Perchlorate mobilization of metals in serpentine soils

Prasanna Kumarathilaka, Christopher Oze, Meththika Vithanage

PII: S0883-2927(16)30381-X

DOI: 10.1016/j.apgeochem.2016.10.009

Reference: AG 3730

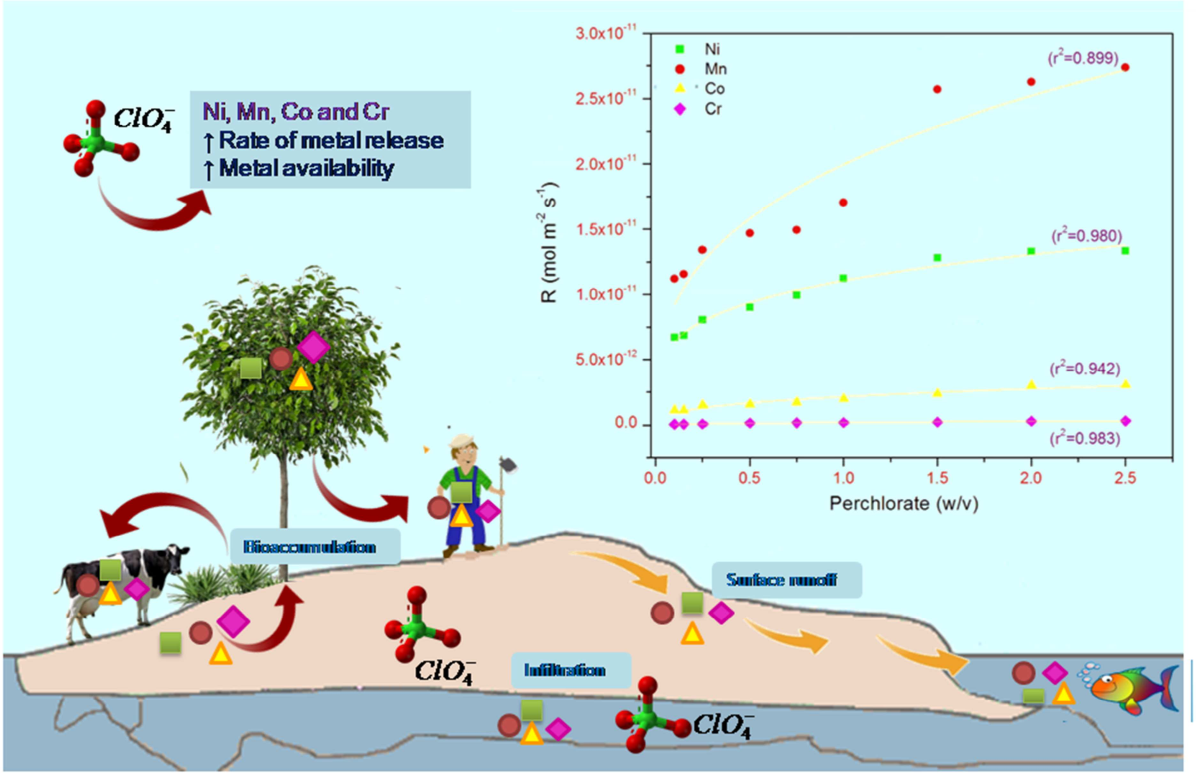
To appear in: *Applied Geochemistry*

Received Date: 2 July 2016

Revised Date: 7 October 2016

Accepted Date: 9 October 2016

Please cite this article as: Kumarathilaka, P., Oze, C., Vithanage, M., Perchlorate mobilization of metals in serpentine soils, *Applied Geochemistry* (2016), doi: 10.1016/j.apgeochem.2016.10.009.



ClO_4^-
Ni, Mn, Co and Cr
↑ Rate of metal release
↑ Metal availability
Bioaccumulation
Surface runoff
Infiltration
ClO_4^-
ClO_4^-
3.0x10^{-11}
2.5x10^{-11}
2.0x10^{-11}
1.5x10^{-11}
1.0x10^{-11}
5.0x10^{-12}
0.0
R (mol m^{-2} s^{-1})
Ni
Mn
Co
Cr
(r^2=0.899)
(r^2=0.980)
(r^2=0.942)
(r^2=0.983)
0.0
0.5
1.0
1.5
2.0
2.5
Perchlorate (w/v)

Perchlorate mobilization of metals in serpentine soils

Prasanna Kumarathilaka[a], Christopher Oze[b], Meththika Vithanage[a,]*

[a]*Chemical and Environmental Systems Modeling Research Group, National Institute of Fundamental Studies, Kandy, Sri Lanka*

[b]*Geology Department, Occidental College, 1600 Campus Rd., Los Angeles, CA 90041, USA*

*Corresponding Author

Tele: +94 812 232 002

Fax: +94 812 232 131

Email: meththikavithanage@gmail.com

ABSTRACT

Natural processes and anthropogenic activities may result in the formation and/or introduction of perchlorate (ClO_4^-) at elevated levels into the environment. Perchlorate in soil environments on Earth and potentially in Mars may modify the dynamics of metal release and their mobilization. Serpentine soils, known for their elevated metal concentrations, provide an opportunity to assess the extent that perchlorate may enhance metal release and availability in natural soil and regolith systems. Here, we assess the release rates and extractability of Ni, Mn, Co and Cr in processed Sri Lankan serpentine soils using a range of perchlorate concentrations (0.10-2.50 w/v ClO_4^-) via kinetic and incubation experiments. Kinetic experiments revealed an increase of Ni, Mn, Co and Cr dissolution rates (1.33×10^{-11}, 2.74×10^{-11}, 3.05×10^{-12} and 5.35×10^{-13} mol m^{-2} s^{-1}, respectively) with increasing perchlorate concentrations. Similarly, sequential and single extractions demonstrated that Ni, Mn, Co and Cr increased with increasing perchlorate concentrations compared to the control soil (i.e., considering all extractions: 1.3 - 6.2 (Ni), 1.2 - 126 (Mn), 1.4 - 34.6 (Co) and 1.2 - 6.4 (Cr) times greater than the control in all soils). Despite the oxidizing capability of perchlorate and the accelerated release of Cr, the dominant oxidation state of Cr in solution was Cr(III), potentially due to low pH (<2) and Cr(VI) instability. This implies that environmental remediation of perchlorate enriched sites must not only treat the direct hazard of perchlorate, but also the potential indirect hazard of related metal contamination.

Keywords: Perchlorate; heavy metals; serpentine soils; dissolution rate; bioavailability

1. Introduction

Perchlorate (ClO_4^-) is a strong oxidizer and an environmental contaminate in soils and related waters (Duncan et al., 2005; Motzer, 2001). Both natural processes and anthropogenic activities may result in the formation and release of perchlorate where it has been detected from trace to micro levels in soils and water in the United States, Chile, Canada, China, South Korea and India (Calderón et al., 2014; Gan et al., 2014; Kannan et al., 2009; Kim et al., 2014; Rao et al., 2007; Wang et al., 2009). Despite a variety of natural pathways related to the formation and accumulation of perchlorate, anthropogenic activities (i.e., fireworks, explosives, stick matches, highway safety flares and military operations) appear to be the major source(s) of perchlorate contamination in the environment (Backus et al., 2005; Gan et al., 2014; Wilkin et al., 2007). Numerous studies have focused on the direct contamination issues of perchlorate (Her et al., 2011; Ye et al., 2013); however, a potential indirect hazard of perchlorate in soils and rocks is the accelerated and enhanced leaching of heavy metals. In Senanayake et al. (2011), the increased dissolution of Ni and Co in the presence of perchloric acid in laterite was examined demonstrating 90 and 98% leaching, respectively, within 6 hr contact time. However, the extent perchlorate can accelerate metal release or modify metal availability in soils have not been systematically addressed.

Soils derived from ultramafic material such as peridotite and serpentinite are termed as serpentine soils and characteristically have elevated Mg concentrations. Additionally, serpentine soils are known for their elevated metal concentrations including Ni, Cr, Mn and Co (Rajapaksha et al., 2012; Vithanage et al., 2014) and these soils provide an opportunity to assess the dynamics of potential metal-perchlorate interactions. Despite the rarity of serpentine soils on Earth, these soils and their related ultramafic sources (i.e., rocks and soil) are common in highly populated and industrialized areas of the Circum-Pacific Margin, Mediterranean, North America, Europe and Australian continents. Additionally, ultramafic rocks and related regolith are common on Mars where perchlorate has been identified at elevated concentrations (~ 1 wt %) (Davila et al., 2013; Kounaves et al., 2014). Here, the aim is to obtain a basic understanding of the reaction kinetics of Ni, Mn, Co and Cr release from serpentine soils utilizing a range of perchlorate concentrations, initially introduced as perchloric acid prior to perchlorate salt formation, based on those identified on Earth and Mars (Catling et al., 2010b; Kounaves et al., 2014). Results garnered here will provide much needed insight if serpentine soil-perchlorate interactions should occur. Finally, this study attempts to elucidate on one of the many environmental problems faced with perchlorate in the environment and its potential impact on soil fertility.

2. Material and methods

2.1. Serpentine soil collection and preparation

Serpentine soil, obtained from Ussangoda (UD) (latitude 6° 05' 54" N and longitude 80° 59' 11" E) and Yudhaganawa (YD) (latitude 7° 71' 67" N and longitude 80° 93' 33" E), Sri Lanka, was used for this study. These soils are direct weathering products of ultramafic rock and were collected from 0-15 cm below from the surface. Soil samples were air-dried and mechanically sieved to <2 mm fraction. Total Ni, Mn, Co and Cr concentrations in the serpentine soils shown in Table 1 were determined by triple acid digestion (HNO_3, HCl and HF) and subsequent analysis by atomic absorption spectrometry and were reported (Vithanage et al., 2014). Specific surface areas of the serpentine soils were determined by using methylene blue test (Yukselen and Kaya, 2008).

2.2 Metal release rates with perchlorate

Perchlorate concentrations of 0.10, 0.15, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00 and 2.50 w/v (0.01, 0.015, 0.025, 0.05, 0.075, 0.1, 0.15, 0.2, 0.25 M, respectively) were used to evaluate

Ni, Mn, Co and Cr removal from the processed serpentine soil. This concentration range was selected based on perchlorate concentrations present on Earth (i.e., Atacama (Catling et al., 2010a)) as well as on the Martian regolith and studies suggested that perchlorate initially deposits as perchloric acid (Davila et al., 2013; Kounaves et al., 2014). Serpentine soil (50 g/L) was placed in polypropylene tubes and 25 ml of perchloric acid (AR, BDH, 70%) was added with different concentrations. These tubes were equilibrated for 11 days at room temperature (~ 25 °C) and agitated at 75 rpm (EYELA B603 shaker). The supernatant was transferred by membrane filtration (0.45 µm) after centrifugation. The filtered solutions were analyzed for Ni, Mn, Co and Cr using flame method of the Atomic Absorption Spectrometry (AAS-Model GBC 933 AA). Each treatment was performed in triplicate. The concentration Cr(VI) was determined by following 1,5-diphenylcarbazide method and the absorbance was measured using a UV-Visible spectrophotometer (UV-160A) at λ 540 nm. The final calibration standard solutions of Cr(VI) ranged from 0.05 to 1 mg/L, providing a linear relationship with a correlation coefficient (R^2 of 0.998).

Nickel, Mn, Co and Cr release rates were studied with respect to perchloric acid concentration and pH to determine the extent of both proton and ligand promoted metal release. Analyses based on the perchloric acid concentration were assessed using Eq. 1 below (Hamer et al., 2003; Rajapaksha et al., 2012).

$$R_T = k_T a_{acid}^{n_T} \tag{1}$$

Here, R_T is the rate of dissolution, k_T is the empirical rate constant for total Ni, Mn, Co and Cr released due to perchlorate, n_T corresponded to experimentally determined factor, and a_{acid} is the concentration of the perchloric acid for that particular experiment. Additionally, the pH dependency of the total Ni, Mn, Co and Cr release rates was evaluated using the following equation (Eq. 2) (Hamer et al., 2003).

$$\log R_T = \log k_T - n_T \, pH \qquad (2)$$

Using Eq. 3, the sum of the rates of hydrogen ion (R_H) and ligand promoted (R_L) dissolution provides the total rate of mineral dissolution (R_T) (Stillings et al., 1996; Welch and Ullman, 1996). Serpentine soils consist of a variety of minerals, therefore, total dissolution or metal release may not be from one particular mineral. Hence, the relationship in Eq. 3, below, is valid whether examining mineral dissolution rates or metal release rates (Rajapaksha et al., 2012).

$$R_T = R_H + R_L \qquad (3)$$

The effect of ligand (R_L) promoted dissolution can be calculated by subtracting hydrogen promoted dissolution (R_H) from total metal release rate (R_T). The enhancement factor (R_T/R_H) allows the comparison of hydrogen ion and ligand promoted dissolution in acids. Typically, low enhancement factors demonstrate hydrogen ion promoted dissolution, whereas, high enhancement factors indicate ligand promoted dissolution (Hamer et al., 2003; Zhang and Bloom, 1999).

2.3. Metal complexation with perchlorate incubation experiments

Soil incubation experiments were performed to evaluate how the addition of different perchlorate concentrations affected the Ni, Mn, Co and Cr complexation and its bioavailability in soil. Three different concentrations (0.50, 0.75 and 1.00 w/w) of perchlorate and a control (i.e., no perchlorate) were used for the treatments. The corresponding samples are referred as US1, US0.75, US0.5 and USC for Ussangoda serpentine soil and YD1, YD0.75, YD0.5 and YDC for Yudhaganawa serpentine soil, respectively. Serpentine soil (100 g) was placed in polypropylene bottles and perchloric acid was added with three different concentrations mentioned above. In addition, water was added to ~70% of water holding capacity of the soil and then allowed for the incubation in airtight condition at room temperature (~ 25 °C) for period of three weeks. Hence, moisture levels were not maintained during the incubation, after the initial addition of water to ~70% of the soil's water holding capacity. Each treatment was performed in triplicate. After three weeks, sequential and single extractions were carried out to evaluate solid phase metal fractionation in serpentine soils. Prior to the sequential and single extractions, serpentine soil was air dried.

Sequential extraction experiments were carried out using the method described by Tessier et al. (1979). A mass of 1 g of air dried serpentine soil was used for the initial extraction. The sample extracted at each steps was centrifuged at 3,500 rpm for 15 min. The supernatant was filtered using 0.45 µm filter paper prior to AAS analysis.

Single extractions were performed on each incubation experiment. Extractable metals in the soil were quantified by the diethylene triamine pentaacetic acid (DTPA) soil test developed by Lindsay and Norvell (1978). Additionally, 0.01 M $CaCl_2$ extraction was performed to assess extractable fraction of heavy metals (Houba et al., 2000). As previously mentioned, the soil solution was centrifuged and filtered through membrane filtration (0.45 µm) prior to AAS analysis.

3. Results

The release of serpentine soil metals in water provides a baseline to assess metal release rates, prior to perchlorate additions. Metal release rates using distilled water were relatively low in Yudhaganawa (Ni - 1.51×10^{-13} mol m^{-2} s^{-1}; Mn - 1.77×10^{-12} mol m^{-2} s^{-1}; Co - 6.85×10^{-13} mol m^{-2} s^{-1}; Cr - 0) and Ussangoda (Ni – 2.31×10^{-13} mol m^{-2} s^{-1}; Mn - 1.68×10^{-13} mol m^{-2} s^{-}

^{1}; Co – 1.37×10^{-14} mol m^{-2} s^{-1}; Cr - 0) serpentine soils. However, rates of Ni, Mn, Co and Cr dissolution increase with addition of perchlorate (Fig. 1). Yudhaganawa serpentine soils yielded higher dissolution rates for Ni (1.33×10^{-11} mol m^{-2} s^{-1}), Mn (2.74×10^{-11} mol m^{-2} s^{-1}) and Co (3.05×10^{-12} mol m^{-2} s^{-1}) compared to the Ussangoda serpentine soils (Ni: 5.12 ×10^{-12} mol m^{-2} s^{-1}, Mn: 5.14×10^{-12} mol m^{-2} s^{-1} and Co: 5.91×10^{-13} mol m^{-2} s^{-1}) in 2.5 w/v perchlorate. Comparing metal release rates, Ni and Mn are preferentially released compared to Co and Cr in both Ussangoda and Yudhaganawa serpentine soil. In the Ussangoda serpentine soil, the Cr dissolution rate was 5.35×10^{-13} mol m^{-2} s^{-1}; however, low Cr dissolution rate was observed in Yudhaganawa serpentine soil (3.39×10^{-13} mol m^{-2} s^{-1}) compared to the Ussangoda serpentine soil in 2.5 w/v perchlorate. Additionally, Cr(VI) was only present at and below trace concentrations (1.44×10^{-15} mol m^{-2} s^{-1} - 2.81×10^{-14} mol m^{-2} s^{-1}) potentially demonstrating that Cr is dominantly present as Cr(III) in solution.

Figure 2 shows the relationship of perchlorate-based pHs and release rates of Ni, Mn, Co and Cr. pH dependencies demonstrate a linear relationship allowing rate constants (k_T) and reaction orders (n_T) for Ni, Mn, Co and Cr release to be obtained (Table 2). We used hydrochloric acid at the same concentration with respect to the perchlorate for estimating the ligand promoted dissolution (Fig. 3a and 3b). Further, R_T (Eq. 3) in hydrochloric acid was assumed to be equal to R_H allowing for the calculation of ligand promoted rate. In this sense, ligand promoted dissolution becomes zero with the presence of hydrochloric acid. Similarly, Rajapaksha et al. (2012) assessed the metal release rate in the serpentine soils using three inorganic and organic acids and assumed $\mathrm{R_T}$ in hydrochloric acid to be equal to $\mathrm{R_H}$ in all acids investigated. The low enhancement factors (<1.15) observed during the experiments revealed that hydrogen ion promoted dissolution dominated the release of Ni, Mn, Co and Cr in both serpentine soils.

Sequential and single extractions provide a proxy for how metals are bound into different fractions of soil and what amount may be available for living organisms as an exchangeable fraction with the presence of perchlorate. Metal fractionation based on sequential extractions for the both serpentine soil locations are presented in Fig. 4. The highest Ni and Cr concentrations in serpentine soils was found to be in the residual fraction, whereas, Mn and Co were dominantly bound in the Fe-Mn oxide phase. Nevertheless, metals in the exchangeable fraction were higher compared to the control soil with addition of perchlorate for both serpentine soils (Fig. 4). Additionally, these metals at different perchlorate concentrations in all soils ranged between 1.8 - 2.5 (Ni), 1.3 - 37.5 (Mn), 1.4 - 5.1 (Co) and 1.6 - 6.4 (Cr) times their respective control, demonstrating that the bioavailability of Ni, Mn, Co and Cr may increase possibly due to the proton component of perchloric acid.

DTPA and $CaCl_2$ single extractions on the incubation experiments provide a representation for evaluating plant bioavailability of metals in soils and solutions (Kashem et al., 2007; Peijnenburg et al., 2007). Both DTPA and $CaCl_2$ extractions demonstrated that release and bioavailability of Ni, Mn, Co and Cr were increased with increasing perchlorate concentrations. Fig. 5a shows that the DTPA extractable fraction of Ni, Mn, Co and Cr ranged between 1.3 - 1.9 (Ni), 1.2 - 10.4 (Mn), 1.6 - 29.7 (Co) and 1.2 - 1.7 (Cr) times greater than the control in all soils. Similarly, Fig. 5b shows that the $CaCl_2$ extraction of Ni, Mn, Co and Cr increased with the presence of perchlorate at 2.9 - 6.2 (Ni), 20 - 126 (Mn), 2.6 - 34.6 (Co) and 1.6 - 2.4 (Cr) times greater than the control.

4. Discussion

Despite high metal concentrations (Table 1), metal release rates are constrained to particular low solubility minerals. Simply, high metal concentrations in serpentine soils do not necessarily mean that there will be high metal release rates. Although the magnitude of metal release is important to characterize, how metal release rates change with increasing perchlorate concentrations provides a more relevant proxy to assess the potential mobility of metals in these systems. In our experiments, metal release rates for Ni, Mn, Co and Cr increased with increasing perchlorate concentrations, thus, demonstrating the proton promoted dissolution of soil/regolith systems. However, it seems that the rate of dissolution change at lower perchlorate concentrations is higher than that of the rate change at higher perchlorate concentrations in particular for Ni and Mn. The enhanced release was dominantly related to proton promoted dissolution where ligand effects were minimal. According to the electron probe microanalysis (EPMA), heavy metals such as Ni, Mn and Cr were not homogeneously distributed in bulk serpentine soil samples, suggesting that those are bound in particular mineral phases (Vithanage et al., 2014). For instance, antigorite is the dominant mineral in the Ussangoda serpentine soil and it possesses a relatively low surface area in comparison with clays or organic matter capable of leading to less release of heavy metals (Vithanage et al., 2014). Overall, perchlorate in acidic soils appears to moderate and/or accelerate metal release and potentially its availability.

Sequential and single extractions of the incubation experiments all demonstrated that perchlorate greatly enhanced the abundance of available metals present in the soil system as well as the metals available for plant uptake. In sequential extractions, the pattern of individual exchangeable metal concentrations was thus Mn > Ni > Co > Cr and hence, Mn showed the highest bioavailability in 1 w/w perchlorate addition. In terms of metal bound fractionations, Fe and Mn oxides bound concentrations, which have the highest concentrations of Mn and Co, showed reduced concentrations with increasing perchlorate concentrations, suggesting that the Fe and Mn oxide bound fractions may have increased the exchangeable fractions’ concentration compared to other fractions. The residual fraction retained the highest concentration of Ni and only slightly varied. Concentrations of Fe and

Mn in the oxide bound fractions were reduced with increasing perchlorate concentrations, potentially increasing the exchangeable fraction of Ni. Additionally, DTPA and $CaCl_2$ single extractions revealed that Mn and Ni are available at higher concentrations compared to the Co and Cr in terms of individual concentrations. Overall, compared to the control soils, the bioavailability of Ni, Mn, Co and Cr appears to have been greatly influenced by proton promoted dissolution of serpentine soils.

Chromium geochemistry related to these experiments provides a means to assess the involvement and potentially oxidative capability of perchlorate. Chromium was present at elevated concentrations (10,707 (Ussangoda) and 14,880 (Yudhaganwa) mg kg^{-1}; Table 1) in both serpentine soils where chromium was dominantly present in the residual fraction (more than likely in spinels such as chromite) as Cr(III). Despite the total Cr concentrations, Cr release rates were the lowest of all the metals analyzed in both serpentine soils. In all the metal release experiments, all aqueous Cr was present as Cr(III) with no Cr(VI) detected. One potential reason for the lack of Cr(VI) may be related to the low pH values which is more conducive to Cr(III) stability (see the Cr Eh-pH stability diagram in (Oze et al. (2004)) in which these experiments were conducted. In essence low pH (<2) soils with perchlorate appear to limit the potential oxidation of Cr(III). Bringing the pH of soil/regolith up to more neutral conditions may result in the production of Cr(VI) if perchlorate is present.

Permissible levels of Ni, Mn and Cr in drinking water are set as low as 20, 400 and 50 µg L^{-1}, respectively (WHO, 2004). The permissible limit of Co is not specified yet by the World Health Organization (WHO) for drinking water. Based on the average metal release rates, metals released in solution from these soils will exceed drinking water standards for Ni, Mn and Cr in less than 1 hr. Other non-serpentine soils and sediments may have less total metal concentrations; however, metals in these soils may be present in less labile phases and potentially capable of releasing metals at faster rates. Regardless, the presence of perchorate accelerates metal release where even low perchlorate concentrations will influence release rates.

Soil-plant systems may be detrimentally affected by increased Ni, Mn, Co and Cr. Although, many metals including Ni, Mn and Co are essential for plant health and development, they are toxic at elevated concentrations. For instance, higher level of Ni in soil can exert direct toxicity in plant tissues and consequently, can indirectly exert toxicity due to induced nutrient deficiencies such as Fe (Aziz et al., 2015). The production of dark specks on leaves and dying at leaf margins are possible symptoms due to the excess Mn uptake (Alves et al., 2011). It seems logical that higher levels of Cr in plants may result in morphological and physiological alterations of plants possibly due to overproduction of reactive oxygen species (Gill et al., 2015). Plants can accumulate trace amount of Co; however, excess metal uptake causes dysfunction of plants (Caillaud et al., 2009). It was well established that antioxidant enzymes (i.e., superoxide dismutase, catalase and ascorbate peroxidase) may play a vital role in the defensive mechanism of plants against heavy metals. However, the antioxidant capacity of plants is not enough to control toxic effect of heavy metal under severe stress conditions (Adrees et al., 2015). In this respect, heavy metal uptake by plants and subsequent introduction into the food chain can cause a potential risk to animals as well as human health. Additionally, heavy metals at higher concentrations may become toxic for soil microflora.

5. Conclusions

The addition of perchlorate, whether from natural or anthropogenic sources, to soils and regolith may modify the rate of metal release and its availability for plant uptake. When remediating perchlorate contaminated soils and regolith, attention needs to be paid to the metals released and/or modified by the remediation process. If this is not taken into account, 'perchlorate-remediated' soils may still remain infertile and/or be capable of producing vegetation unfit for human consumption.

Implications of high perchlorate concentrations (~ 1 wt%) in Martian regolith and its conversion crop cultivation is of significant concern with regard to the future human habitation of Mars. Martian perchlorate has been posited to be produced from photochemical reactions in the upper atmosphere via hydrochloric acid from volcanic eruptions and/or through gas-phase reactions (i.e., chloride bearing aerosols reaction with O_3 or H_2O_2). Perchlorate is subsequently deposited as perchloric acid on the surface with suspended dust. However, the high solubility of perchlorate in water may concentrate it in patches in Martian regolith. When utilizing Martian regolith as a growing medium, it will not only be a matter of removing the perchlorate, but also about addressing metal release and availability. Increased metal accessibility, as shown in our experiments, may result in plant infertility.

References

Adrees, M., Ali, S., Iqbal, M., Aslam, B.S., Siddiqi, Z., Farid, M., Ali, Q., Saeed, R. and Rizwan, M. (2015). Mannitol alleviates chromium toxicity in wheat plants in relation to growth, yield, stimulation of anti-oxidative enzymes, oxidative stress and Cr uptake in sand and soil media. *Ecotox. Environ. Safe.* 122, 1-8.

Alves, S., Trancoso, M.A., Goncalves, M.D.L.S. and Santos, M.M.C.D. (2011). A nickel availability study in serpentinised areas of Portugal. *Geoderma* 164, 155-163.

Aziz, R.A., Rahim, S.A., Sahid, I. and Idris, W.M.R. (2015). Speciation and availability of heavy metals on serpentinized paddy soil and paddy tissue. *Procedia Soc. Behav. Sci.* 195, 1658-1665.

Backus, S.M., Klawuun, P., Brown, S., D'sa, I., Sharp, S., Surette, C. and Williams, D.J. (2005). Determination of perchlorate in selected surface waters in the Great Lakes basin by HPLC/MS/MS. *Chemosphere* 61, 834-843.

Caillaud, J., Proust, D., Philippe, S., Fontaine, C. and Fialin, M. (2009). Trace metals distribution from a serpentinite weathering at the scales of the weathering profile and its related weathering microsystems and clay minerals. *Geoderma* 149, 199-208.

Calderón, R., Palma, P., Parker, D., Molina, M., Godoy, F. and Escudey, M. (2014). Perchlorate levels in soil and waters from the Atacama Desert. *Arch Environ Contam Toxicol* 66, 155-161.

Catling, D., Claire, M., Zahnle, K., Quinn, R., Clark, B., Hecht, M. and Kounaves, S. (2010a). Atmospheric origins of perchlorate on Mars and in the Atacama. *J. Geophys. Res-Planet.* 115.

Catling, D., Claire, M., Zahnle, K., Quinn, R., Clark, B., Hecht, M. and Kounaves, S. (2010b). Atmospheric origins of perchlorate on Mars and in the Atacama. *Journal of Geophysical Research: Planets* 115.

Davila, A.F., Willson, D., Coates, J.D. and McKay, C.P. (2013). Perchlorate on Mars: a chemical hazard and a resource for humans. *Int. J. Astrobiology* 12, 321-325.

Duncan, P.B., Morrison, R.D. and Vavricka, E. (2005). Forensic identification of anthropogenic and naturally occurring sources of perchlorate. *Environ. Forensics* 6, 205-215.

Gan, Z., Sun, H., Wang, R. and Deng, Y. (2014). Occurrence and exposure evaluation of perchlorate in outdoor dust and soil in mainland China. *Sci. Total Environ.* 470–471, 99-106.

Gill, R.A., Zang, L., Ali, B., Farooq, M.A., Cui, P., Yang, S., Ali, S. and Zhou, W. (2015). Chromium-induced physio-chemical and ultrastructural changes in four cultivars of *Brassica napus* L. *Chemosphere* 120, 154-164.

Hamer, M., Graham, R.C., Amrhein, C. and Bozhilov, K.N. (2003). Dissolution of ripidolite (Mg, Fe-Chlorite) in organic and inorganic acid solutions. *Soil Sci. Soc. Am. J.* 67, 654-661.

Her, N., Jeong, H., Kim, J. and Yoon, Y. (2011). Occurrence of perchlorate in drinking water and seawater in South Korea. *Arch. Environ. Contam. Toxicol.* 61, 166-172.

Houba, V., Temminghoff, E., Gaikhorst, G. and Van Vark, W. (2000). Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Commun. Soil Sci. Plan.* 31, 1299-1396.

Kannan, K., Praamsma, M.L., Oldi, J.F., Kunisue, T. and Sinha, R.K. (2009). Occurrence of perchlorate in drinking water, groundwater, surface water and human saliva from India. *Chemosphere* 76, 22-26.

Kashem, M., Singh, B., Kondo, T., Huq, S.I. and Kawai, S. (2007). Comparison of extractability of Cd, Cu, Pb and Zn with sequential extraction in contaminated and non-contaminated soils. *Int. J. Environ. Sci. Te.* 4, 169-176.

Kim, D.-H., Yoon, Y., Baek, K., Han, J. and Her, N. (2014). Occurrence of perchlorate in rice from different areas in the Republic of Korea. *Environ. Sci. Pollut. Res.* 21, 1251-1257.

Kounaves, S.P., Carrier, B.L., O'Neil, G.D., Stroble, S.T. and Claire, M.W. (2014). Evidence of martian perchlorate, chlorate, and nitrate in Mars meteorite EETA79001: implications for oxidants and organics. *Icarus* 229, 206-213.

Lindsay, W.L. and Norvell, W.A. (1978). Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42, 421-428.

Motzer, W.E. (2001). Perchlorate: problems, detection, and solutions. *Environ. Forensics* 2, 301-311.

Oze, C., Fendorf, S., Bird, D.K. and Coleman, R.G. (2004). Chromium geochemistry of serpentine soils. *Int. Geol. Rev.* 46, 97-126.

Peijnenburg, W.J., Zablotskaja, M. and Vijver, M.G. (2007). Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. *Ecotox. Environ. Safe.* 67, 163-179.

Rajapaksha, A.U., Vithanage, M., Oze, C., Bandara, W. and Weerasooriya, R. (2012). Nickel and manganese release in serpentine soil from the Ussangoda ultramafic complex, Sri Lanka. *Geoderma* 189, 1-9.

Rao, B., Anderson, T.A., Orris, G.J., Rainwater, K.A., Rajagopalan, S., Sandvig, R.M., Scanlon, B.R., Stonestrom, D.A., Walvoord, M.A. and Jackson, W.A. (2007). Widespread natural perchlorate in unsaturated zones of the southwest United States. *Environmental Science & Technology* 41, 4522-4528.

Senanayake, G., Childs, J., Akerstrom, B.D. and Pugaev, D. (2011). Reductive acid leaching of laterite and metal oxides - a review with new data for Fe(Ni,Co)OOH and a limonitic ore. *Hydrometallurgy* 110, 13-32.

Stillings, L.L., Drever, J.I., Brantley, S.L., Sun, Y. and Oxburgh, R. (1996). Rates of feldspar dissolution at pH 3–7 with 0–8 m M oxalic acid. *Chem. Geol.* 132, 79-89.

Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51, 844-851.

Vithanage, M., Rajapaksha, A., Oze, C., Rajakaruna, N. and Dissanayake, C.B. (2014). Metal release from serpentine soils in Sri Lanka. *Environ. Monit. Assess.* 186, 3415-3429.

Wang, Z., Forsyth, D., Lau, B.P.Y., Pelletier, L., Bronson, R. and Gaertner, D. (2009). Estimated dietary exposure of Canadians to perchlorate through the consumption of fruits and vegetables available in Ottawa markets. *J. Agr. Food Chem.* 57, 9250-9255.

Welch, S. and Ullman, W. (1996). Feldspar dissolution in acidic and organic solutions: compositional and pH dependence of dissolution rate. *Geochimica et Cosmochimica Acta* 60, 2939-2948.

WHO (2004). *Guidelines for drinking-water quality*. World Health Organization, Geneva.

Wilkin, R.T., Fine, D.D. and Burnett, N.G. (2007). Perchlorate behavior in a municipal lake following fireworks displays. *Environ. Sci. Technol.* 41, 3966-3971.

Ye, L., You, H., Yao, J., Kang, X. and Tang, L. (2013). Seasonal variation and factors influencing perchlorate in water, snow, soil and corns in Northeastern China. *Chemosphere* 90, 2493-2498.

Yukselen, Y. and Kaya, A. (2008). Suitability of the methylene blue test for surface area, cation exchange capacity and swell potential determination of clayey soils. *Engineering Geology* 102, 38-45.

Zhang, H. and Bloom, P.R. (1999). Dissolution kinetics of hornblende in organic acid solutions. *Soil Sci. Soc. Am. J.* 63, 815-822.

Tables

Table 1

Total metal concentrations (mg kg^{-1}) in Ussangoda and Yudhaganawa soils.

Table 2

Rate constants (k_T), reaction orders (n_T), total rate of dissolution (R_T) and ligand promoted dissolution (R_L) with the presence of perchlorate.

Figure Legends

Fig. 1. Metal releasing rate for Ni, Mn, Co and Cr in Ussangoda (a) and Yudhaganawa (b) serpentine soil with the presence of different perchlorate concentrations.

Fig. 2. Metal releasing rate (in log R) for Ni, Mn, Co and Cr in Ussangoda (a) and Yudhaganawa (b) serpentine soil with the presence of different pH in perchlorate.

Fig. 3. Metal releasing rate (in log R) for Ni, Mn, Co and Cr in Ussangoda (a) and Yudhaganawa (b) serpentine soil with the presence of different pH in hydrochloric acid.

Fig. 4. Effect of perchlorate on different phases of heavy metals: (a) Ni, (b) Mn, (c) Co and (c) Cr.

Fig. 5. Bioavailability of heavy metals with the presence of different perchlorate concentrations: (a) DTPA extraction, and (b) $CaCl_2$ extraction.

Tables

Table 1

Total metal concentrations (mg kg^{-1}) in Ussangoda and Yudhaganawa soils.

Location	Metal concentrations (mg kg^{-1})				Specific surface area (m^2 g^{-1})
	Ni	Mn	Cr	Co	
Ussangoda	6,776	1,117	10,707	157	70.99
Yudhaganawa	6,567	2,609	14,880	555	67.32

Table 2

Rate constants (k_T), reaction orders (n_T), total rate of dissolution (R_T) and ligand promoted dissolution (R_L) with the presence of perchlorate.

Location	**Metal**	**Log k_T**	**n_T**	**R_T**	**R_L**	**R_T/R_H**
				mol m^{-2} s^{-1} × 10^{-12}		
Ussangoda	Ni	-11.23	-0.10	4.39	0.01	1.00
	Mn	-11.26	-0.08	4.35	0.00	1.00
	Co	-12.20	-0.10	0.46	0.15	0.99
	Cr	-11.53	-1.08	0.16	0.15	0.68
Yudhaganawa	Ni	-10.73	-0.23	9.46	1.20	1.15
	Mn	-10.41	-0.29	16.12	0.07	1.05
	Co	-11.36	-0.31	1.73	0.03	1.02
	Cr	-12.22	-0.44	0.16	0.03	0.61

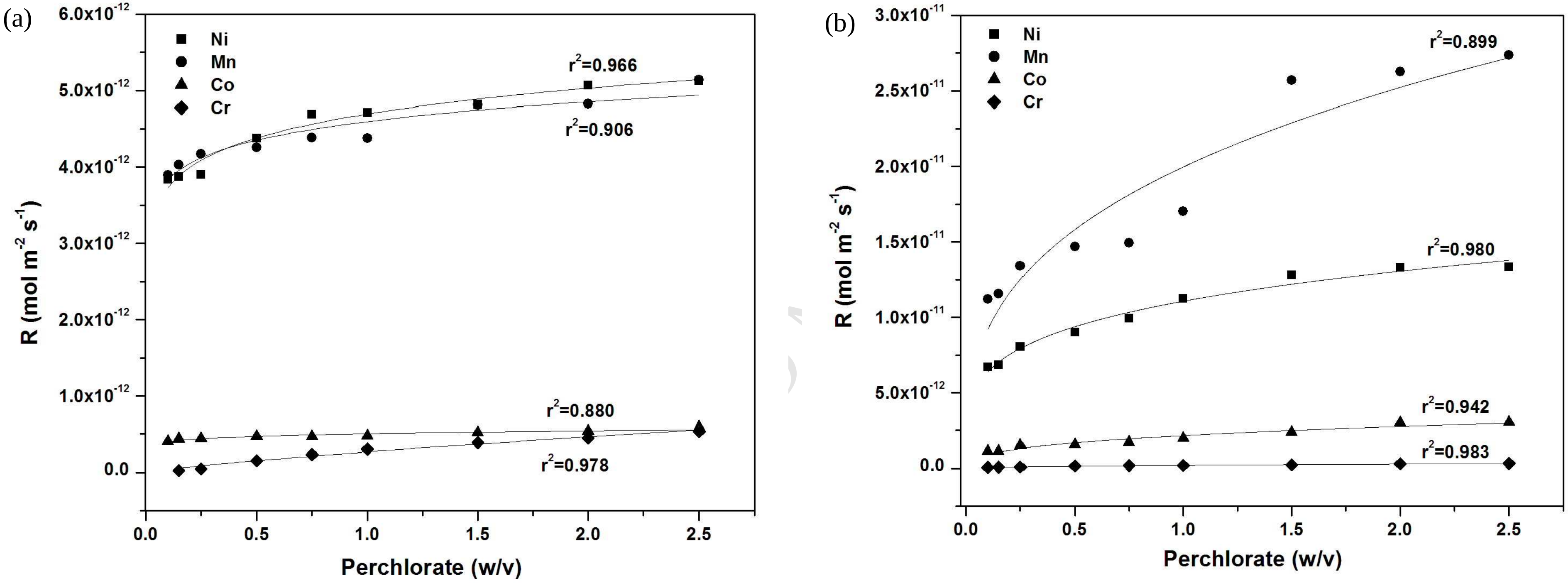


Fig. 1. Metal release rates for Ni, Mn, Co and Cr in Ussangoda (a) and Yudhaganawa (b) serpentine soil with a variety of perchlorate concentrations.

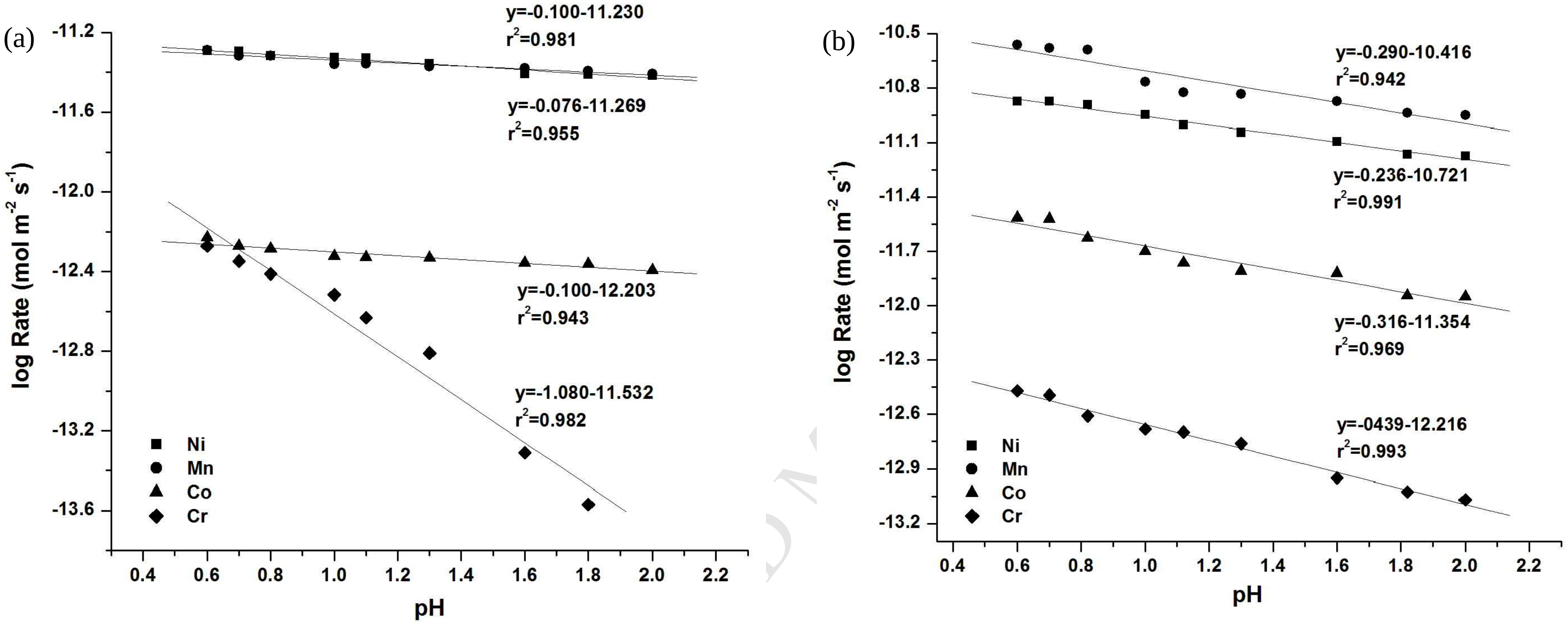


Fig. 2. Metal releasing rate (in log R) for Ni, Mn, Co and Cr in Ussangoda (a) and Yudhaganawa (b) serpentine soil with the presence of different pH in perchlorate.

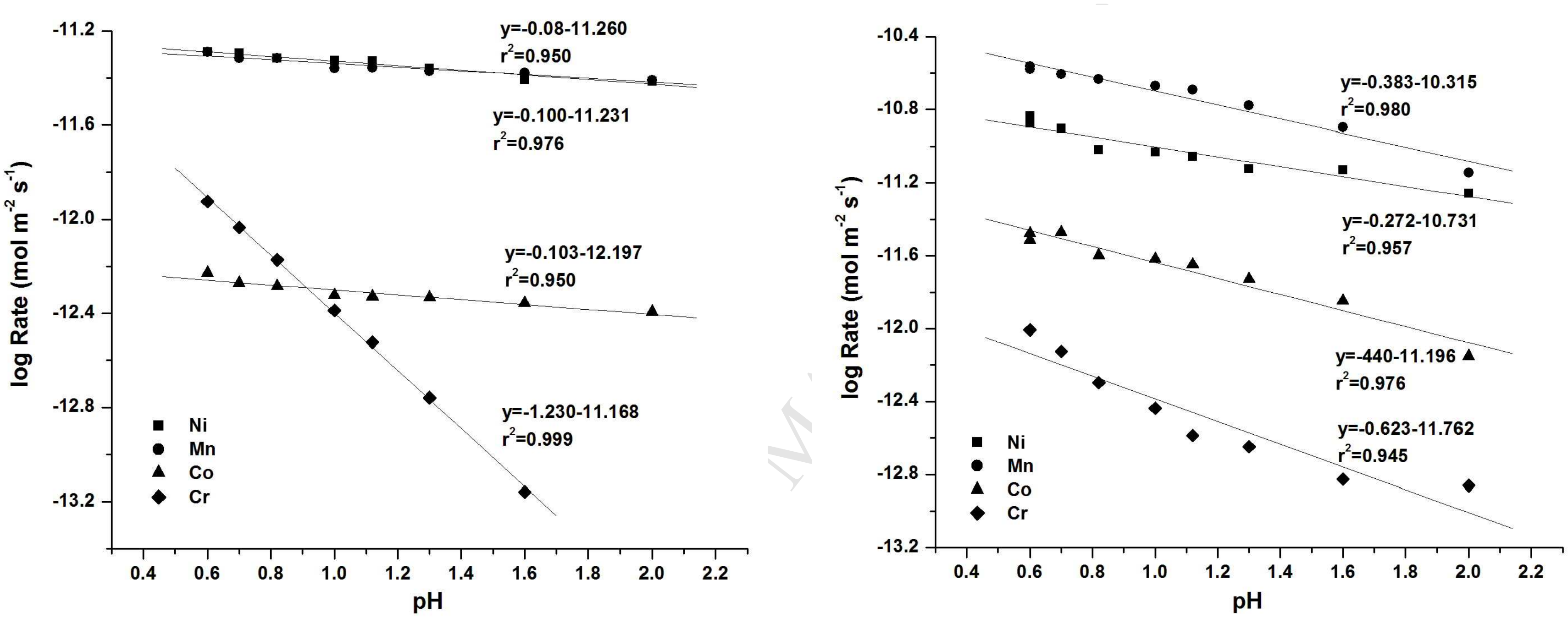


Fig. 3. Metal release rate (in log R) for Ni, Mn, Co and Cr in Ussangoda (a) and Yudhaganawa (b) serpentine soil with the presence of different pH in hydrochloric acid.

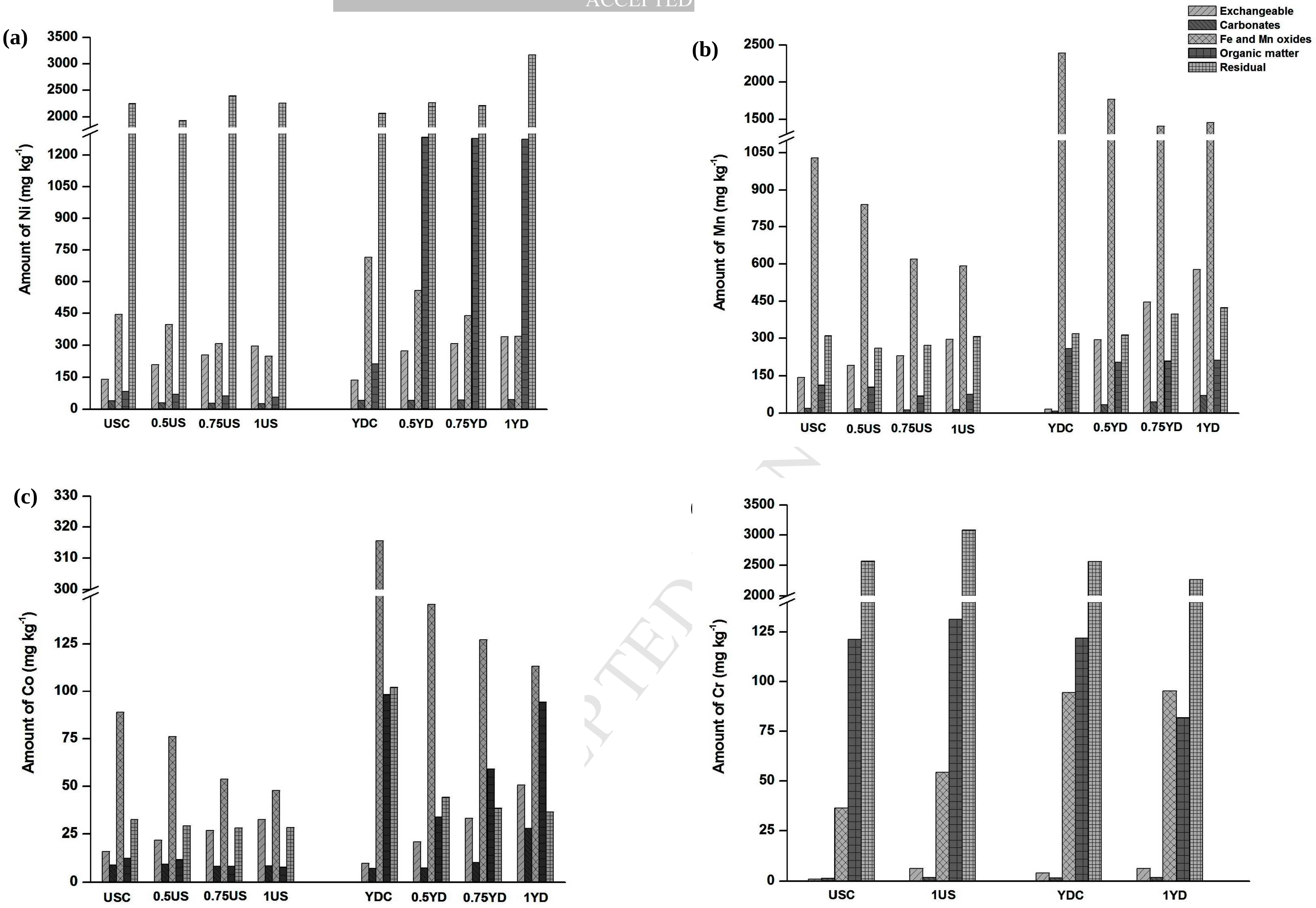


Fig. 4. Effect of perchlorate on different phases of heavy metals: (a) Ni, (b) Mn, (c) Co and (d) Cr.

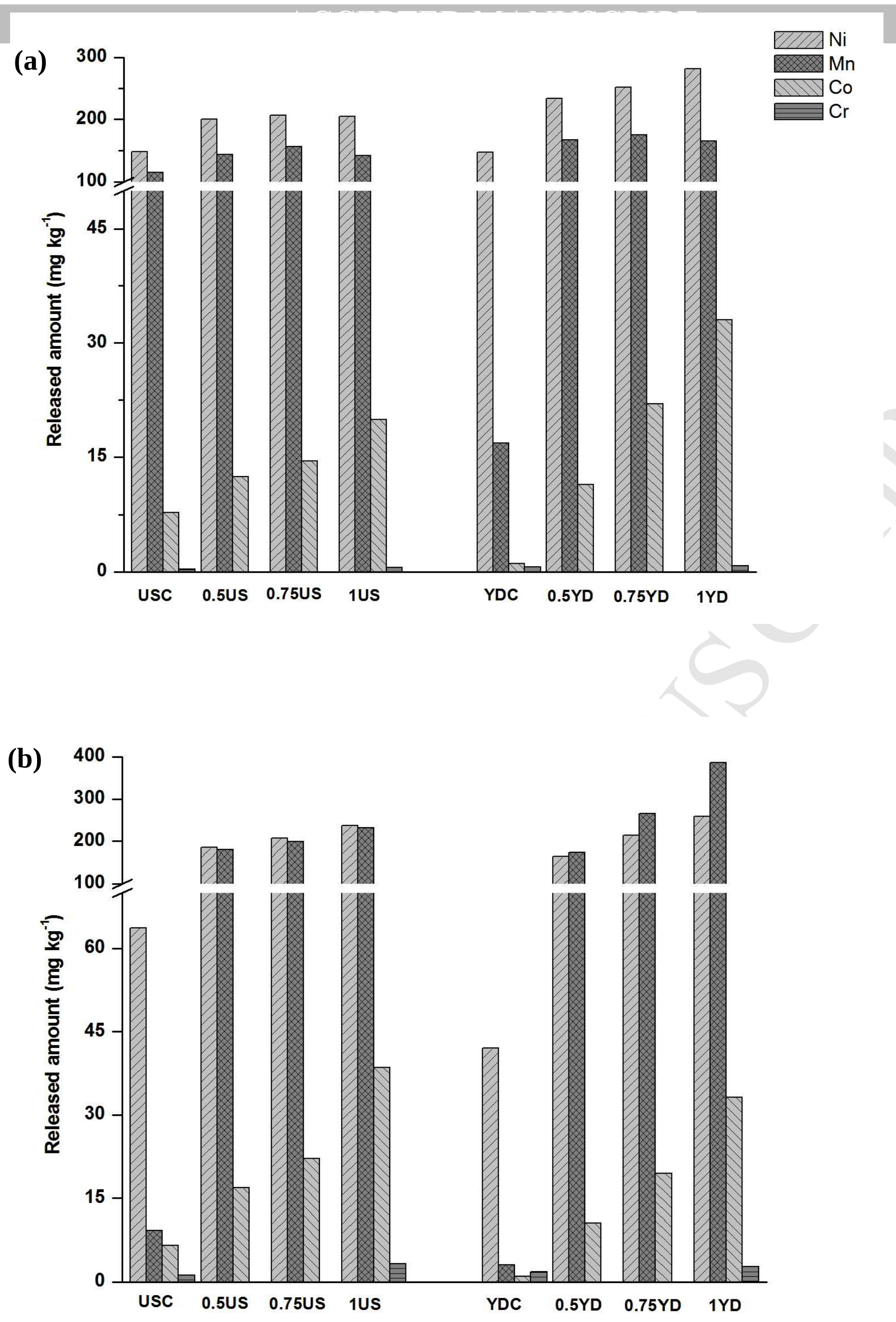


Fig. 5. Bioavailability of heavy metals with the presence of different perchlorate concentrations: (a) DTPA extraction, and (b) $CaCl_2$ extraction.

HIGHLIGHTS

- Perchlorate vs serpentine soil interactions were assessed
- Total dissolution rates of Ni, Mn, Co and Cr increased with perchlorate addition
- Exchangeable and extractable fractions of heavy metals increased by perchlorate
- Formation of Cr(VI) was trivial due to its instability and low pH