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# Nickel Speciation in Soil and the Relationship with Its Concentration in Fruits

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Interest in the potential link between cancer and some inorganic nickel compounds (Nriago 1980) has drawn attention to the Ni concentration in food and other environmental samples. The studies of the uptake and chemical behavior of Ni in plants are related mainly to its toxicity having possible implications with respect to animals and man. On the basis of a report published by the International Committee on Nickel Carcinogenesis in Man (ICNCM) (Report 1990), the International Agency for Research into Cancer concluded that (i) there is sufficient evidence to establish a correlation between nickel sulfate and combinations of nickel sulfides and oxides and the incidence of lung and nasal cancers; (ii) there is inadequate evidence to establish a similar correlation for metallic nickel and nickel alloys; and (iii) limited evidence in experimental animals for the carcinogenicity of Ni compounds including metallic nickel, alloys and various nickel salts. The anthropogenic nickel sources of soil are the metal processing operations and the combustion of coal and oil because organic matter reveals a strong ability to absorb Ni; so, this metal is likely to be concentrated in coal and oil. In particular, nickel in sewage sludge that is present mainly in organic chelated forms is readily available to plants and therefore may be highly phytotoxic.

The general approach for the soil speciation studies has been to separate the soil into different chemical reagent or solvent fractions and, by analyzing each fraction, to determine the amount of element combined or associated with each soil fraction or phase (Ure 1991). A number of extractants, including ethylenediaminetetraacetic acid (EDTA), diethylenetriamine pentaacetic acid (DTPA), acetic acid, ammonium acetate, calcium chloride and hydroxylamine hydrochloride have been tested to identify metal species as exchangeable, carbonate-bound, Fe and Mn oxide-bound, organically bound, and to estimate the plant available trace metals. Flame atomic absorption spectrophotometry (FAAS) has proved to be a reliable, convenient and rapid method for analysis of toxic and nutritional metals in food, biological and environmental matrices, as direct or, particularly, in combination with preconcentration method (Morales et.al. 1993; Gucer and Yaman 1992; Yaman and Gucer 1994, 1995a, 1995b and 1998; Yaman 1997, 1998 and 1999; Alegria et. al. 1988). In this study, nickel concentrations in the fruit samples were determined by FAAS after

preconcentration on activated carbon. Soil samples were dissolved by using the extractants such as the mixture of nitric acid/hydrogen peroxide, oxalic acid, $Na_2EDTA$, acetic acid and citric acid and the extracts were analyzed for Ni by using direct FAAS measurements. So, the relation between the fruit nickel contents and the soil extractants-Ni contents was investigated. In addition, the possible chemical forms of Ni in soil were evaluated.

## MATERIALS AND METHODS

An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (AAS) equipped with ATI UNICAM Hollow cathode lamp was used for the determinations. The optimum conditions for FAAS are given in Table 1. The pH was measured with an EDT GP 353 ATC pH meter. In the enrichment and digestion procedure Snijders magnetic stirrer with heater and a Hettich EBA III centrifuge were used. Unless stated otherwise, all chemicals used were of high-purity reagent grade. Throughout all analytical work, doubly distilled water was used. All glass apparatus have been kept permanently full of 1 M nitric acid when not in use. In the digestion and extraction procedures, concentrated nitric acid (65%, Merck), hydrogen peroxide (35%, Merck), oxalic acid (Merck), citric acid (Merck), ethylenediaminetetraacetic acid disodium salt ($Na_2EDTA$, Merck) and acetic acid (96%, Merck) were used. A stock solution of Ni (1000 mg $L^{-1}$) was prepared by dissolving nickel nitrate (Merck) in 1.0 mol $L^{-1}$ nitric acid. A buffer solution of pH 4.4±0.2 was prepared by adding 0.1 mol $L^{-1}$ HCl solution to 0.1 mol $L^{-1}$ sodium citrate solution. A solution of 0.2% N-nitrosophenyl hydroxylamine (cupferron) was prepared by dissolving 0.2 g of reagent in 100 mL of ethyl alcohol. Preparation of activated carbon suspension was described elsewhere (Yaman 1999).

**Table 1**. Operating parameters for FAAS

| Parameter | |
|---|---|
| Wavelength, nm | 232.0 |
| HCL current, mA | 14.5 |
| Acetylene flow rate, L/min | 0.5 |
| Air flow rate, L/min | 4.0 |
| Slit width, nm | 0.2 |

Seven sites were selected from the major agricultural areas in Elazig, Turkey. The soil samples were taken from seven different locations, with the sampling at a depth of about 10 cm below the surface. The fruit samples were also gathered at each of these locations, at distances not more than 200 cm from the location of the soil sample. Morello cherry, cherry, mulberry, strawberry and pear were chosen for the present study because they are the common consumed fruit available in Turkey. The fruits chosen were washed separately and thoroughly with running tap water and further rinsed twice with distilled water and then allowed draining on a filter paper. Then, both fruit and soil samples were dried at 85 °C. 2.0-3.0 g

samples of oven dried materials were placed into evaporating dishes and ashed at 480 °C in an ashing furnace for 4 h. This process was repeated if necessary until a white ash was obtained. The mixtures of nitric acid-hydrogen peroxide (2+1) (for 1.0 g of dried matter, 1.5 mL of mixture were used) were added to the ashed samples and dried with occasionally stirring on a hot plate with low heat. Then, the residue was dissolved with 1.5 mol $L^{-1}$ nitric acid and diluted to 30 mL. The clear digests were preconcentrated as described below. A blank digest was carried out in the same way.

Chelation and adsorption on activated carbon was chosen as enrichment method because high separation efficiency was obtained when the metal ions were encapsulated in organic structures prior to the adsorption step. Particularly, if the complexing agent has an aromatic structure, π-orbital overlap interaction between the aromatic structures of the molecule and the activated carbon surface is possible, resulting in larger adsorption energy. Therefore, cupferron, which has an aromatic structure, was used as a chelating reagent. For the chelation and adsorption conditions on activated carbon, the optimized enrichment steps in the previous work (Yaman and Gucer 1998) were as follows with slight modification.

The pH of nickel solutions or the clear digestions of fruit samples (30 mL) was adjusted to 4.4±0.2 by adding $HNO_3$ and NaOH at the necessary concentrations. The buffer solution of 10 ml, cupferron solution of 20 ml and the activated carbon suspension of 4 mL were added and the pH of the solution was adjusted again, as necessary. The mixture was stirred mechanically for 45 minutes and filtered through a filter paper (Advantec Toyo 5B white ribbon). The residue was dried at 105 oC for 1 h. Concentrated nitric acid (4 mL) was added to the residue in a glass beaker and evaporated to dryness. Then, 2.0 ml of 1.5 mol $L^{-1}$ $HNO_3$ was added and, after centrifuging twice, the clear solution was separated for measurements. The nickel content of the solutions obtained was determined by means of the FAAS.

Soil pH was measured on soil suspension using soil: distilled water at 1:5 (w/v). The mixture of nitric acid-hydrogen peroxide (2+1) of 3 mL were added to the soil samples of 1.0 g and dried with occasionally shaking on a hot plate. After cooling, 2 ml of 1.5 mol $L^{-1}$ nitric acid was added to the remainder and centrifuged. The clear digests were analysed by using FAAS. A blank digest was carried out in the same way.

The soil extracts were obtained by shaking, separately, 1.0 g of soil samples with 2.0 mL of 0.05 mol $L^{-1}$ $Na_2EDTA$, 1.0 mol $L^{-1}$ oxalic acid and concentrated acetic acid. The mixture was evaporated with occasionally shaking on a hot plate. Then, 2 mL of 1.5 mol $L^{-1}$ nitric acid was added and centrifuged (this procedure was mentioned as hot extraction in this text). In addition, 2.0 mL of 0.05 mol $L^{-1}$ $Na_2EDTA$, 1.0 mol $L^{-1}$ oxalic acid, concentrated acetic acid and 1.0 mol $L^{-1}$ citric acid were also, one by one, added to 1.0 g of soil samples at the room temperature (this procedure was mentioned as cold extraction in this text). The clear digests

**Table 2.** Recoveries of Ni from fruit and from soil by using $HNO_3/H_2O_2$ mixture (Dried weight basis). The results are mean values as mg $kg^{-1}$; n=4

| Sample* | Ni levels in Fruit | | | Ni levels in Soil | | |
|---|---|---|---|---|---|---|
| | Added, mg $kg^{-1}$ | Found, mg $kg^{-1}$ | Recovery, % | Added, mg/kg | Found, mg/kg | Recovery, % |
| Strawberry 1 | 0 | 1.10±0.10 | - | 0 | 380±20 | - |
| Strawberry 1 | 1.0 | 2.00±0.12 | 90 | 50 | 428±23 | 96 |
| Cherry 6 | 0 | 1.20±0.09 | | 0 | 370±17 | - |
| Cherry 6 | 1.0 | 2.12±0.12 | 92 | 50 | 416±20 | 92 |
| Morello 3 | 0 | 0.70±0.07 | | 0 | 38±2 | - |
| Morello 3 | 1.0 | 1.63±0.10 | 93 | 50 | 87±5 | 98 |

*Numbers such as 1, 3 and 6 mean the region taken the soil and fruit.

were analysed by using FAAS. The blank digests were carried out in the same ways.

## RESULTS AND DISCUSSION

Dry ashing method was preferred because this method is simple and smaller quantities of reagents were needed which reduces the possibility of extraneous pollution. In addition, the results between the dry ashing and wet ashing methods for Ni showed no statistically significant differences (Yaman and Gucer 1998). For the fruit analysis, the parameters that are thought to affect the enrichment and measurement steps in the analytical scheme were taken from the previous work as described above which interference effect of Mg on the Ni absorbance measured was overcome by using this method (Yaman and Gucer 1998).

The added nickel amounts to the fruits and soils were recovered to check accuracy of analyses performed (Table 2). It was found that at least 90 % of the nickel added to the fruit samples was recovered. The recoveries obtained for Ni added to soil matrices were higher than 92 % by using $HNO_3/H_2O_2$ digestion. The effect of contamination was eliminated by subtracting values obtained for blanks. Adsorption loss can be excluded as the procedure was followed in exactly the same way, using the same glassware and the same reagents that were used throughout. Therefore, the effect of contamination or adsorption may be reliably overlooked.

Calibration curve for soil samples was obtained by using the nickel solutions of 0.25; 0.50; 1.0; 1,5; 2.0 and 4.0 mg $L^{-1}$. The graph obtained was rectilinear in the concentration range of described above and the equation of the curve was as follow:

$$Y = 42.371\ X + 1.125 \qquad R^2 = 0.99$$

**Table 3.** Results of Ni contents of fruits and soils by using the enrichment method-FAAS and different extractants, respectively (dried weight basis). n=4; pH±0.2

| Sample of Fruit and Soil on grown ** | Ni in Fruit $mgkg^{-1}$ | Ni in soil, mg/kg | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $HNO_3/H_2O_2$ | Oxal. a 1 M * | Oxal. a 1 M | EDTA 0.01M * | EDTA 0.01M | Ace.acid Concen. * | Citric a. 1 M | soil pH |
| M cherry1 | 0.8±0.07 | 85±5 | 62±4 | 3±0.21 | 5±0.3 | 1.2±0.08 | 4±0.3 | 0.8±0.06 | 6.4 |
| M cherry2 | 0.6±0.06 | 27±1.6 | 20±1.4 | 2±0.15 | 2.5±0.15 | 0.4±0.04 | 2.6±0.2 | 0.9±0.09 | 6.3 |
| M cherry3 | 0.7±0.07 | 38±2 | 16.5±1 | 2.7±0.18 | 3.1±0.20 | 0.7±0.05 | 2.5±0.2 | 1.1±0.08 | 6.4 |
| M cherry4 | 0.4±0.05 | 15±0.8 | 14±0.7 | 1.4±0.11 | 1.9±0.14 | 0.8±0.06 | 2.0±0.17 | 0.5±0.04 | 6.2 |
| M cherry5 | 0.5±0.08 | 18±1.2 | 10±0.7 | 1.3±0.1 | 2±0.14 | 0.4±0.04 | 1.3±0.1 | 0.8±0.06 | 6.1 |
| Cherry 6 | 1.2±0.09 | 370±17 | 250± 14 | 29±2 | 48±3 | 2±0.13 | 38±2.0 | 5.8±0.3 | 6.6 |
| Cherry 4 | 0.6±0.05 | 15±1.0 | 13±1.0 | 1.5±0.12 | 2.2±0.15 | 0.8±0.07 | 2.0±0.16 | 0.5±0.05 | 6.3 |
| Mulberry 1 | 1.4±0.12 | 90±5 | 65±4 | 2.9±0.2 | 5±0.3 | 1.3±0.11 | 3.9±0.25 | 0.9±0.08 | 6.4 |
| Mulberry 3 | 1.1±0.1 | 32±2 | 9±0.6 | 1.8±0.15 | 1.8±0.12 | 0.4±0.04 | 1.4±0.11 | 0.8±0.08 | 6.4 |
| Mulberry 4 | 1.2±0.09 | 13±0.8 | 12±0.9 | 1.3±0.1 | 2.7±0.15 | 0.8±0.06 | 2.5±0.16 | 0.9±0.07 | 6.4 |
| Mulberry 5 | 1.2±0.1 | 20±1.2 | 13±0.8 | 1.4±0.09 | 2.5±0.2 | 0.5±0.05 | 1.7±0.12 | 0.9±0.07 | 6.5 |
| Strawberry 1 | 1.1±0.10 | 380±20 | 295± 16 | 35±1.6 | 65±4 | 2.3±0.15 | 30±1.5 | 8.8±0.5 | 6.5 |
| Strawberry 6 | 0.9±0.10 | 215±10 | 208±9 | 10±0.6 | 22±1.3 | 5±0.3 | 14.5±1.0 | 3.1±0.2 | 6.6 |
| Pear 7 | 1.0±0.09 | 18±1.0 | 13±0.8 | 3.4±0.17 | 4.2±0.3 | 0.4±0.05 | 4.0±0.3 | 1.5±0.11 | 6.5 |

*: After dried of reagent, 2 ml of 1.5 M $HNO_3$ was added and centrifuged (mentioned as hot extraction).
** Numbers such as 1, 3, 4 and 7 mean the region taken the soil and fruit.

Calibration curve for fruit samples was obtained by using 30 mL of Ni solutions in concentration range of 30-200 μg $L^{-1}$. The described enrichment procedure was applied to these solutions (pH 4.4± 0.2). The clear solutions were analysed by means of FAAS. The graph obtained was rectilinear in the concentration range of described above and the equation of the curve was as follow:

$$Y = 0.5569\ X + 0.841 \qquad R^2 = 0.99$$

The relative standard deviation was found to be 3% at the concentration of 50 μg $L^{-1}$ for 10 replicate enrichment procedure. Table 3 gives the nickel concentrations of fruit samples by using dry ashing and the soil samples by using different extraction reagents. The mean total Ni concentrations for all studied fruits were in the range of 0.4-1.4 mg $kg^{-1}$. Soil EDTA-extractable metal concentrations are commonly used to indicate of the likely availability of metals to plant uptake. Our results are also showing that these evaluations for Ni are nearly valid for the studied fruits. Other interpretations about Table 3 are as follows:

The Ni concentrations of morello cherry did linearly change dependent on the soil Ni contents using the mixture of $HNO_3/H_2O_2$ ($R^2$=0.78), hot $Na_2EDTA$ ($R^2$=0.83) and cold oxalic acid ($R^2$=0.91) extractions (Fig. 1 and 2). The changes at the nickel contents of the cherry and strawberry samples were dependent on the soil Ni

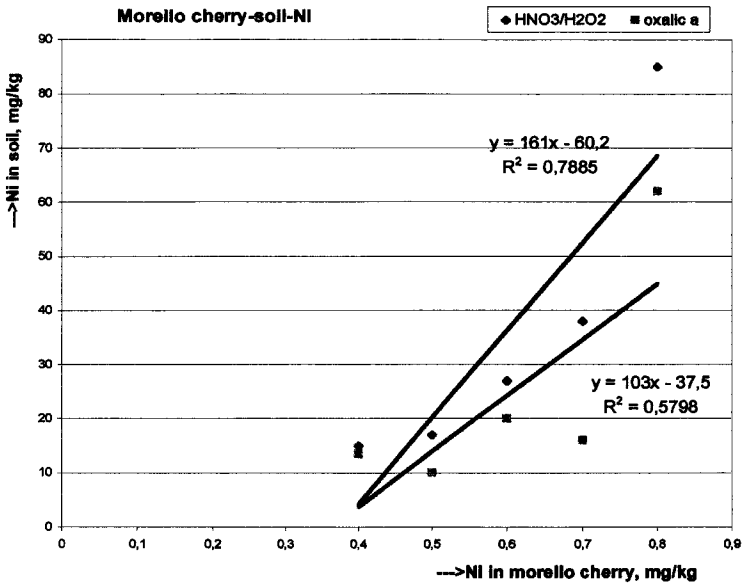


**Figure 1**. Relationship between the amounts of morello cherry-Ni and $HNO_3$/ $H_2O_2$-dissolved and oxalic acid-extractable-Ni of the soils studied.

concentrations for all studied extractants. The nickel contents of the mulberry samples did linearly change dependent on hot $Na_2EDTA$ ($R^2$=0.96), hot acetic acid ($R^2$=0.91) and citric acid ($R^2$=0.79) results (Fig. 3). Ni concentrations of some studied soils were significantly found higher than the permitted concentration of 100 mg $kg^{-1}$ described by Pendias (1986).

The Ni concentrations in the hot oxalic acid extraction solutions from soil were found higher than the Ni concentrations in both hot $Na_2EDTA$ and concentrated acetic acid extraction solutions for all studied soils. In addition, nickel concentrations in hot oxalic acid extracts of soil were approximately close to the Ni concentration in $HNO_3/H_2O_2$ digestion for all studied soils except the soils taken from location with 3 and 5 numbers. One possible explanation of these results, chemical form of Ni in these soils may exist as a reducible form or occluded on minerals such as Fe and Mn oxides. So, oxalic acid plays the role both as acid and as complexing agent which form complexes with both Fe and Mn, and so, Ni releases from minerals. In the literature, it is described that the soil nickel is strongly associated with Mn and Fe oxides or/and occurred organically bound forms (Pendias et. al. 1986). More additional interpretation can be done on the results in Table 3.

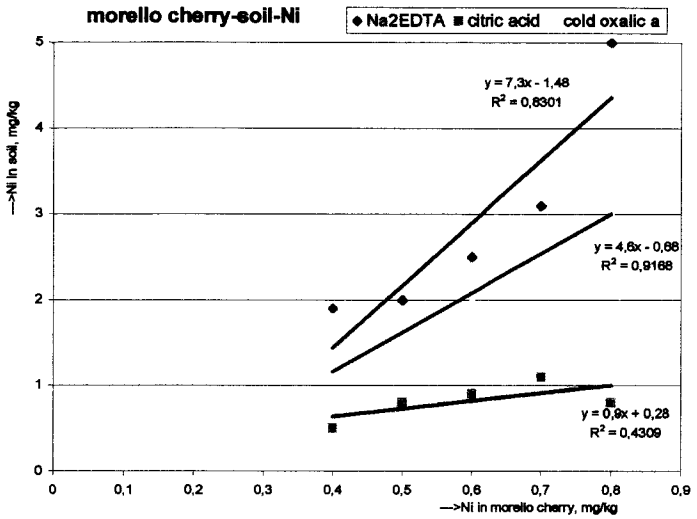


**Figure 2**. Relationship between the amounts of morello cherry-Ni and $Na_2EDTA$, citric acid and cold oxalic acid-extractable-Ni of the soils studied.

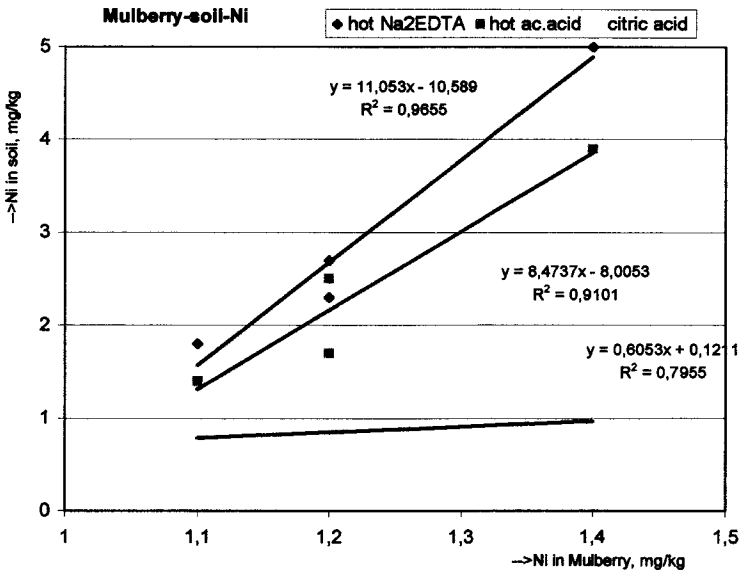


**Figure 3**. Relationship between the amounts of mulberry-Ni and hot $Na_2EDTA$, hot acetic and citric acids-extractable-Ni of the soils studied.

An attempt was made to identify the Ni species that is most responsible for the plant-available Ni. The comparative data using various extraction reagents were found useful to study speciation of nickel in soils and to estimate Ni uptake of fruits from soils. The results obtained show that Ni contents of fruits are dependent to the different extractants-soil Ni concentrations as related to fruit types.

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