The role of pedogenic processes and soil characteristics on nickel distribution in some Oxicaquic Paleudalfs

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Abstract

Soil properties and pedogenic processes can significantly affect heavy metals accumulation and distribution in soils. In order to study the effective factors on nickel distribution, seven soil profiles containing Fe-Mn concentrations with Oxicaquic Paleudalfs classification were investigated. Nitric acid extractable iron (Fe$\text{t}$), manganese (Mn$\text{t}$), free iron oxides (Fe$\text{o}$), amorphous iron (Fe$\text{a}$) and some soil properties (OC, CEC, Clay, and pH) were measured and their correlations with nitric acid extractable Nickel (Ni$\text{t}$) were investigated. In addition, Fe and Mn concentrations and their adjacent soils were separated and then Fe$\text{t}$, Mn$\text{t}$, Ni$\text{t}$, Fe$\text{a}$ and Fe$\text{o}$ were measured in them. Mineralogical study showed that vermiculite, smectite, mica and kaolinite were dominant clay minerals in the studied soils. Lepidocrocite, goethite, ferrihydrite and birnessite were the minerals existed in the Fe-Mn concentrations. The results showed that Ni$\text{t}$ had a significant and positive correlation with Fe$\text{d}$ and clay as well as significantly and negatively correlated with OC, Mn$\text{t}$ and Fe$\text{o}$. The mean accumulation coefficient (K) of Ni in the Fe-Mn concentrations was 1.5, indicating the ability and role of pedogenic microzones in Ni accumulation. With regard to the results, the co-migration of clay and crystalline iron oxides (Lessivage) and Fe-Mn concentrations genesis can be considered as two main processes in the Ni distribution in the studied soil profiles.

Keywords: Fe-Mn concentrations, free iron oxides, soil profile

Abbreviations: CDB: citrate dithionate bicarbonate; CEC: Cation exchange capacity; DTPA: diethylenetriamine penta-acetic acid; EC: Electrical conductivity; OC: organic carbon; PSD: Particle-size distribution.

Introduction

The entrance of heavy metals to the ecosystem, including water, soil and air has become a serious problem that threatens the healthy life of organisms. Soil plays an important role in the heavy metals cycle in ecosystem. Soil is a complicated bio-physico-chemical environment and one of the basic components of ecosystem, which appear to be separated, but it is similar to a ring of chain related to environmental processes (Alloway, 1995).

Ni is the 24th most abundant metal in the earth crust and the 5th most plentiful element by weight after iron, oxygen, magnesium and silicon, which can naturally enter soil by bedrock, volcanic emission or artificially by fertilizers, industrial waste, etc. (Massoura et al., 2006). Several factors, such as pH by affecting carbonates, oxides and hydroxide solubility, complexes formation, changing the surface charges and OC solubility can be effective on the heavy metals distribution (e.g. Ni) (Rooney et al., 2006; Appel and Ma., 2001). Iyaka (2011) stated that nickel adsorption intensity with increasing pH. Organic matters, clay content, carbonates, and iron and manganese oxides can be effective on the heavy metal distribution by influencing the soil adsorption characteristics, participating in specific and nonspecific adsorption, co-precipitation processes and isomorphic substitutions. Furthermore, the quantity and quality of these factors can be changed by pedogenic processes, such as leaching, lessivage, carbonation, oxidation and reduction, etc. (Alloway, 1995). Kabaka-Pendas and Pendas (2001) stated that Ni content in soil fairly depends on parent material, but its distribution is the reflection of pedogenic processes.
Organic matters with high cation exchange capacity (CEC) are able to adsorb large amounts of heavy metals (Adriano, 2001). Organic matters have a reciprocal role on the solubility of heavy metals. Organic components with high molecular weight form the metal - organic matter complexes, leading to the less mobility of elements such as Cu, Pb, Ni, Zn, etc. (Sparks et al., 1997; Karapanagiotis et al., 1991). In contrast, Temmingho et al. (1998) found that humic acids increased the mobility of heavy metals in soils.

Oxidation and reduction processes in solutions are controlled by the activity of free electrons (Sposito, 1983). Some elements, for example Mn and Fe have different valences and many heavy metals such as Cu, Co, Cr, and Ni are associated with their oxides. Singh and Gilkes (1992) found that hematite and goethite adsorbed the highest amount of nickel among inorganic adsorbents. Vodyanitskii et al. (2002) and Vodyanitskii (2006) reported that Ni could substitute in goethite and lithiophorite structures. During reduction conditions, iron and manganese have more solubility that leads to the release of metals such as Ni (Liu et al., 2002). Mellis et al. (2004) studied Oxisols and Alfisols and reported that organic matters and iron oxides had the highest involvement in the Ni adsorption. Mury et al. (2004) stated that high clay content horizons generally have more ability than low clay content ones for heavy metals accumulation and adsorption. Gomes et al. (2001) also reported the same results.

Fe-Mn concentrations, which are important in both soil genesis and environment, appear in different shapes in soil such as nodules, concretions, mass, etc. These concentrations are indicators of imperfect soil drainage and also their characteristics reflect weathering soil conditions (Wiederhold et al., 2007). The formation of Fe - Mn concentrations as pedogenic agents has an important effect on the distribution of heavy metals in soils affected by redox conditions. Palumbo et al. (2001) reported higher amounts of Zn, Cu and Ni in Fe-Mn nodules compared to soil matrix. Cornu et al. (2005) achieved similar results about lead, zinc, nickel and cobalt. Teemofeeva and Golov (2007) reported a high amount of Ni in Fe-Mn nodules and stated that the Ni accumulation in these concentrations decreases its mobility in soil profile.

Overall, there are not sufficient researches on pedogenic processes affecting the heavy metals distribution and extensive studies are needed. Moreover, comprehensive understanding of factors influencing the behavior and distribution of heavy metals are essential for maintaining the environmental quality.

The purpose of this study was to investigate the effects of pedogenic processes on the distribution of nickel in some soil profiles of Alfisols affected by redox conditions.

Materials and Methods

The studied area is located in Noshahr in the north of Iran (36°27’ to 36°40’northern latitudes and 51°32’ to 51°43’ eastern longitudes). Mean annual precipitation in this region is above 1000 mm. Soil moisture and temperature regimes, calculated according to the Newhall Simulation Model (Newhall and Berdanier, 1996), were udic, mesic and thermic. After investigating the geological and topography maps, the location of 7 soil profiles affected by redox conditions, containing Fe - Mn concentrations determined as well as description and sampling were performed according to the field book for describing and sampling soils (USDA-NRCS, 2002). Then, they were classified according to the Soil Taxonomy (Soil Survey Staff, 2010). Bedrock was limestone in the studied area. All analyses were performed on air-dried soil samples passed through a 2 mm sieve (Pansu and Gautheryrou, 2006). pHsp was determined using a pH meter applied to the soil saturated to a paste using deionised water. Electrical conductivity (ECsp) was measured in the saturated extracts. Particle-size distribution (PSD) was measured by hydrometer method. Organic carbon (OC) was determined using wet oxidation (Pansu and Gautheryrou, 2006). Cation exchange capacity (CEC) was determined by ammonium acetate method (pH=7) (Carter and Gregorich, 2008). diethylenetriamine penta-acetic acid (DTPA) was used for the extraction of soluble and exchangeable forms of Ni (Lindsay and Norvell, 1978), citrate dithionate bicarbonate (CDB) for the measurement of free iron oxides (Feo) (Mehra and Jackson, 1960), ammonium oxalate in the dark for the measurement of amorphous iron oxides (Feo) (McKeage and Day, 1966) and nitric acid 4 N for the measurement of total iron (Feo), manganese (Mno) and nickel (Nio) (Richards et al, 1998).

Fe-Mn concentrations separated from the adjacent soils and Feo, Mno, Nio, Feo, and Feo were measured in them.

The contents of extracted elements determined by atomic adsorption spectrophotometer (Shimadzu, 670-AA). Accumulation coefficients (K) were calculated for the extracted elements according to the equation 1:

\[ K = \frac{C_n}{C_s} \]  

Where Cn and Cs are the contents of elements in the Fe - Mn concentrations and the soil (without Fe-Mn concentrations), respectively. Pretreatments for clay mineralogical analysis were carried out according to Kunze and Dixon ( 1989). Iron and manganese (oxy)hydroxides were distinguished using random oriented powder method (Moore and Reynolds., 1989). Minerals were determined by X-ray diffraction using a
Siemens D5000 diffractometer via CuK (\(\lambda=1.5409\) A\(^\circ\)) and 30 kV voltage and 30 mA. Statistical analysis was performed by SPSS.18 software.

**Results and Dissections**

PH range changed from neutral to slightly alkaline in the studied soils. Lime in the soil was intensively leached and its amount was very small. The amount of OC decreased with increasing the depth and varied between 4.45% in the A horizon of profile 7, and 0.17% in the Bt3 and Btg horizons of profiles 5 and 7. Clay increased in the subsoil horizons, which resulted in the increase of CEC in them. The range of Mn\(_t\) was from 562 to 2386 mg/Kg. The highest Fe\(_o\) was 1.08% in the A horizon of profile 7.

The range of variations of Fe\(_d\) was between 1% in the A horizon of profile 1 and 3.5% in the Btg horizon of profile 7. The amount of FET was in the range 2.35 to 5.07%. The Ni\(_t\) content changed from 25 mg/Kg in the A horizon of profile 7 to 63.9 mg/Kg in the Btg2 horizon of profile 4. The content of Ni rose with increasing the depth and accumulated in the horizons with high clay content (Table 1). DTPA-extractable Ni was low and could not be measured by atomic absorption spectrophotometer.

Ni\(_t\) positively and significantly correlated with pH, clay, CEC, Fe\(_o\), Mn\(_t\) at 1% level, while there was a negative correlation between Ni\(_t\) with OC, Fe\(_o\) and Mn\(_t\). Fe\(_o\) and Mn\(_t\) showed a positive and significant correlation with OC at 1% level. Fe\(_o\), Fe\(_d\), and Mn\(_t\) correlated positively and significantly with pH, CEC and clay at 1% level (Table 2).

Fe-Mn concentrations were in the form of nodules and concretions and showed a clear boundary with soil matrix (Table 3). The maximum Fe\(_o\) in the redoxomorphic concentrations of Fe and Mn and soil matrix was 54.3 and 41.4 g/Kg, respectively and the mean accumulation coefficient (K) was 1.19. Mn\(_t\) in the concentrations and the soil varied between 3.5 to 4.5 g/Kg and 0.15 to 0.45 g/Kg, respectively and the mean accumulation coefficient was 12.3. Fe\(_o\) was between 6 to 11 and 2.4 to 3.5 g/Kg in the concentrations and the soil matrix, respectively and the mean accumulation coefficient was 19.2. The Fe\(_o)/Fe\(_d\) ratio varied between 0.08 to 0.27 and 0.19 to 0.38 in the soil and in the concentrations, respectively (Table 4).

The clay minerals of studied soils were mainly consists of vermiculite, smectite, mica, and kaolinite. Predominant iron minerals in the Fe-Mn concentrations were lepidocrocite, goethite and ferrihydrite. The existence of birnessite as a manganese mineral in them is probable (Figure 2).

Figure1. Fe-Mn concentrations sample (Btg horizon of profile 3)
Table 1. Some physical and chemical properties of studied soil samples

<table>
<thead>
<tr>
<th>Fe_{d} / clay (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Fe_{d}^{*} Ni</th>
<th>Fe_{d}^{*} Ni</th>
<th>Mn_{d}^{*} Ni</th>
<th>CEC Ni</th>
<th>OC Ni</th>
<th>pH clay</th>
<th>texture</th>
<th>depth (cm)</th>
<th>horizon</th>
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<td>Profile 1: Very fine, mixed, active, mesic, Oxiaquic Paleudalfs</td>
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<tr>
<td>A</td>
<td>0.7</td>
<td>0.5</td>
<td>0.1</td>
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<tr>
<td>B</td>
<td>0.7</td>
<td>0.5</td>
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Table 2. Correlation between Ni and some physico-chemical soil properties.
Correlation is significant at the 0.01 and 0.05 level, respectively

**Table 3. Morphological properties of Fe and Mn concentrations**

<table>
<thead>
<tr>
<th>Profile</th>
<th>horizon</th>
<th>color</th>
<th>contrast</th>
<th>boundary</th>
<th>shape</th>
<th>size</th>
<th>quantity</th>
<th>Kind</th>
</tr>
</thead>
<tbody>
<tr>
<td>Btg1</td>
<td>black</td>
<td>Prominent</td>
<td>Sharp</td>
<td>Spherical and irregular</td>
<td>Coarse and very Coarse</td>
<td>Common</td>
<td>Nodules and Concretions</td>
<td></td>
</tr>
<tr>
<td>Btg2</td>
<td>black</td>
<td>Prominent</td>
<td>Sharp</td>
<td>Spherical and irregular</td>
<td>Coarse and very Coarse</td>
<td>Common</td>
<td>Nodules and Concretions</td>
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</table>

**Table 4. Comparison of iron, manganese and nickel content between soil and Fe-Mn concentrations**

<table>
<thead>
<tr>
<th>Profile</th>
<th>Horizon</th>
<th>Ni&lt;sub&gt;t&lt;/sub&gt;</th>
<th>Fe&lt;sub&gt;d&lt;/sub&gt;/Fe&lt;sub&gt;t&lt;/sub&gt;</th>
<th>Fe&lt;sub&gt;o&lt;/sub&gt;</th>
<th>Fe&lt;sub&gt;d&lt;/sub&gt;</th>
<th>Mn&lt;sub&gt;t&lt;/sub&gt;</th>
<th>Ni&lt;sub&gt;t&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>soil</td>
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<td>mg/kg</td>
<td>g/kg</td>
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<tr>
<td>Btg1</td>
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<tr>
<td>soil</td>
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<td>mean</td>
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</table>
Since the studied area was intact, it seems the main source of nickel was bedrock. The lack of pedogenic lime in the field and chemical studies as well as clay transportation evidence indicated that pedogenic processes were developed.

Fe\textsubscript{d} includes iron associated with organic matters, amorphous iron and crystalline iron. Crystalline iron increased with increasing the depth in most profiles (Table 1), which caused higher amounts of Fe\textsubscript{d} in subsoil horizons compared with the surface horizons. Fielder and Sumer (2004) also confirmed these results. The clay / Fe\textsubscript{d} ratio showed a nearly consistent trend in the soil profiles (Table 1), which represented the co-migration of iron and clay to the subsoil horizons. The correlation between Fe\textsubscript{d} and clay also confirmed these results (Table 2). The same trend between Fe\textsubscript{d} and clay shows a mechanical transportation of small mineral particles from A to B horizons in the profile, which is called Lessivage (Jao et al., 1974). The positive and significant correlation between Fe\textsubscript{d}, clay and CEC indicated that the clay minerals and crystalline forms of iron were main factors affecting CEC (Table 2). The positive correlation between CEC, pH, Fe\textsubscript{d} and Fe\textsubscript{t} (Table 2) indicated the probable presence of some pH dependent charges in these samples. The significant and negative correlations between Mn\textsubscript{t}, pH, clay content and CEC (Table 2) showed that there was no association between manganese oxides and clay transportation.

The positive correlation between Mn\textsubscript{t} and OC, as well as its increase in the subsoil horizons containing high clay content with the reduction conditions (Table 1), which prevent Mn mineral crystallization and lead to the higher Mn movement, showed the presence of manganese in the forms linked with organic matters and amorphous forms. McKenzie (1988) stated that manganese is mainly present in the forms of amorphous and complexed with organic matters in soils. Fe\textsubscript{o} was higher in the surface horizons than the subsoil horizons (Table 1), which was due to more suitable conditions for weathering of primary and clay minerals as well as the presence of organic matters that prevented the crystallization of iron in the surface horizons (Schwertmann and Taylor, 1989). Fe\textsubscript{o} including iron associated with organic matters and amorphous iron, proved the Fe\textsubscript{o} correlation with organic carbon. Notwithstanding decreasing OC in the subsoil horizons, the increase of Fe\textsubscript{o} was seen in some profiles (Table 1) that could be attributed to the existence of reduction conditions in the subsoil horizons. Cornell and Schwertmann (2003) stated that reduction conditions lead to the instability of crystalline forms of iron and an increase in the amorphous iron forms. According to the results, there was a positive correlation between Ni\textsubscript{t} and pH. Bergkvist (1987) also reported that the relation between Ni and pH was positive, but it was not linear. Alloway (1995) stated that Ni solubility decreases with increasing pH. pH in studied soils in the range of neutral to alkaline (Table 1) could lead to a decrease in the solubility of Ni and an increase the adsorption characteristic of soil such as CEC. On the other hand, it could lead to the lower solubility of iron and manganese oxides that resulted in the fixation of Ni by these components. Hernandez et al. (2003) reported a positive relationship between Ni, CEC and pH. Furthermore, small amounts of DTPA extractable Ni could be related to soil alkaline pH. The positive correlation between Ni\textsubscript{t}, Fe\textsubscript{t} and Fe\textsubscript{d} resulted in the accumulation of this element in the horizons with high clay content and iron minerals. Hseu (2006) reported that the highest amount of Ni associated with silicate minerals and iron oxides. Hseu et al. (2007) stated that during the initial stages of weathering, Ni exits from the structure of primary mineral and substitutes in the structure of clay minerals. Garnier et al. (2009) stated that when elements, such as Si, Ca and Mg are leached, elements like Ni remain in the soil profile and precipitate with iron oxides. The positive correlation between Ni\textsubscript{t}, crystalline iron forms and clay minerals as well as the negative correlation between Ni and amorphous forms indicated the presence of Ni in the crystalline forms. Regarding the evidence about co-migration of crystalline iron oxides and clays (lessivage), the effect of this process in the distribution of Ni was highly possible. The mean accumulation coefficient of Ni (Table 3) in the Fe-Mn concentrations also showed the influence of these pedogenic concentrations in the distribution of nickel in the soil profiles. The existence of Fe-Mn concentrations reflected the redox conditions originated from high clay content in the subsoil horizons and also the presence...
of effective microflora in the iron and manganese cycles (Teemofeeva and Golov, 2010). Iron and manganese oxides exist in the Fe-Mn concentrations in neutral to alkaline pH have a high capacity for specific and nonspecific adsorption of elements such as Ni (Liu et al., 2002).

Lepidocrocite is widespread in the Fe-Mn concentrations. Alloway (1995) stated that lepidocrocite is an evidence for the frequency of reduct conditions. On the other hand, geothite is the dominant mineral in the oxide conditions (atmospheric conditions) (Vempati and Lopert, 1988). The presence of these two minerals in the concentrations represented a combination of oxidation and reduction conditions in the genesis of these microzones. Alternative oxidation and reduction conditions lead to the creation of alternate layers of iron and manganese. Gasparatos et al. (2005) stated that because of the difference between iron and manganese redox potentials, the Fe-Mn concentrations have a layered structure, which shows an alternate formation of these concentrations. This formation mechanism can trap heavy metals such as Ni and isolate them from the soil environment. Smaller accumulation coefficient (K) of Fe compared to Fe in the Fe-Mn concentrations increased the Fe/Fe ratio in them in comparison to the soil matrix. Higher amounts of Fe in the concentrations showed the existence of more amorphous structures and organic compounds (Huang et al., 2008). Amorphous structures have a high specific surface area providing the opportunity for the substitution of heavy metals in these structures.

In conclusion, the relationship between crystalline iron, clays, and Ni as well as the influence of co-migration of iron oxides and clays on Ni and Ni accumulation in the redoxomorphic Fe-Mn concentrations were the most important factors in the Ni distribution in the studied soil profiles. These results indicated the importance of pedogenic processes in the heavy metals distribution. In other words, considering soil and pedogenic processes is necessary and vital to maintain soil quality and consequently environment sustainability.

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