Evaluation of the relative contribution of gravel and fine-earth fractions to the chemical properties of a scoriaceous Haplic Regosols, Japan

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Summary

The objectives of this study were to compare soil chemical properties of gravel fractions (>2 mm) and fine-earth fractions (≦ 2 mm) in a weakly-weathered Regosol derived from basaltic scoria, and to evaluate the relative contributions of these fractions to the chemistry of the whole soil. The gravel fraction was found to contribute to chemical properties of the whole soil as follows: contributions to T-C and Al_o were 21.3% and 21.4%, respectively; and the contributions to cation exchange capacity (CEC) and each exchangeable cation were 17.4% and 16.7-21.5%, respectively. In the initial stages of formation of Regosols at least over 125 years, it is evident that most soil chemical properties are associated with the fine-earth fraction. However, some organic carbon and available nutrients also accumulated concomitantly in gravel fractions. In order to evaluate the chemical properties of Regosols derived from basaltic scoria, which is a porous parent material, it is necessary to recognize that the gravel fraction as well as the fine-earth fraction contributes to the whole-soil properties.

1. Introduction

In the chemical analysis of soil, air dried samples of the ≦ 2 mm fraction, the so-called fine-earth fraction, have been conventionally used. Soil samples are soil materials partially sampled from a continual natural body. Therefore, analysts must always be aware of the relationship between the soil samples and the natural soil body upon performing chemical analyses. There have been some studies on methodologies for analyzing soil samples in which the relationship between the soil body (undisturbed sample) and the soil's sieved fine-earth fraction was critically evaluated with respect to such factors as soil moisture content, pH, and extraction methods (Mclean and Owen, 1969; Barrow and Shaw, 1975; Barton and Karathanasis, 1997). However, all of these studies were conducted on clayey soils and not on Regosols containing abundant coarse rock fragments >2 mm (typically gravel or coarser clasts). In the case of weakly-weathered volcanogenous Regosols derived from porous volcanic ejecta, it has been assumed that the >2 mm fraction contributed little to various soil physicochemical properties. Basaltic scoria is a pyroclastic material and many pores (vesicles) were formed on its surface at the time of eruption. Because nanocrystalline (short-range order) and crystalline clay minerals are generated on the weathered surface of the pores of scoria (Singer *et al.*, 2004), it is plausible that weathering, argillisation and other soil-forming processes occur on the surfaces of fragments of the pores of scoria. Kato *et al.* (2005) examined the initial soil formation for volcanogenous Regosols using whole soil samples, and found that a root had been twisted around the porous surface on the scoria. It is clear that weathering and soil-forming process including argillisa-

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tion are promoted by association of the root with the particle surfaces (Berner, 1992; Drever, 1994; Jackson, 1996; Augusto et al., 2000; Hinsinger et al., 2001). Thus, it is suggested that the chemical characteristics present in fine-earth fractions would appear on the pore surfaces inside scoria fragments of >2 mm. However, Kato et al. (2005) did not show the contribution for soil chemical properties of the >2 mm (gravel) fraction. Moreover, analytical data on whole soil samples are often required when the plant-soil relationship is investigated in the field, especially in ecological studies (e.g. Kamijo et al., 2002). These studies also provide important information for research into carbon accumulation and loss in soil with respect to greenhouse warming (Jones et al., 2008). Our study aims to clarify the contribution of the >2 mm fraction to the whole soil in weakly-weathered volcanogenous Regosols deriving from porous basaltic scoria by comparison of soil chemical properties between gravel (>2 mm) and fine-earth ($\leqq$ 2 mm) fractions.

2. Materials and Methods

2.1) Soil samples

Soil samples were taken from the A horizon of a soil derived from basaltic scoria fragments resulting from an eruption that took place in 1874 on Miyake-jima Island, about 180 km south of Tokyo, Japan (Kato et al., 2005). On Miyake-jima Island prior to the eruption 2000, basaltic scoria was emitted by a comparatively small eruption (the eruption height was <10 km), which normally would cause a scoria cone to form around a crater (Aramaki and Hyakawa, 1984). The soil from which the sample was taken was on a basaltic scoria cone formed in an eruption in 1874 (Kato et al., 2005). The soil samples were taken in September, 1999 and soil forming time was for 125 years (Kato et al., 2005). This study site has a humid warm-temperate climate, and the soil is today under a mixed broad-leaved evergreen and broad-leaved deciduous forest (Kato et al., 2005). It is classified in the Regosols according to the Unified Soil Classification System of Japan (Fourth committee for soil classification and nomenclature, 2002), and as an Haplic Regosol (Hyperochric) according to the World Reference Base for Soil Resources (IUSS working group WRB, 2006). The parent material comprises porous

basaltic (basic) rock fragment $\leqq$ 64 mm (Aramaki, 1995). In volcanogenous Regosols on scoria, the concentration of the gravel fraction (>2 mm) is high, and whole soil samples are quite heterogeneous in terms of the size distribution and the nature of the fragments. In our study, the A horizon sample after air dried was divided into >2 mm and $\leqq$ 2 mm fractions by sieving. These >2 mm and $\leqq$ 2 mm fractions, hereafter referred to as gravel and fine-earth fractions, respectively, were used for the chemical analyses.

2.2) Analytical methods

Particle size distribution was analyzed by the conventional pipette method in which ultrasonic dispersion (10 KHz, 15 min) after H_2O_2 treatment was carried out in water to which a small amount of NaOH had been added (Committee of Soil Environment Analysis, 1997). Exchangeable bases were extracted with CH_3COONH_4 (1 mol L^{-1}) using a soil/solution ratio of 1:50, and determined by atomic absorption spectrophotometry (Committee of Soil Environment Analysis, 1997). Total carbon and total nitrogen contents were measured using an NC analyzer (Sumika Chemical Analyses Service, NC-900). Acid ammonium oxalate extraction was conducted by the method proposed by Blakemore et al. (1987) in which 50 mL of oxalate solution (0.2 mol L^{-1}, pH 3.0) was added to 500 mg of the samples and shaken end-to-end in the dark (25 ℃, 4 hour). After extraction, 0.5 mL of 0.1% Accofloc solution was added to the extract, and the supernatant was separated by centrifugation. Then, the supernatant was filtered though a 0.45 μm membrane-filter and analyzed for Al, Fe and Si (designated as Al_o, Fe_o and Si_o) by ICP-AES. Cation exchange capacity (CEC) was determined by the method put forward by Wada and Harada (1969).

3. Results and Discussions

3.1) Particle-size distributions

In the whole soil sample after air dried that was divided by 2 mm sieving, the particle size distribution of gravel (>2 mm) and fine-earth ($\leqq$ 2 mm) fractions were 46.4% and 53.6%, respectively. The particle size distribution of both gravel (>2 mm) and fine-earth ($\leqq$ 2 mm) fraction samples are shown in Table 1. A fraction comprising finer than coarse sand made up 21.6% of the total gravel

Table 1. Particle size distribution of after dry sieving.

sample fraction	gravel	coarse sand	fine sand	silt	clay
			% (w/w)		
gravel (>2 mm)	78.4	7.7	4.3	8.5	1.1
fine-earth (≦ 2 mm)	N.A	64.2	30.3	4.9	0.6

Table 2. Amount of T-C, T-N, Al_o, Fe_o and Si_o in gravel (>2 mm) and fine-earth (≦ 2 mm) fractions.

sample fraction	T-C	T-N	C/N ratio	Al_o	Fe_o	Si_o	Al_o/Si_o ratio
	g kg^{-1}			g kg^{-1}			
gravel (>2 mm)	17.8	1.07	17	0.84	1.86	0.31	2.7
fine-earth (≦ 2 mm)	56.9	3.36	17	2.68	4.32	0.80	3.4

fraction. This fraction was considered to have been generated by ultrasonic and H_2O_2 treatments, and probably the particles came from the surfaces and vesicles of the sucoriaceous gravels. In the fine-earth fraction, sand comprised 94.5%. Moreover, silt and clay derived from the gravel fraction were higher than in fine-earth fraction. As for the scoria surface, it is found that many pores are formed with the gaseous release that occurs when erupting on land (Singer *et al.*, 2004). These results showed that basaltic scoria contained considerable amounts of sand, silt and clay particles inside a pore of the scoria clast. Thus the gravel fraction contains finer particles which can likely affects chemical properties of soil (even though it is dominated by gravels) more than would be expected.

3.2) Chemical properties

The amount of T-C, T-N, Al_o, Fe_o and Si_o in the gravel and fine-earth fractions are shown in Table 2. The T-C content of the fine-earth fraction was larger than in the gravel fraction by about 3 times, indicating that most of the soil organic matter accumulated in fine-earth fraction. The Al_o, Fe_o and Si_o contents were greater in the fine-earth fraction than in the gravel fraction, and it would be conceivable that many nanocrystalline (or amorphous)

materials, or their precursor materials such as hydoxy aluminum and hydoxy alumino silicate precipitates, or both, were contained in the fine-earth fraction. However, it was clear that T-C, T-N, Al_o, Fe_o and Si_o were also contained in the gravel fraction. It could be considered that the quality of the organic matter in both fractions was almost the same because C/N ratios for gravel and fine-earth fractions were both 17. On the other hand, the Al_o/Si_o ratio of the gravel fraction was 2.7 and that of the fine-earth fraction was 3.4.

The CECs and the amount of exchangeable bases of the gravel and fine-earth fractions are shown in Table 3. The CEC of the fine-earth fraction was 4.1 times higher than that of the gravel fraction. The fine-earth fraction has a high content of exchangeable bases. As noted earlier, the clay content of the gravel fraction was higher than that of in the fine-earth fraction. However, the fine-earth fraction had most of the soil organic matters and nanocrystalline materials. Kato *et al.* (2005) showed that the CEC of Regosols was controlled by the amounts of soil organic matters and amorphous substances. Consequently, it was considered that very rapid weathering of the soil has resulted in the fine-earth faction having a high CEC.

The base saturation index of gravel fraction was 137.0%, almost the same as that for the fine-earth fraction

Table 3. Amount of CEC and exchangeable bases of gravel (>2 mm) and fine-earth (≦ 2 mm) fractions.

sample fraction	CEC	Exchangeable cations				Bass-saturation index
		Na^+	K^+	Mg^{2+}	Ca^{2+}	
	$cmol_c$ kg^{-1}	$cmol_c$ kg^{-1}				%
gravel (>2 mm)	1.55	0.098	0.082	0.472	1.472	137.0
fine-earth (≦ 2 mm)	6.37	0.310	0.266	2.037	5.810	132.4

of 132.4%. The contributions of each exchangeable cation to the total were calculated. In the gravel fraction, exchangeable Na^+ was 4.6%, exchangeable K^+ was 3.9%, exchangeable Mg^{2+} was 22.2% and exchangeable Ca^{2+} was 69.3%. In the fine-earth, exchangeable Na^+ was 3.7%, exchangeable K^+ was 3.1%, exchangeable Mg^{2+} was 24.1% and exchangeable Ca^{2+} was 68.7%. It was suggested that exchangeable bases composition of gravel and fine-earth fraction samples was almost the same.

The large quantities of organic matters and nanocrystalline material formed in the fine-earth fraction, plus high exchangeable bases and CEC values, indicate that soil genesis has progressed rapidly in this fraction comprising fine-grained particles with a relatively large surface area. However, it is also evident, surprisingly, that significant amounts of organic matter and noncrystalline materials have been formed in the gravel fraction, inducing negative charges (CEC) and associated exchangeable cations, and these make a substantial contribution to the chemistry of the whole soil. The fact rate of accumulation of organic matter in ~ 150 years exceeds those reported in other studies (Guenat et al., 1999; Egli et al., 2008; Mavris et al., 2010). The enrichment of Al or Fe in the initial formation of soil derived from basaltic lava is well recognised (Egli et al., 2008). Zarin and Johnson (1995) showed that when initial conditions are oligotrophic, both pools of nutrient salts and the base saturation index can increase on the surface of minerals. Although these studies are using fine-earth ($\leqq$ 2 mm) fraction, it is clear that accumulation of soil organic matters and formation of amorphous substance are fast advanced in initial soil formation. It is suggested that initial soil formation process has occurred inside pore of scoria particles in the gravel fraction.

In order to estimate the relative contribution of the gravel fraction to the whole soil, we sieved and weighed air-dried samples of the gravel (>2 mm) fraction, which comprised 53.6%, and of the fine-earth ($\leqq$ 2 mm) fraction, which comprised 46.4%. These values were then multiplied by the results from the chemical analyses of the same size fractions (Fig. 1). The gravel fraction contributed 21.3% of the T-C of the whole soil. Similarly, the Al_o, Fe_o and Si_o in the gravel fraction contributed 21.4%, 27.1% and 25.4%, respectively, of the whole soil. From these results, it was
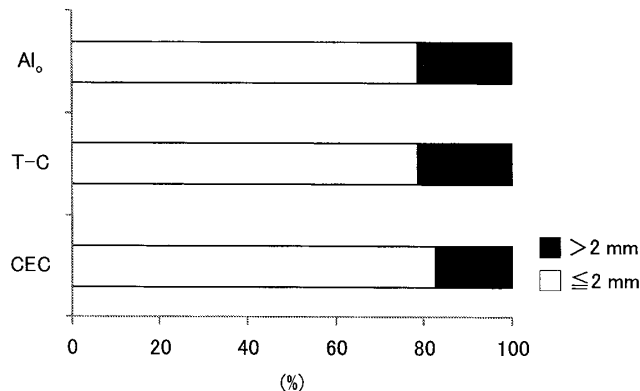

Fig. 1. Relative contributions (weighted) of Al_o, T-C and CEC as assayed from gravel (>2 mm) and fine-earth ($\leqq$ 2 mm) fractions.

inferred that the soil formation process, especially accumulation of an organic matter and mineral weathering, has taken place in gravel fraction as well as the fine-earth fraction. Moreover, CEC in the gravel fraction has contributed 17.4% of the CEC of the whole soil. The contributing rates of the gravel fraction of exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ to the whole soil were 18.0%, 16.7%, 21.1%, and 21.5%, respectively.

Thus in this young Haplic Regosol (125 years old and under humid warm-temperate climate) on scoria, the gravel fraction (>2 mm) contributes about 20% of the chemical properties of whole soil. Previously, it has often been assumed that there may be almost no contribution from the gravel fraction in such soils. Our analysis shows that it is important to evaluate the composition of the gravel fraction as well as the fine-earth ($\leqq$ 2 mm) fraction. We suggest that studies such as ours on scoria should be undertaken on soil developed on pumice and partially consolidated gravelly sediments because the gravel fractions in them may also contains significant quantities of organic matter and nanocrystlline minerals and exchangeable cations. Thus, an evaluation of the amount of carbon storage or nutrients in a young soil needs to be made by analyzing both fine-earth and gravel fractions.

Acknowledgments

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