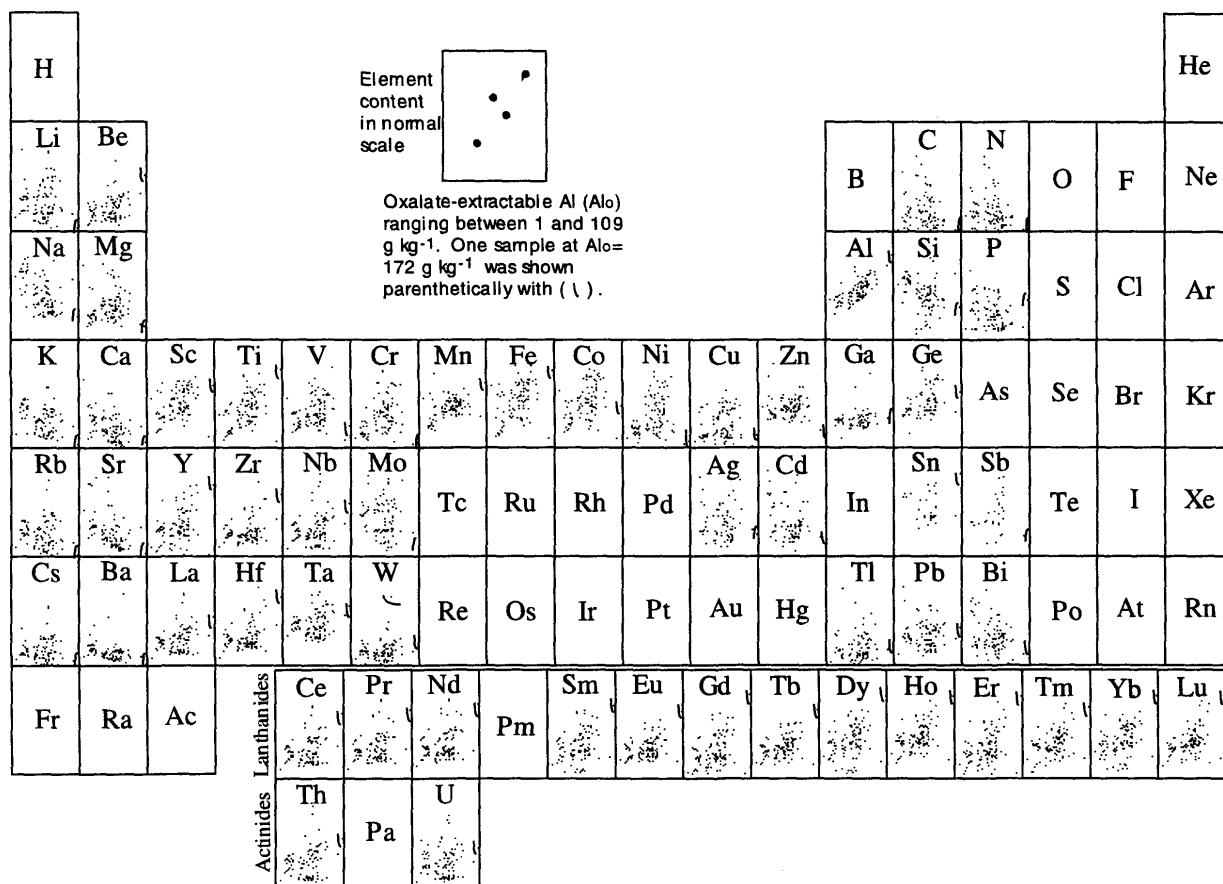


Figure 3. Relationships between content of oxalate-extractable Al (Al_0) and that of major, trace and ultratrace elements in volcanic ash soils of Japan.

Results and Discussion

Total content of elements

The ranges and means of the total element content are shown in Figure 2 on a logarithmic scale. The number of analytical data obtained for Tl and Bi was 92, for Mo 86, for Ga, Ge, Ag and Cd 74, for Sn and Sb 33 due to their low content compared with their background noise and for the other elements 95. The concentration of Cr, Zr, Hf and the heavy rare earth elements might have been somewhat underestimated because minerals containing these elements such as garnet, chromite, magnetite and zircon are highly acid-tolerant (Yamasaki et al., 2001). The obtained element content was highly variable and the values of maximum/minimum ranged between 2 and 300. The maximum/minimum values for Si, Al and Fe were rather narrow ranging between 2 and 4. The contents of many other elements varied widely and many factors such as weathering, leaching, biological activities, rock types of tephra, human activities are involved in the variation of the element concentration. The mean content of the 12 major

elements (C, N, Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe) was more than $1\ g\ kg^{-1}$ and the others were less than these. The Oddo-Harkins' law that the content of the even atomic number elements is greater than those for the neighboring odd atomic number ones was clearly shown for the lanthanoid elements of which the atomic number was from 57 (La) to 71 (Lu). These results were almost within the range reported by Yamasaki et al. (2001) using 514 samples from 78 pedons which covered many soils in Japan. Various correlations, very strong and weak, were observed examining the correlation matrix of 57 elements as reported by Nanzyo et al., (2002).

Relationship between total content of elements and active Al and Fe

Table 1 shows the correlation coefficient between oxalate-extractable soil components [Si (Si_0), Al (Al_0) and Fe (Fe_0)] and total contents of 57 elements. Scatter graphs of 57 elements as a function of Al_0 and Fe_0 are shown in Figures 3 and 4, respectively. Significant negative correlation was found between

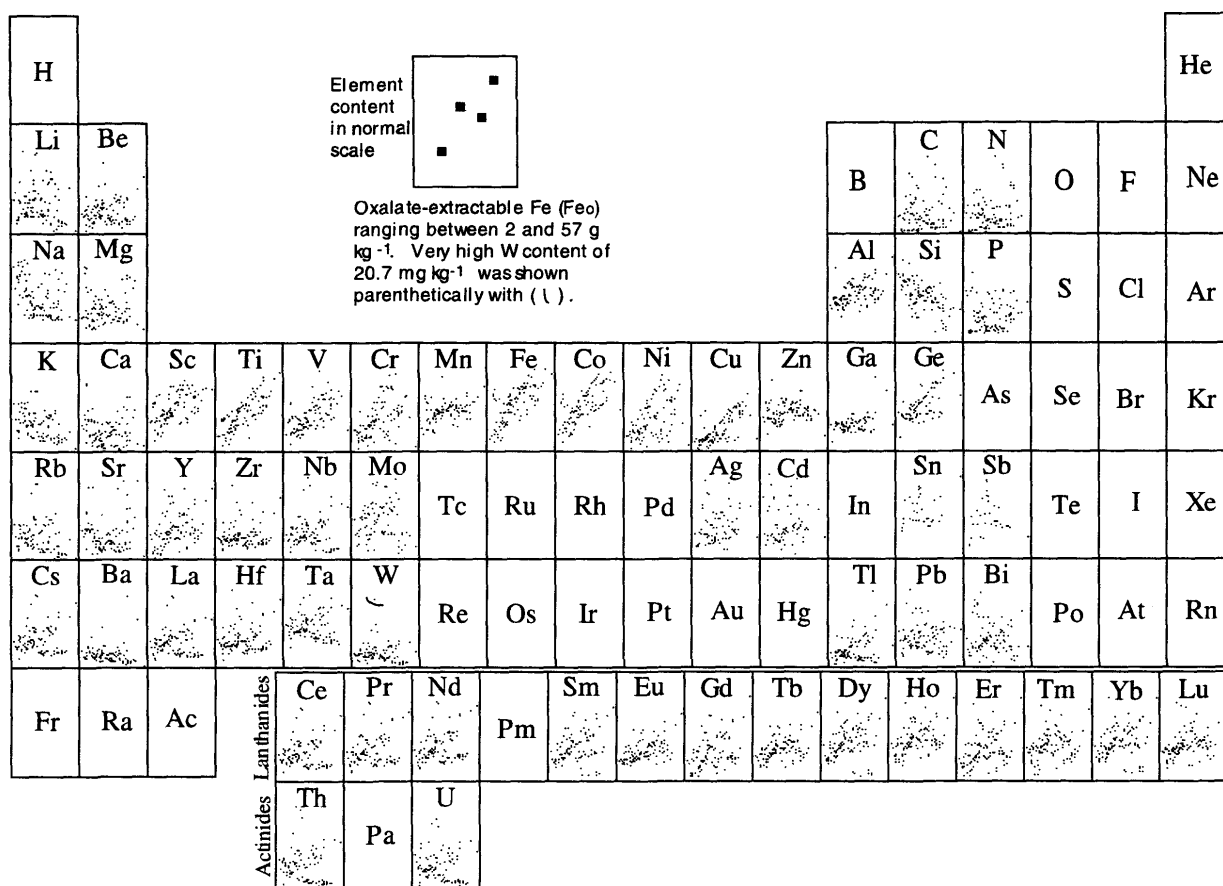


Figure 4. Relationships between content of oxalate-extractable Fe (Fe_o) and that of major, trace and ultratrace elements in volcanic ash soils of Japan.

Si_o and 4 elements (C, N, Na and Sr), between Al_o and 3 elements (Na, Ca and Sr) and between Fe_o and 3 elements (Na, Si and K) at $p=0.1\%$. These elements are alkali and alkaline-earth elements except C, N and Si. Some other alkali and alkaline-earth elements also tended to show negative correlation with Si_o , Al_o and Fe_o although not as strong. Thus, many alkali and alkaline-earth elements are lost with Andosolization. The relatively strong negative correlation between Si_o and humus content (C and N) can be explained due to inhibition of allophane formation by humus. The strong negative correlation between Fe_o and Si is partly attributable to the properties of parent materials as well as the Andosolization process. Negative correlation between Fe and Si content is basically found in fresh tephros having a wide range of rock types.

Significant positive correlation was found between Si_o and 24 elements (Be, Al, Sc, Ti, Mn, Fe, Y, Zr, Nb, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf and Ta), between Al_o and 22 elements

(Be, Al, Sc, Ti, Fe, Ge, Y, Zr, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Hf), and between Fe_o and 18 elements (Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Ge, Y, Eu, Gd, Tb, Ho and Er). These elements are concentrated in Andisols during Andosolization. Due to very high correlation between Si_o and Al_o , 21 elements among 23 strongly correlated with Si_o , also showed high correlation with Al_o . Mn and Ta, strongly correlated with Si_o , also showed significant positive correlation with Al_o at $p=1\%$.

Ten elements (Al, Sc, Ti, Fe, Y, Eu, Gd, Tb, Ho and Er) that showed strong correlation with either of Si_o and Al_o also correlated with Fe_o . However, 11 elements (Be, Ce, Pr, Nd, Sm, Dy, Tm, Yb, Lu and Hf) among 21 elements that correlated with both Si_o and Al_o did not correlate very strongly with Fe_o . Other 8 elements (V, Cr, Mn, Co, Ni, Cu, Ga and Ge) correlated strongly with Fe_o in spite that they did not correlate with either Si_o or Al_o very strongly. All the members of first transition metals from Sc to Cu showed strong correlation with Fe_o , adding Sc, Ti

and Fe that correlated also with Si₀ and Al₀.

Thus, many trace elements are concentrated in Andisols in spite that these soils are formed with strong leaching possibly due to strong affinity to noncrystalline materials. Rock type of parent tephros also affect the elemental composition of Andisols.

References

- Aubert, H. And Pinta, M. 1977. Trace Elements in Soils. *Developments in Soil Science* 7, Elsevier, Amsterdam, 1-395.
- Blakemore, L.C., Searle, P.L. and Daly, B.K. 1981. *Methods for Chemical Analysis of Soils*. New Zealand Soil Bureau Scientific Report 10A. Department of Scientific and Industrial Research, New Zealand.
- Childs, C.W., Matsue, N., and Yoshinaga, N. 1990. Ferrihydrite in volcanic ash soils of Japan, *Soil Sci. Plant Nutr.*, 37, 299-311.
- Gobran, G.R., Wenzel, W.W. and Lomb E. 2001. Trace elements in the rhizosphere, CRC Press, Boca Raton, USA, 1-321.
- Goody, D.C., Shand, P., Kinniburgh, D.G., and Van Riemsdijk, W.H. 1995. Field-based partition coefficients for trace elements in soil solutions, *Eur. J. Soil Sci.*, 46, 265-285.
- Inoue, K., and Mizota, C. 1988. Eolian origin of 2 : 1 layer silicates and fine quartz in Andosols and red-yellow soils developed on limestones and basalts, *J. Clay Sci. Soc. Jpn*, 28, 30-47.
- Kato, Y. 1983. Mechanism of volcanic ash soil formation. In : Y. Yoshinaga (ed.) *Volcanic Ash Soils -Genesis, Properties and Classification*, Hakuyuusha, Tokyo, 5-30.
- Kitagishi, K. And Yamane, I. 1981. *Heavy Metal Pollution in Siols of Japan*, Japan Scientific Press, Tokyo, 1-302.
- Mortvedt, J.J., Cox, F.R, Shuman, L.M. and Welch, P.M. 1991. *Micronutrients in Agriculture* 2nd Ed. Soil Sci. Soc. Am., Inc. Madison, Wisconsin, USA, 1-760.
- Nanzyo, M. , Yamasaki, S. and Honna. T. 2002. Changes in content of trace and ultratrace elements with an increase in noncrystalline materials in volcanic ash soils of Japan. *Clay Sci.* 12, 25-32.
- Parfitt, R.L. and Henmi, T. 1982. Comparison of an oxalate extraction method and an infrared spectroscopic method for determining allophane in soil clays, *Soil Sci. Plant Nutr.*, 28, 183-190
- Parfitt, R.L., and Kimble, J.M. 1989. Conditions for formation of allophane in soils, *Soil Sci. Soc. Am. J.*, 53, 971-977
- Saigusa, M., and Matsuyama, N. 1998. Distribution of allophanic Andosols and Non-allophanic Andosols in Japan, *Tohoku J. Agric. Res.*, 48, 75-83.
- Shoji, S., Nanzyo, M., and Dahlgren, R.A. 1993. *Volcanic Ash Soils - Genesis, Properties and Utilization*. *Developments in Soil Science* 21, Elsevier, Amsterdam, 1-288.
- Soil Survey Staff. 1999. *Soil Taxonomy, A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, 2th Ed. *Agriculture Handbook No. 436*, United States Department of Agriculture, U.S. Government Printing Office, Washington DC 20402, 271-328.
- Ugolini, F.C., Dahlgren, R., Shoji S., and Ito. T. 1988. An example of andosolization and podzolization as revealed by soil solution studies, Southern Hakkoda, northeastern Japan. *Soil Sci.*, 145, 111-125.
- Wada, K. 1980. Mineralogical characteristics of Andosols. p.87-107. In B.K.G. Theng (ed.) *Soils with variable charge*. New Zealand Soc. Soil Sci., Lower Hutt, N.Z.
- Wada, K. 1986. *Ando Soils in Japan*, Kyushu University Press, pp.276.
- Yamasaki, S. 1996. Inductively coupled plasma mass spectrometry, In : Eds. T.W. Boutton and S. Yamasaki, *Mass Spectrometry of Soils*, Marcel Dekker, Inc. New York, 459-491.
- Yamasaki, S. 2000a. Soil Analysis by inductively coupled plasma mass spectrometry, *BUNSEKI KAGAKU*, 49, 217-224.
- Yamasaki, S. 2000b. Inductively coupled plasma mass spectrometry in environmental analysis, In : Ed. R.A. Meyers, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons Ltd, Chichester, 2672-2692.
- Yamasaki, S., Takeda, A., Nanzyo, M., Taniyama, I., and Nakai, M. 2001. Background levels of trace and ultra-trace elements in soils of Japan, *Soil Sci. Plant Nutr.* 47, 755-765