Geoderma 327 (2018) 97–106

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Geochemical fractionation of chromium and nickel in serpentine soil profiles along a temperate to tropical climate gradient

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ARTICLE INFO

Keywords:
Bioavailability
Heavy metal
Sequential extraction
Soil geochemistry
Ultramafics

ABSTRACT

Serpentine soils contain high levels of geogenic Cr and Ni, which may pose potential risks to the environment due to the increase of bioavailability of the metals during soil weathering. This study determined the lability of Cr and Ni by sequential selective extraction (SSE) and illustrated its relationships to mineral composition and physicochemical properties of serpentine soils for eight pedons along a climate gradient including temperate, subtropical, and tropical regions in Austria, Japan, Taiwan, and Indonesia. Although the mineral origin of Cr was different from that of Ni, Cr significantly accompanied Ni in various climates. Geochemical Cr and Ni fractions (by SSE) followed the order: residual (F4) > Fe/Mn oxide (F2) > organic matter (F3) > acid soluble (F1). Soil properties associated with changes in climate/weathering state, including pH, organic carbon, exchangeable Ca/Mg, and dithionite-citrate-bicarbonate extractable Fe, correlated with all fractions of Cr and Ni. Individual and the sum of all labile pools (ΣF1–F3) of Ni were much higher than those of Cr in all pedons. Cr and Ni associated with Fe/Mn oxides (F2) was higher in the tropical soils than in the temperate soils, while Cr and Ni associated with organic matter (F3) was higher in the temperate soils than in the tropical soils along this gradient. Our results demonstrate that Cr and Ni are gradually transformed into labile pools in the soils as chemical weathering progresses from temperate to tropical climate.

1. Introduction

Serpentine soils are derived from ultramafic rocks or serpentinites and may show high geochemical background of Cr and Ni, which is of environmental concern (Proctor and Woodell, 1975; Oze et al., 2004; Kierczak et al., 2007, 2016; Cheng et al., 2011). Additionally, serpentine soils may have severe fertility limitations because of low contents of P and K, low Ca/Mg ratios as well as Cr and Ni enrichment (Reeves et al., 2007; McGahan et al., 2009; D'Amico and Previtali, 2012). These soils further exhibit a unique flora and unique physical properties (Alexander, 2014; Kanellopoulos et al., 2015). Serpentinites are metamorphic rocks formed by low temperature hydrothermal alteration of ultramafic rocks such as peridotites and pyroxenites (Guillot and Hattori, 2013). Serpentinites mainly consist of serpentine group minerals (antigorite, lizardite, and chrysotile) and chlorite, with lower amounts of chromite, talc, and brucite (Hseu et al., 2015). Chromite is the primary mineral origin of Cr (Garnier et al., 2009; Hseu and Iizuka, 2013), while Ni is substituted for Mg^{2+} in olivine and pyroxenes (Becquer et al., 2006). Nickel released by weathering of these primary minerals can substitute for Mg in clay minerals such as smectite and vermiculite during the early stages of serpentine soil development (Bonifacio et al., 2010; Raous et al., 2013). However, as chemical weathering progresses, these clay minerals destabilize (Hseu et al., 2015). Highly mobile elements such as Ca and Mg are preferentially leached whereas Cr and Ni remain in the profiles and accumulate along with Fe and Mn (Becquer et al., 2006; Cheng et al., 2011; Hseu and Iizuka, 2013; Hseu et al., 2015).

Serpentine rocks and soils cover only a small area of the Earth's terrestrial surface, but they are abundant in ophiolite belts and have been typically found in regions of the Circum-Pacific margin and Mediterranean Sea (Oze et al., 2004). The principles of geochemistry and weathering processes of serpentine soils have been generalized in previous studies, comparing Cr and Ni contents in different weathered horizons along soil profiles with the metal compositions of the parent rocks (Kierczak et al., 2007; Caillaud et al., 2009; Cheng et al., 2009; Kelepertzis et al., 2013). However, pedogenesis differs from location to

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https://doi.org/10.1016/j.geoderma.2018.04.030
Received 27 January 2018; Received in revised form 25 April 2018; Accepted 29 April 2018

Table 1
Geographic information and classification of the studied pedons.

Pedon	Location	Elevation	MAR[a]	MAT[b]	Slop position	Slope	Soil classification[c]
		m	mm	°C		%	
AT-1	N 48°37′28″, E 15°33′46″	360	700	8.0	Lower backslope	5	Lithic Udorthent
AT-2	N 47°24′38″, E 16°17′19″	620	760	8.0	Upper backslope	6	Typic Udorthent
JP-1	N 35°21′00″, E 134°38′17″	760	1680	14	Upper backslope	8	Typic Eutrudept
JP-2	N 35°21′37″, E 134°38′53″	450	1680	14	Lower backslope	4	Typic Eutrudept
TW-1	N 23°42′32″, E 121°24′40″	120	2100	23	Upper backslope	2	Lithic Udorthent
TW-2	N 23°03′04″, E 121°11′58″	380	2100	23	Lower backslope	8	Typic Hapludert
TW-3	N 22°47′32″, E 121°09′30″	300	2100	23	Footslope	10	Typic Hapludalf
IN-1	S1°51′02″, E116°02′46″	92	2260	27	Lower backslope	2	Typic Hapludult

[a] Mean annual rainfall.
[b] Mean annual temperature.
[c] Soil Taxonomy (Soil Survey Staff, 2014).

location due to the wide distribution and occurrence of serpentine soils in contrasting climatic zones as well as the different nature of the parent materials and other factors including topography, biota, and time of soil development (Proctor and Woodell, 1975; Chardot et al., 2007; Cheng et al., 2011; Vithanage et al., 2014). Contents of Cr and Ni vary widely in global serpentine soils. Chromium contents of up to 30 g kg^{-1} have been found in serpentine soils of New Caledonia (Amir and Pineau, 1998). Average Ni content in soils is approximately 16 mg kg^{-1} varying normally between 2 and 750 mg kg^{-1} (McGrath, 1995), but certain serpentine soils exhibit extremely high Ni contents exceeding 10,000 mg kg^{-1} (Oze et al., 2004; Rinklebe and Shaheen, 2017a, 2017b). The behavior of Cr and Ni merit increased study to determine their mineral origin and vertical distribution in serpentine soil profiles under different climates (Burt et al., 2001; Kierczak et al., 2007; Cheng et al., 2009). Gouch et al. (1989) explored the processes influencing Cr and Ni distribution in soil profiles in a serpentine landscape in California. According to their results, the surface horizons contained more Cr than the parent materials in highly-developed serpentine soils, and the highest contents of Ni occurred in B horizons. However, Cr and Ni contents did not show clear depth functions in profiles of serpentine soils sampled from a toposequence in Taiwan (Cheng et al., 2011).

Geogenic heavy metals in serpentine soils tend to be fixed by the mineral structures rather than the particle surfaces, but the release of Cr and Ni into ecosystems during mineral weathering suggests that serpentine soils are a source of non-anthropogenic metal contamination (Chardot et al., 2007; Ünver et al., 2013). The potential environmental risk of serpentine soils seems to involve an increase in the bioavailability of Cr and Ni (Kierczak et al., 2008; Cheng et al., 2011; Hseu and Iizuka, 2013; Kelepertzis and Stathopoulou, 2013). Serpentine soils have been studied in diverse climatic regions, but few studies have attempted to correlate their weathering state and geochemical properties with differences in regional climate. Slight weathering of ultramafic rocks under temperate or Mediterranean climate resulted in the moderate leaching of Mg and Si and formation of secondary Mg-rich or Fe-rich clay minerals, such as Ni- and Cr-bearing smectites, vermiculites and/or chromite–silicate mixtures (Bonifacio et al., 1997; Caillaud et al., 2009; Kierczak et al., 2007; Oze et al., 2004). In tropical soils, non-crystalline Fe oxides and goethite formed by weathering of clay minerals often accumulate and play a role as hosts for Ni and Cr sequestration (Becquer et al., 2006; Cheng et al., 2011; Hseu et al., 2015). In soils with ultramafic parent materials but different weathering degrees, the bioavailability, mobility, and potential toxicity of these two elements are largely dependent on their chemical binding forms (Cheng et al., 2011; Kierczak et al., 2008; Quantin et al., 2008; Rinklebe and Shaheen, 2017b; Shaheen et al., 2017). Serpentine soils offer good opportunities for the study of the mobility of Cr and Ni of geogenic origin (Kelepertzis and Stathopoulou, 2013; Kelepertzis et al., 2013; Vithanage et al., 2014; Hseu et al., 2017). Of special interest is the fractionation of Cr and Ni and its relationships to mineral composition and physicochemical properties of serpentine soils under different climates. This study evaluated the hypothesis that geogenic Cr and Ni would be re-distributed in distinct biogeochemical fractions in serpentine soils depending on their state of weathering. This hypothesis was tested by analyzing horizon samples of serpentine soil profiles from temperate to tropical regions including Austria, Japan, Taiwan, and Indonesia for soil properties indicative of weathering state as well as Cr and Ni fractionation. The aims were to: (1) investigate Cr and Ni contents in the serpentine soils from different climates, (2) evaluate the potential mobility of Cr and Ni by sequential extraction for the soils along the climate gradient, and (3) illustrate the relationship between the different metal fractions and soil properties.

2. Materials and methods

2.1. Study sites and soil collection

The serpentine soils under study were collected from a climate gradient from temperate to tropical regions including Austria, Japan, Taiwan, and Indonesia. The study sites were selected to reflect the development of soils on serpentinites under the different climates. As far as possible, the soil profiles examined (1) occupied stable portions of the landscape and (2) were developed on serpentinites unaffected by additions or mixing of materials with non-ultramafic lithologies. Table 1 gives site and geographic information for the 8 pedons selected for this study; these soils include Entisols, Inceptisols, Vertisols, Alfisols, and Ultisols according to U.S. soil taxonomy (Soil Survey Staff, 2014). Entisols and Inceptisols are incipient in their development, Vertisols and Alfisols are intermediate, and Ultisols represent highly weathered soils. The soil moisture regime was udic for all studied pedons. All pedons were located in montane landscapes with slopes from 2 to 10%. Pedons AT-1 and AT-2 were from eastern Austria, with low mean annual rainfall (< 800 mm) and low mean annual temperature (< 10 °C) and the dominant vegetation was *Picea abies* (L.). Pedons JP-1 and JP-2 were located in western Japan, where the mean annual temperature and rainfall are 14 °C and 1680 mm, respectively. The dominant vegetation was *Quercus serrata*. Pedons TW-1, TW-2, and TW-3 were located in eastern Taiwan, where climate is extremely humid with mean annual temperature of approximately 22.5 °C. The annual rainfall in eastern Taiwan ranges between 1800 and 2400 mm and is concentrated from May to September. Tropical broad-leaf evergreen forests are the dominant vegetation including *Acacia confusa*, *Calocedrus formosana* Florin, and *Trema orientalis*. Pedon IN-1 was in East Kalimantan, Indonesia, where mean annual temperature and rainfall are 27 °C and 2260 mm, respectively, and the vegetation was dominated by *Harpullia arborea*. Of all the study sites, IN-1 exhibits the highest air temperature and rainfall and is the only one from the Southern Hemisphere, but closest to the equator. The soil samples were taken according to genetic horizons, air-dried, gently crushed, and passed through a 2-mm sieve for subsequent laboratory analyses.