Solid Phases Formation and Solution Chemistry of Nickel in Some Soils at Abou-Rawash Area, Egypt

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Nickel contaminated soils from various origins were sampled and analyzed for total Ni, DTPA-extractable Ni, mobility pattern in soil profile, speciation in soil solutions, predicted Ni activities, and to identify the possible solid phases which control Ni solubility in the tested soils.

The results showed that the highest total-Ni values were seen in samples originating from sewage sludge effluent (x̄=24.76 ppm), followed in decreasing order by well water-irrigated soil (x̄=1.21 ppm) and Nile water-irrigated soil (x̄=0.85 ppm). Also, the lowest value of bioavailable Ni was recorded in sewage effluent-treated soil. This may be because the sludge can low metal solubility via complexing by soluble ligands or colloidal surface. The distribution patterns of Ni along the tested soil profiles showed a significant downwards movement to 30-60 cm in sewage effluent-treated soil, followed by decreasing pattern. Meanwhile, in the other soils, the distribution pattern was uniformity. The predicted Ni²⁺ concentrations in the tested soils were 4.07*10⁻⁶ M, 1.44*10⁻⁶ M, and 4.43*10⁻⁷ M in sewage effluent-treated soil, Nile water irrigated soil, and well water-irrigated soil, respectively. Speciation of Ni in the tested soil showed that the free portion (Ni²⁺) was the predominant species in Nile water-irrigated soil (98% of Niₗ) followed by sewage effluent-treated soil (88% of Niₗ) and ground water-irrigated (34% of Niₗ). Ni also complexes with sulfate ions, in ground water irrigated soil, NiSO₄(AQ) accounts (63.8% of Niₗ), while this form constitutes about (9.1% of Niₗ), in sewage effluent-treated soil. NiCl⁺ species also constitutes about (2.2% of Niₗ), meanwhile it accounted (ca. 1.5% of Niₗ) in the other soils. The predicted Ni²⁺ activities suggested that Ni₂SiO₄ in equilibrium with soil-SiO₂ and Ni₃(PO₄)₂ in equilibrium
with strengite-soil Fe are two possible minerals that control the activities of Ni in the tested soils.

**Keywords:** Egypt, Ni, Speciation, Mobility, Activity, Identification of Ni minerals.

That terrestrial ecosystems continue to accept an increasing pollution load is a patent truth (Aboulroos et al., 1989; FAO, 1992; Zenbin and Shuman, 1997 and McBride, 1998). In order to assess the environmental impact of heavy metals in soils, it is important to study the chemistry of these pollutants in soils. Speciation of heavy metals in soil solution is considered a prerequisite in understanding the interactions and interpreting the observed mobility of these metals (Bripa, 1997; Sauve et al., 1997; El-Gendi, 1998 and Jensen et al., 1999). Moreover, the quantity of metal absorbed by plant or remaining in soil solution is governed by soil-solid phases of these metals in soil. In the recent years, interest is focused on whether one or another of possible solid phase, the pollutant can form is likely under given soil conditions (Emmerich et al., 1982; Sadiq and Enfield, 1984; El-Falaky et al., 1991 and Aboulroos et al., 1996). They also added that the positive identification of soil-solid phases, along with knowledge of their solubility and kinetics of dissolution and precipitation, would provide sufficient information to make reliable predictions about these metals.

The objective of this study is to understand the chemistry of Ni (concentrations, bioavailability, mobility along soil profile, activities, and to identify the soil-solid phases which control the solubility of this metal) in some soils at Abou-Rawash area, Egypt.

**Material and Methods**

**Soils**

The soil samples in this study were collected from Abou-Rawash area, Giza, Egypt. Six soil profiles were dug to the depth of 160 cm as the following; two profiles representing area irrigated with Nile water; two profiles representing area irrigated with well water; and two representing soil irrigated continuously with sewage effluent for period up to 20 years. Each soil profile was sampled at...
20 cm increments to the depth of 160 cm. Six sub-samples were taken from each soil increment and transported to the laboratory and prepared for the relevant analysis.

Methods

General properties
Selected soil properties, pH, total carbonates, organic carbon and clay content were determined for all tested soil samples according to procedure outlined by Black (1965).

Total Ni content
Total content of Ni was determined by acid digestion using a mixture of HClO₄ and HF (5:1 v/v) as described by Tessier et al. (1979).

DTPA-extractable
Available Ni was determined using 0.005 DTPA (diethylene triamine pentaacetic acid) extract as described by Lindsay and Norvell (1978).

Speciation of Ni in the tested soils
Speciation of Ni in the studied soil samples was measured into saturated soil pastes, which were prepared with distilled water and left for equilibrium for 24 hr.

Concentrations of 11 trace metals (Ni, Pb, Cu, Co, Zn, Si, Fe, Cr, P, Mn, B) and concentrations of Na, K, Ca, Mg, Cl, CO₃²⁻, HCO₃⁻, SO₄²⁻ were determined in the clear extractants. The trace metals were measured by Inductively Coupled Spectrometer Plasma (ICP) Plasma 400. The rest elements were determined according to Black (1965). The results are listed in Table 1.

Data treatments
The speciation of Ni in aqueous solutions was calculated using the geochemical speciation program MINTEQA2 ver 3.11 (Allison et al., 1991). The calculated results are illustrated in Fig. 2.

Construction of stability diagrams of Ni minerals
The stability diagrams for the various Ni minerals which may control the solubility of Ni in the tested soils were constructed according to Lindsay (1979).
Results and Discussion

General characteristics of the soils

Table 1 contains the general properties of the tested soils. The results in the table showed that the pH values varied from 7.23 to 7.62. The highest pH value is recorded in the soil irrigated with well water, followed with decreasing with Nile water-irrigated soil, while sewage effluent-treated soil had the lowest value (7.23). Total carbonates content of the tested soils ranged from 1.4 % to 2.87 %. The sewage effluent - treated soil had the lowest carbonate content (1.4%). These results may be attributed to the dissolution of CaCO$_3$ as a result of interaction with organic acids present in sewage effluent. On the other hand, organic carbon (OC) and clay-size fraction content values show that the sewage effluent-treated soil had the highest values, followed by Nile water-irrigated soil and ground water-irrigated soil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Nile water-irrigated soil</th>
<th>Well water-irrigated soil</th>
<th>Sewage effluent-treated soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay %</td>
<td>31.96</td>
<td>30.45</td>
<td>37.2</td>
</tr>
<tr>
<td>O.M%</td>
<td>2.54</td>
<td>1.46</td>
<td>9.46</td>
</tr>
<tr>
<td>TCC</td>
<td>2.87</td>
<td>1.99</td>
<td>1.40</td>
</tr>
<tr>
<td>pH</td>
<td>7.40</td>
<td>7.82</td>
<td>7.23</td>
</tr>
<tr>
<td>Ni determinations: (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.846</td>
<td>1.216</td>
<td>24.76</td>
</tr>
<tr>
<td>DTPA-extractable</td>
<td>0.29</td>
<td>0.43</td>
<td>2.58</td>
</tr>
<tr>
<td>Soluble in water</td>
<td>0.086</td>
<td>0.071</td>
<td>0.269</td>
</tr>
<tr>
<td>Active portion (ML$^{-1}$)</td>
<td>1.44*10$^{-6}$</td>
<td>4.43*10$^{-7}$</td>
<td>4.07*10$^{-8}$</td>
</tr>
</tbody>
</table>

Total Ni content

Total content of Ni in the tested soils are given in Table 2. The results reveal that the highest level is recorded in sewage effluent-treated soil ($x^- = 24.76$ppm). followed in decreasing order by well water- irrigated soil ($x^- = 1.21$ ppm) and Nile water-irrigated soil ($x^- = 0.85$ ppm).

These results obviously show that the use of sewage effluent water for irrigation has a potential risk for human safety. This agrees to some extent with the studies of Aboulroos et al. (1991); El-Gendi et al. (1999) and Badawy & Helal (2002). They also added that the metals in sludge, Cu, Ni, and Zn are considered the ones most likely to cause phytotoxicity.

It is also worth to mention here that the Ni contents in the tested soils are within the range established by U.S. EPA (1993). This organization set up 40.0 ppm for Ni as the maximum permitted value. Furthermore, Badawy and Helal (2002) added that we have to deal with the standards of heavy metals as a guideline only that is due to the high solubility and mobility of sewage-burden metals which, contradicted to sewage sludge, may facilitate uptake of heavy metals into crops. Conversely, McBride (1995) mentioned that the adsorptive properties of sludge often prevent excessive uptake of many heavy metals.

**Metal bioavailability**

Since total Ni in soil is not a reliable index of plant availability and mobility, the extractable fraction is commonly used for this purpose. DTPA extractable -Ni

in the tested soils are given in Table 1. The data reveal that the highest value is recorded in sewage effluent-treated soil ($x^- = 2.58$ ppm), followed by well water-irrigated soil ($x^- = 0.43$ ppm) and Nile water-irrigated soil ($x^- = 0.29$ ppm).

A glance at the table indicates that the bioavailable portion of Ni amounted 10.42% of its total in sewage soil, meanwhile this portion constitutes about 34% and 35% of their totals in Nile-irrigated soil and well-irrigated soil, respectively. These results support the findings of McBride (1995) who mentioned that adsorption properties of sludge might prevent excessive uptake of heavy metals. Also, Paul et al. (1994) mentioned that the low portion percentage extracted of Ni in sewage effluent-treated soil may be because to the sludge constituents can low metal solubility via complexing by soluble ligands or colloidal surface.

**Metal movement**

Distribution of total-Ni with depth as a percent of surface layer content in each profile of the tested profiles are illustrated in Fig. 1. The figure reveals that the majority of Ni had accumulated in the upper layers of the tested profiles, in spite of the quality of irrigation waters. These findings are confirmed by Dowdy et al. (1991) and Dowdy and Volk (1983) who mentioned that minimal or no movement of trace metals below the sludge soil layer.

![Fig. 1. Distribution of total Ni content with depth as percent of surface layer content.](image)

*Fig. 1. Distribution of total Ni content with depth as percent of surface layer content.*

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Also, the figure shows clearly that the distribution patterns of Ni in both Nile-irrigated soil and in well water-irrigated soil are almost uniform. The uniformity pattern of Ni distribution in the former soils may be due to: (1) low contents of Ni in that soils (Table 1), (2) the employed irrigation regime (flood regime) which may facilitate the uniformity; and the coarse texture of that soils which modulate the distribution of Ni along the tested profiles. Returning again to the sludge amended soil, the present figure reveals that the distribution pattern of Ni shows a significant downward movement to the 30-60 cm layer of the soil profile, followed by decreasing pattern. Another important point may be detected from the figure that is below the second layers of the tested profiles the lowest portions of Ni are observed in sewage amended soil compared with the other soils.

The percent of Ni in the third, fourth and fifth layers in the sewage amended soil accounted 80%, 63%, and 57% of the total content of Ni in the upper layer, respectively. The corresponding values are 89%, 82%, and 72% in well-irrigated water, meanwhile it constitutes about 88%, 80%, and 79% in Nile water-irrigated soil. That may be because the sludge itself plays a significant role in controlling the metal mobility and bioavailability. This role may be: (1) precipitate or co-precipitate form of these metals with Fe, Al, Mn or Ca; (2) the strength of bonding to organic and mineral adsorption sites; (3) the potential of adsorbing power of sludge and the presence of dissolved ligands capable of complexing the trace metals.

Clearly there is some contradiction apparent in literature concerning the role of sludge on partitioning of heavy metals along soil profiles. Also, the important question that need an answer is what happens to heavy metals over the long-term (up to 20 years) following the cessation of using sewage effluent in irrigation. So, a comprehensive study is needed to cover these arguments.

**Metal bioavailability**

Since total Ni in soil is not a reliable index of plant availability and mobility, the extractable fraction is commonly used for this purpose. DTPA extractable-Ni in the tested soils are given in Table 2. The data reveal that the highest value is recorded in sewage effluent-treated soil \( (x^- = 2.58 \text{ ppm}) \), followed by well water irrigated soil \( (x^- = 0.43 \text{ ppm}) \) and Nile water irrigated soil \( (x^- = 0.29 \text{ ppm}) \).
A glance at the table indicate that the bioavailable portion of Ni amounted 10.42 % of its total in sewage soil, meanwhile this portion constitutes about 34% and 35% of their totals in Nile soil and ground soil, respectively. These results support the findings of McBride (1995) who mentioned that adsorption properties of sludge might prevent excessive uptake of heavy metals. Also, Paul et al. (1994) mentioned that the low portion percentage extracted of Ni in sewage effluent treated soil may be because the sludge constituents can lower metal solubility via complexing by soluble ligands or colloidal surface.

In the same connections, McBrid (1995) added that even sludge is applied to soil for sufficiently long to convert the surface soil almost completely into sludge residue, the uptake of heavy metals would be, at worst, linear function of accumulative sludge application, because the sludge itself adds adsorptive capacity to the soil.

**Ni speciation in the tested soils**

The input data of the tested soils used for calculating the various species of Ni are tabulated in a Table 2. The predicted Ni species calculated as percentages of their sums are illustrated in Fig. 2. The figure shows that the predominant species of Ni in the Nile water-irrigated soil solution is the free species (Ni$^{2+}$). This form constitutes more than 98% of total dissolved Ni (Ni$_t$). The same situation is also existed in sewage effluent-treated soil, the free form accounts more than 88% of total Ni (Ni$_t$).

![Fig. 2. Percentages of various species of Ni in the tested soils.](image)

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Using the GEOCHEM computer program, Emmerich et al. (1982) predicted that the free form of Ni in the soil solution for the Ramona soil treated with sewage sludge was about 52% of (Ni₁), while it was account 68%, in the mineral soil below the sludge layer. The reduction of the free form of Ni in sewage effluent-treated soil comparing with Nile water-irrigated soil may be due to the presence of inorganic and organic ligands found in the former soil which create web of interactions, consequently, decrease the percentage of the free portion. In the same connections, Stumm and Morgan (1976) stated that (Ni²⁺) is the most important species of the dissolved Ni in soil solutions. They also added that Ni²⁺ may be hydrolysis and form mononuclear species, NiOH⁺, Ni(OH)₂⁺, Ni(OH)₃⁻, and Ni(OH)₄²⁻. Whereas, the poly nuclear species may be formed only at high Ni²⁺ concentrations before precipitation of Ni(OH)₂ occurs. In well water-irrigated soil, the figure shows that only a small portion of Ni is existed as free species (about 34%). These findings may be attributed to: 1) high concentration of sulfate ligands in that soil, (Tables 1 and 2), the pH of the soil (7.82). Htal et al. (1996) studied the effect of pH on speciation of cadmium and reported that the pH of the soil solution can control metal speciation. They also added that pH also affects the bonding of metal to particulate because hydrogen ions can influence adsorption and ion exchange by competing for active sites. Also, Gambrell et al. (1980) mentioned that the pH also modify the adsorption sites, or change the degree of protolysis of sorbing material, thereby affecting the speciation of a metal in solution. The figure indicates that Ni also complexes with sulfate ions, especially in well water-irrigated soil (83% of Ni₁), followed in decreasing order by Nile water effluent-treated while Nile water-treated soil had only 1.3% as NiSO₄(AQ). El- Gendi (1988) stated that the second dominant species in uncontaminated soil solution was the sulfate from about 18.71% of (Ni₁).

**Predicted Ni activities**

The activities of Ni in the tested soils are listed in Table 1. The table shows that the mean values of Ni activities in the soils are; 10⁻⁵.₃⁹ M in (sewage water-treated soil), followed in decreasing order by Nile water-irrigated soil (x = 10⁻⁵.₈⁴ M) and well water-irrigated soil (x = 10⁻⁶.₃₅ M). It clearly shown that the highest value of Ni activities is obtained in sewage effluent-treated soil and these values are inversely correlated with pH values.

Aboutroos et al. (1996) mentioned that the activities of Ni in some soils using competitive chelation method, as described by Workman and Lindsay (1990) and reported that Ni activities ranged from (10⁻⁶.₈₂ to 10⁻⁸.₇₈ M). They also added that these values were inversely correlated with pH.
The solid phases of Ni which controlling the solubility of Ni in the tested soils

The predicted values of Ni$^{2+}$ plotted on the stability diagrams of the various Ni minerals as shown in Fig 3. The figure reveals that the predicted values of Ni$^{2+}$ activities are undersaturated with respect to Ni oxides, hydroxide and NiCO$_3$ minerals. As obviously shown from the figure that Ni oxide and hydroxide are too soluble and unlikely to form in the tested soils. In the same connection, Aboulroos et al. (1996) stated that NiCO$_3$ could not precipitate in soils that is because it requires high Ni concentration along with high level of CO$_2$ (reached to 0.3 Kpa) and this situation in normal soil is unlikely occurs. Thereby, neither oxides nor carbonate are the possible Ni mineral which control Ni$^{2+}$ in the tested soils.

![Figure 3. Plot of the predicted Ni(2+) on the stability diagrams of Ni minerals.](image)

On other hand, the values of Ni activities of the tested soils, as shown from the figure, are very close to Ni$_3$(PO$_4$)$_2$ and Ni$_2$SiO$_4$ solubility lines. Aboulroos et al. (1996) reported that NiFe$_2$O$_4$ (trevorite) in equilibrium with amorphous Fe(OH)$_3$ and geothite was the likely Ni mineral that can control Ni$^{2+}$ activities in soils. But, they also added that the solubility of NiFe$_2$O$_4$ could be expected to vary from soil to another, due to variation of pH, degree of crystallization and chemical composition. Meanwhile, in the present study, the results suggested that Ni$_3$(PO$_4$)$_2$ in equilibrium with strengite-soil Fe and Ni$_2$SiO$_4$ in equilibrium with soil-SiO$_2$ are the two possible Ni minerals that control the activities of Ni in the tested soils, regardless of the origin or the level of nickel.

Reference


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دراسة الصور الصلبة للأنيكل وكذلك المفصولات الكيميائية له في المحول الأرضي في بعض الأراضي المصرية

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تم تجميع عينات ندية من منطقة أبو روش - محافظة الجيزة لدراسة تأثير الرذيب من صامد مختلف وتشمل الرذيب بياض الصرف الصحي - مياه الآبار - مياه النيل على تراكم النديك في تلك الأراضي. وتشمل دراسة النديك الكمية الكلية - الجزء الناشئ من حركة النديك في القطاع الأرضي - المفصولات الكيميائية المختلفة للنديك في المحول الأرضي - قياس نشاط النديك - تحديد المعدن المتحكم في ذوبان النديك في تلك الأراضي. أوضحت النتائج أن الكمية الكلية للنديك كانت أعلى قيمة لها في الأراضي المروية بياض الصرف الصحي (كمتوسط عام = 17.7 جزء في المليون) بيلبيها في الترتيب الأرضي المروية بياض الآبار (المتوسط = 85 جزء في المليون) ثم أخيرا الأراضي المروية بياض النيل (المتوسط = 78 جزء في المليون). وكانت أدنى قيمة للجزء الناشئ من النديك في مصنفات التربة المروية بياض الصرف الصحي وقد يفسر ذلك كنتيجة لما تحتويه تلك المياه من مكونات غنية مختلفة والتي يمكن أن تؤثر في ذوبان النديك كنتيجة لتكوين معقدات. دراسة توزيع شكل النديك على طول القطاع أوضحت أنه في الأراضي المروية بياض الصرف الصحي هناك تراكم داخلها في 2-10 سم يتبين ذلك انخفاض في تركيز النديك في حين كان التوزيع سواء في الأراضي المروية بياض النيل أو بياض الآبار كان التوزيع متجانس على طول القطاع. أوضحت دراسة المفصولات الكيميائية الناشئة في المحول الأرضي أن الجزء الناشئ هو الصورة السائدة في كل الأراضي المروية بياض النيل (حيث يمثل 88% من مجموع الصور الدائمة) في حين كان يمثل 88% من مجموع الصور الدائمة للنديك في الأراضي المروية بياض الصرف الصحي و17% (17%) فقط في الأراضي المروية بياض الآبار. كذلك

ผลกระทบ النيكل بانونات الكبريتات - نفث الأراضي المروية بعياب
الأبار كانت الصورة الأجوفية NiSO₄(AQ) تمثل (8.8٪) من
مجموع الصورة الذائبة. في حين كانت هذه الصورة تمثل (1.9٪)
في الأراضي الم الروية بعياب الصرف الصحي. أوضحت النتائج أن
الصورة الأجوفية NiCl⁺ تمثل (1.9٪) من مجموع الصورة الذائبة
في الأراضي المروية بعياب الأبار. بينما هذه الصورة تمثل فقط
حوالي 0.1٪ في الأراضي الأخرى.

أوضحت النتائج أن أعلى قيمة لنشاط النيكل كانت في
الأراضي المروية بعياب الصرف الصحي (7.4×10⁻⁵ مول) تليها
الأراضي المروية بعياب النيل (4.4×10⁻⁵ مول) ثم الأراضي المروية
بعياب الأبار (4.3×10⁻⁵ مول).

تنخفض قيم نشاط النيكل في الأراضي المروية على منحنى
الذوبان لمعادن النيكل المختلفة يتضح أن معدن NiSiO₄ عند اتزانه
Strengite-soil Fe وكذلك معден Ni₃(PO₄)₂ و معден Soil-SiO₂ مع
هما أكثر المعادن تأثيرا على نشاط النيكل في تلك الأراضي.