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Distribution of Nickel in Different Phases of Soil Samples and Plant Parts Taken From Serpentine and Copper Mining Area

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Speciation is important to determine the mobility, bioavailability and/or toxicity of trace elements in soils because the total metal concentrations are not adequate for determination of these properties. In this study, four stage sequential extraction procedures were used to determine different Ni phases in soil samples. Soil samples and plants grown in these soils were collected from serpentine and copper-mining area in Maden-Elazig-Turkey. The extracted fractions are: exchangeable/carbonate, reducible-iron/manganese oxides, oxidizable-organic matter and sulfides and residual except silicates. In addition, selective extraction procedures were applied to the same samples and the results were compared. The concentrations of Ni in soil and plant samples were determined by flame atomic absorption spectrometry (FAAS) and inductively coupled plasma-mass spectrometry (ICP-MS). Considerable Ni concentrations in hydroxylamine hydrochloride extracts were found compared to other selective extracts. Because of translocation factor higher than 1, *Rumex* (Sorrel) leaves can be used as hyperaccumulator.

Key Words: Speciation, Nickel, Soil, Plant, Atomic absorption spectrometry.

INTRODUCTION

Nickel is the metal component of the seven microbial enzymes including urease, hydrogenase, CO-dehydrogenase, methylcoenzyme M reductase, Ni-superoxide dismutase, glyoxylase I and *cis-trans* isomerase. As a result, it is considered to be essential to plants and some domestic animals. On the other hand, some nickel-containing enzymes have also been studied for their relationship to human diseases. More attention has been focused on the toxicity of nickel because it can cause allergic reactions and certain nickel compounds have carcinogenic effects[1-3]. The essentiality, toxicity and carcinogenicity of nickel were well reviewed in recent times[4]. Hence, the studies of the uptake and chemical behaviour of nickel in plants are related mainly to its toxicity to animals and humans. Although typical nickel concentrations in plants were in ranges of 0.1 to 5 mg kg^{-1}, on a dry-weight basis,

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toxicity thresolds were reported between 24-246 mg kg^{-1} depending on the species[5]. Maximum allowable Ni levels in agricultural soils were described in the range of 20-100 mg kg^{-1} according to different countries[6,7]. Consequently, there is a growing interest in the determination of Ni in the environment and food samples due to its carcinogenicity and high toxicity for human.

It is well known that the pollution degree of soil by heavy metals is depending on chemical forms than the total metal concentration[8]. Thus, the identification of the chemical forms (called as speciation) of trace metals in soil are necessary for estimating their biological availability, physico-chemical reactivity and transport in the environment and food chain. The speciation is important to determine the mobility, bioavailability and/or toxicity of trace elements in soils because the total metal concentrations are not adequate for determination of these properties. According to the speciation[9], the species are defined by their function, as, for example, 'plant available forms', 'exchangeable cations' or 'labile species'. However, this procedure has been expressed as fractionation[10]. In unpolluted soils, trace metals are mainly bound to silicates and primary minerals forming relatively immobile species, whereas in polluted ones, trace metals are generally more mobile and bound to other soil phases. The metals in mobile phases of soils are available to plants and may be readily taken up by plants. The determination of the different binding kinds gives more information on trace metal mobility, as well as on their availability or toxicity than the total element content. The fractionation may be performed by selective extraction of the soil with chemical reagents or solvents designed to extract the elements bound in, or associated with, a particular soil phase or component[11-15]. For example, the extraction reagents were used to release, metals on exchange sites, or metals bound or associated with soil organic matter and bound to carbonate phases. Thus, the levels of mobile or potentially mobile species can be assessed by applying selective extraction methods.

Sequential extraction procedures designed to isolate a number of soil phases offer a considerable improvement in phase-specificity. Although these procedures are not still perfect and both, tedious and difficult to use. Sequential extraction methods can be also used in more fundamental studies such as: to elucidate the soil chemistry, to assess the structure and composition of soil components and to improve understanding of the processes in the soil that control the mobilization and retention of nutrient and toxic elements as well as to illuminate their transport mechanisms. The specificity of many reagents can be improved by combining a series of them in a sequential extraction scheme in which the residue from a first extraction is used as the material for a second extraction and so on through a number of stages. The soil phase attacked by each extracting reagent is thus restricted by the preceding extraction in the series and is thereby made more specific[8].

Among various sequential and selective extraction procedures, 3 stage sequential extraction procedure (TSSEP) recommended by the Commission of the European Communities Bureau of Reference (BCR), now the Standards, Measurements and

Testing Programme, were standardized for applying to speciation of metals to sediment samples[16]. Tokalioglu *et al.*[17] investigated the heavy metal uptake of vegetables growing in contaminated soils. They used modified BCR sequential extraction method and they determined soil Ni concentrations of 66 % in the residual phase which total Ni contents were in range of 40.1-44.5 mg/kg. Bacon *et al.*[18] determined Ni concentrations in the labile fractions remained similar for all three soils and the increased concentration in the residue was reflected in the higher total concentration in an upland catchment soil in Scotland by using BCR. The soils of Almería were studied by Sierra *et al.*[19] for determination of trace elements to evaluate of environmental risk. In these soils, Ni concentrations were found in range of 7-80.1 mg/kg (0-20 cm depth) and 4.9-94.8 mg/kg (20-40 cm). Sasmaz and Yaman[20] and Sasmaz *et al.*[21] examined soils and *Euphorbia*, *Verbascum* and *Astragallus* plants grown on abondened Zn-Pb-Ag mining area to determine the relationship between Cr, Ni, Co and Tl concentrations in soil and in plants. They found Ni concentrations in ranges of 4.6-49.3 mg/kg for soil and 2.73-13.1 mg/kg for roots and 0.97-2.23 mg/kg for shoots of *Euphorbia* plant.

In this study, selective and sequential extraction procedures modified from three stage sequential extraction procedure (TSSEP) were applied to soil samples for speciation of nickel. The plant species grown in this serpentine and copper-mining area were also analyzed. Ni concentrations in soil extracts and plant digests were determined by FAAS and ICP-MS, respectively. ICP-MS was also used to determine the reliability of results.

EXPERIMENTAL

A Model 929 ATI UNICAM flame AAS equipped with an ATI UNICAM hollow cathode lamp was used for nickel determination. The optimum instrumental conditions were used as described in manual handbook: wavelength; 232 nm, HCl current; 7.5 mA, the flow rate of acetylene and air; 0.5 and 4.0 L/min, respectively and slit width; 0.2 nm. Plant samples were analyzed by Perkin-Elmer Elan 9000 inductively coupled plasma-mass spectrometer (Perkin-Elmer SCIEX, Concord, Ontario, Canada). The operation conditions as recommended by the manufacturers are given in Table-1.

TABLE-1
OPERATING PARAMETERS FOR ICP-MS

Inductively coupled plasma	Perkin-Elmer Elan 9000
Nebulizer	Crossflow
Spray chamber	Ryton, double pass
RF power	1000 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Carrier gas flow rate	0.9 L min^{-1}
Sample uptake rate	1.0 mL min^{-1}
Detector mode	Auto

All chemicals used were of analytical-reagent grade. Throughout the analytical work, doubly distilled water was used. All glass apparatus were kept permanently full with 1.0 mol L^{-1} nitric acid when not in use. In the digestion and extraction procedures, concentrated nitric acid (65 %, Merck), hydrogen peroxide (35 %, Merck), ethylenediaminetetraacetic acid disodium salt (Merck), acetic acid (96 %, Merck), sodium acetate (Merck), ammonium acetate (Merck), potassium nitrate (Merck), hydroxylamine hydrochloride (Merck), sodium pyrophosphate (Merck) were used. The stock solutions of nickel (1000 mg L^{-1}) were prepared by dissolving its nitrate salts in 1.0 mol L^{-1} nitric acid.

Digestion and selective extraction of soil samples: The soil samples were sampled from serpentine and copper-mining area in Maden, Elazig, Turkey. Soil samples were collected from the surface (10-20 cm depth). Stones and plant fragments were removed by sieving with a 2 mm sieve. The sieved samples were dried at 60 ºC and grinded in a mortar. To determine total Ni concentrations except silicates, 3 mL of a mixture of nitric acid-hydrogen peroxide (1:1) were added to the samples of 0.25 g and dried with occasionally shaking on a hot plate. After cooling, 3 mL of 1.0 mol L^{-1} nitric acid were added to the remainder and centrifuged. The clear digests were analyzed by using direct FAAS. Blank digests were prepared and analyzed in the same way.

The selective extracts were obtained by, separately, shaking 1.0 g of soil samples with 5.0 mL of following reagents, separately: 1.0 mol L^{-1} potassium nitrate, 1.0 mol L^{-1} sodium acetate and 1.0 mol L^{-1} ammonium acetate for the exchangeable and weakly adsorbed fraction, 0.04 and 1.0 mol L^{-1} of $NH_2OH.HCl$ solutions for fractions bound to Fe and Mn oxides, 0.1 mol L^{-1} of Na_2EDTA solution for organically and carbonate bound, 1.0 mol L^{-1} acetic acid solutions for the carbonate and exchangeable fractions, 0.2 mol L^{-1} of sodium pyrophosphate solution for the easily soluble organic and exchangeable fractions, acetic acid-acetate buffer solution (pH 5.0) for carbonate fraction. The mixtures were separately shaken by magnetic stirrer for 10 min and then, centrifuged. The clear digests were analyzed by using FAAS. The blank digests were prepared in the same way and analyzed.

Sequential extraction: The modified three step sequential extraction procedure recommended by BCR was studied as described below.

Step-1: 40 mL of 0.11 mol L^{-1} acetic acid was added to 1.0 g of soil and shaken for 16 h on magnetic stirrer at room temperature. The extract was separated from the residue by filter paper and stored in a polyethylene container in a refrigerator at 4 °C prior to analysis. The residue was washed with 20 mL of distilled water by shaking for 15 min. The washings were discarded.

Step-2: The residue was extracted for 16 h with 40 mL of 0.1 mol L^{-1} hydroxylamine hydrochloride acidified (at pH 2) with nitric acid. The extract was separated and the residue was washed as described above.

Step-3: The washed residue was digested with 10 mL of 8.8 mol L^{-1} hydrogen peroxide at 80 °C in a water bath. The flask was covered with a watch glass during

the digestion and was occasionally shaken to dryness. The procedure was repeated. After cooling, the residue was extracted, 16 h, with 50 mL of 1.0 mol L^{-1} ammonium acetate adjusted to pH 2 with nitric acid. The extract was separated and the residue was washed as described above. The blank digests were prepared in the same way.

Step-4: At the end of the third step, a 8 mL of nitric acid- hydrogen peroxide (1:1) was added to the residual and the mixture was dried with shaking, occasionally, on a hot plate. After cooling, 5 mL of 1.0 mol L^{-1} nitric acid was added to the residue and centrifüged. The clear digests were analyzed using FAAS. The blank digests were analyzed in the same way.

Preparation and digestion of plant samples: Plant samples, *Rumex* (Sorrel), *Euphorbia* (Spurge) and *Brassicasea* (Isatis), were collected at the same sampling sites from which the soil samples were taken. The plant samples were separated to root, stem and leaves and washed with tap and distilled water. After drying at 60 ºC for 24 h up to constant weight, a 1.0 g of plant sample was placed into a glass (Pyrex) beaker and ashed at 480 ºC in an ashing furnace for 4 h. This process was repeated, if necessary, until a white ash was obtained. The mixture of nitric acid/ hydrogen peroxide (2+1) was added to the ash and dried with occasionally stirring on a hot plate at low heat. Then, the residue was dissolved with 3 mL of 1.0 mol L^{-1} nitric acid and centrifugated. After centrifugation, the clear digests were analyzed for Ni by FAAS and ICP-MS. Blank digests were prepared in the same way.

RESULTS AND DISCUSSION

Related to the calibration curve, the graphic obtained was rectilinear in the concentration range described and the equation of the curve was as follow:

$$Y = 85\ X + 0.5 \quad R^2 = 0.99 \text{ for Ni (0.2-2.0 mg/L)}$$

Selective extraction: Using CH_3COONH_4, CH_3COONa and KNO_3 as exchangeable fraction, exchangeable metal ions are released most readily into the environment. Metals corresponding to the exchangeable fraction usually represent a small portion of the total metal content in soil, sewage sludges and sediments and can be replaced by neutral salts. Thus, this fraction generally accounted for less than 2 % of the total metals in soil present. Readily exchangeable fraction, also described as non-specifically adsorbed fraction, can be released by the action of cations such as K, Ca, Mg or (NH_4) displacing metals weakly bound electrostatistically on organic or inorganic sites[8]. From the Table-2, the obtained Ni concentrations in the exchangeable fraction were found in range of 0.6-19 mg kg^{-1}. Some of these concentrations are higher than 2% of the total Ni in soil.

EDTA as complexing extractant can displace metals from insoluble organic or organometallic complexes as well as those sorbed on inorganic soil components. From the Table-2, Ni concentrations in EDTA extracts were found higher than both in the acetic acid and in acetic acid-acetate buffer solution at pH 5 extracts except soil 2. So, it can be concluded that Ni in these soils are predominant in the organic fractions. An alternative approach uses sodium or potassium pyrophosphate (0.1 M

TABLE-2
NICKEL(II) CONTENTS IN SOIL SAMPLES BY USING DIFFERENT SELECTIVE EXTRACTS AND HNO_3/H_2O_2 DIGEST (EXCEPT SILICATES) (AS mg kg^{-1} BASED ON DRIED WEIGHT), n = 3

Soil	pH	Extraction reagent									
		1.0 mol L^{-1} CH_3COONH_4	1.0 mol L^{-1} CH_3COONa	1.0 mol L^{-1} KNO_3	1.0 mol L^{-1} CH_3COOH	0.1 mol L^{-1} EDTA	0.2 mol L^{-1} $Na_4P_2O_7$	Acetate buffer pH 5	1.0 mol L^{-1} NH_2OH HCl*	0.04 mol L^{-1} NH_2OH HCl*	HNO_3/H_2O_2 (ICP-MS)
Soil 1	4.65	1.5±0.30	0.6±0.11	0.8±0.15	11±2.0	13±2.0	0.50±0.09	3.6±0.60	24±4.0	19±3.0	230±32 (219±32)
Soil 2	7.15	11±2.00	8.0±1.50	19±3.00	9.0±1.5	18±3.0	13±2.00	19±3.00	26±4.0	18±3.0	784±86 (762±85)
Soil 3	6.20	1.0±0.20	1.0±0.20	1.2±0.20	bdl	1.4±0.2	1.3±0.20	1.0±0.20	2.4±0.4	1.0±0.1	85±11 (82±10)
Soil 4	6.80	6.7±1.00	2.4±0.30	3.6±0.50	17±2.0	34±5.0	17±2.00	12±2.00	84±15.0	71±12.0	1021±105 (1002±102)
Soil 5	6.25	0.70±0.12	0.50±0.09	0.70±0.13	bdl	1.8±0.3	0.50±0.08	0.50±0.08	5.0±0.6	2.9±0.4	51±8 (48±7)
Soil 6	6.80	2.2±0.30	0.90±0.17	1.0±0.10	14±3.0	20±3.0	3.0±0.50	5.0±0.70	55±7.0	64±6.0	1339±120 (1303±137)

*Hydroxylamine hydrochloride solutions were prepared in 25 % acetic acid; bdl = below detection limit.

TABLE-3
NICKEL(II) CONCENTRATIONS IN SOIL SAMPLES BY USING SEQUENTIAL EXTRACTION AND PLANT SAMPLES (AS mg kg^{-1} BASED ON DRIED WEIGHT), n = 3

Soil	Setp				Sum	Ni in plant parts, using ICP-MS			Plant
	1st step	2nd step	3rd step	4th step		Root	Stem	Leaf (FAAS)	
Soil 1	43±6	59±9	36±6	91±14	229	6.4±1.0	2.9±0.5	8.9±1.5 (8.8±1.6)	*Rumex* 1
Soil 2	45±7	94±14	67±11	835±100	1041	28±5	10±2	107±15 (104±14)	*Rumex* 2
Soil 3	bdl	5.0±0.7	bdl	64±8	69	15±2	4.4±0.7	8.1±1.3 (8.0±1.2)	*Euphorbia*
Soil 4	121±15	270±28	107±14	604±54	1102	39±6	0.56±0.11	35±5 (34±5)	*Brassicasea* 1
Soil 5	bdl	6.5±0.9	5.5±0.9	42±4	54	0.81±0.13	0.30±0.05	0.85±0.10	*Brassicasea* 2
Soil 6	107±17	232±25	103±12	826±74	1268	16±3	3.7±0.6	19±3 (17±3)	*Brassicasea* 3

bdl = below detection limit

at pH 10) to disperse colloidal organic material by complexing the floculating Ca, Al or Fe cations. This reagent is more selective for the easily soluble organic fraction, metals associated with humic and fulvic acids[8]. Ni concentrations bound to organic matters were found in the ranges of 1.4-34 mg kg^{-1} using 0.1 mol L^{-1} EDTA and 0.5-17 mg kg^{-1} using 0.2 mol L^{-1} $Na_4P_2O_7$ (Table-2).

It was described that the acidified hydroxylamine hydrochloride solution at its high concentrations releases the metals from the Mn and Fe oxides[8]. The amorphous oxyhydroxides of iron and manganese strongly sorb trace elements, initially in exchangeable forms, but increasingly with time are transformed to less mobile, specifically adsorbed forms. Acidified hydroxylamine hydrochloride (0.1 M) releases metals mainly from amorphous manganese oxide phases with little attack on iron oxide phases. Increasing the hydroxylamine hydrochloride concentration to 0.5 M and decreasing the pH from 2 to 1.5 provides effective attack on the iron oxide phases while still releasing metals from manganese oxide phases. So, Ni concentration in 0.04 M hydroxylamine hydrochloride extract is related to the amorphous manganese oxide phases. As it could be expected, an increase in Ni concentrations was found when the concentration of hydroxylamine hydrochloride was increased from 0.04 mol L^{-1} to 1.0 mol L^{-1} except soil 6. The highest Ni concentrations among the studied extraction reagents were found in 1.0 mol L^{-1} hydroxylamine hydrochloride as 84 mg Ni kg^{-1}. For hydroxylamine hydrochloride extract, the percentage up to 10 % of total Ni concentrations was observed.

The concentrations determined by the mixture of concentrated HNO_3-H_2O_2 (total metal concentration except silica phases) were higher, at least, 10-times than this each extract. In soil samples, Ni concentrations of 30 mg kg^{-1} for pH < 6 and 75 mg kg^{-1} for pH > 6 were the accepted limit values. The observed pH of soil samples was higher than 6 except soil 1. Although total Ni concentrations in all soil samples were found higher than these limit values, there isn't any risk because these high Ni concentrations are in immobile phases regarding with Ni levels in the other soil extracts.

Finally, it can be concluded that the observed Ni concentrations using selective extraction reagents are useful to determine the risk factor originated from nickel element in soil. The observed Ni concentrations by selective extraction procedure were given in Table-2 and illustrated in Fig. 1.

Sequential extraction: The sequential extraction is more advantage than the selective extraction because each reagent has a different chemical nature such as a dilute acid, reducing or oxidising agent and the steps are performed roughly in order of increasing 'vigour'. In a typical procedure, the first species to be isolated are those already in the soil solution, perhaps, together with those loosely attached at cation-exchange sites in the matrix. This is generally followed by stepwise attack on the carbonate phase, iron and manganese oxyhydroxides and organic matter. The most widely used procedure involves the oxidation of organic material by hydrogen peroxide with a subsequent extraction with ammonium acetate to prevent

readsorption or precipitation of released metals. The organic fraction released in the oxidizable step is not considered mobile or available since it is thought to be associated with stable high molecular weight humic substances that release small amounts of metals in a slow manner. Amounts of trace metals bound to sulfides might also be extracted during this step.

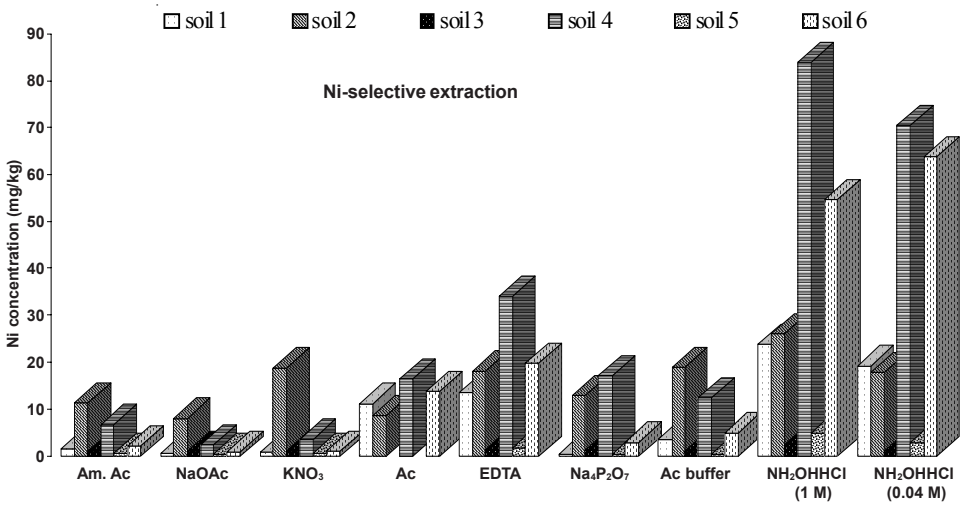

Fig. 1. Partitioning of Ni among various extraction reagents in selective extraction in samples

1.0 g of sample

↓

Exchangeable and carbonate fraction

Setp-1 → 40 mL 0.11 mol L^{-1} CH_3COOH; Extraction time: 16 h

↓

Reducible fraction

Setp-2 → 40 mL 0.1 mol L^{-1} NH_2OHHCl pH 2; Extraction time: 16 h

↓

Oxidizable and organic fraction

Setp-3 → 10 mL 8.8 mol L^{-1} H_2O_2 at 80 ºC (2 times)

50 mL 1.0 mol L^{-1} CH_3COONH_4 pH 2; Extraction time: 16 h

↓

Residual

3 mL HNO_3/H_2O_2 heating on a hot plate to dryness

Setp-4 → 5 mL HNO_3/H_2O_2 heating on a hot plate to dryness

5 mL 1.0 mol L^{-1} HNO_3

Fig. 2. Sequential extraction scheme modified from BCR for metal speciation

The results obtained using sequential extraction for soil samples were summarized in Table-3. Fig. 3 shows the extracted percentages of Ni in all steps of the sequential extraction procedures. The highest percentages of nickel in exchangeable and carbonates fractions were observed to be 18.8 % for soil 1 while it was found to be 25.8 % in Fe-Mn oxide fractions and 15.7 % in organic and sulfide phases for the same soil.

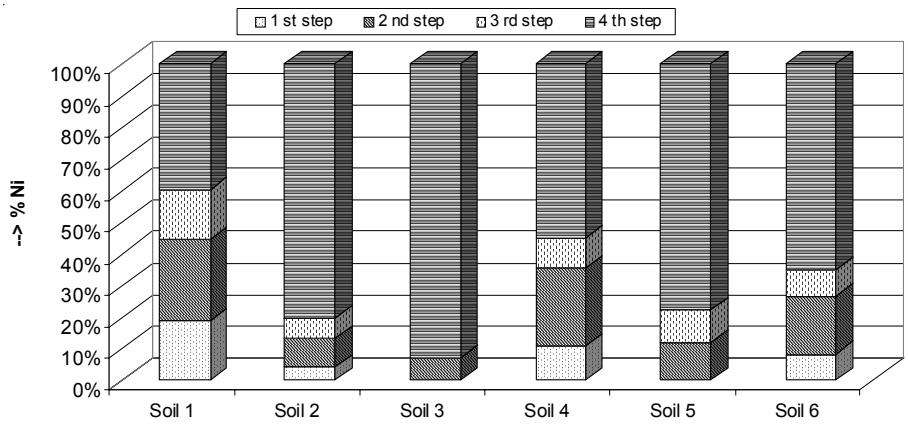

Fig. 3. Partitioning of Ni among steps in sequential extraction of soil samples

In the examined soils, Ni levels are in ranges < DL-121 mg kg^{-1} in first step, < DL-270 mg kg^{-1} in second step and < DL-107 mg kg^{-1} in third step. The maximum Ni concentrations for all steps were obtained from soil 4.

The results of Ni concentrations in samples of plant parts were also given in Table-3. The observed Ni concentrations of all studied plants were in the range of 0.81-39 mg kg^{-1} for roots, 0.3-10 for stems and 0.85-107 for leaves.

A major limitation to the widespread adoption of sequential extraction for trace element sequestration is the lengthy sample processing time[22] and BCR sequential extraction schemes require an overall operation time of about 18 and 51 h, respectively. Hence, some authors have attempted to develop more rapid means of extraction, involving ultrasonic or microwave assistance and also continuous flow extraction techniques and rotating coiled columns[23]. The goal of such studies is generally to obtain performance similar to that of a well-established methods. As a result, different shaking times lower than the 16 h (the time for BCR method) were applied to a typical soil (soil 2) in this study. Comparing different shaking times (Fig. 4), it was found that Ni concentrations increased for shaking 16 h compared to 2 h and 5 h while no increase in 5 h than 2 h.

Translocation factor and enrichment coefficient (bioaccumulation factor): One of the characteristics of hyperaccumulator plants is the ability to accumulate high concentrations of metal or metalloid in the above ground biomass. Translocation factor (TF) *i.e.*, the ratio of element concentrations in shoot and/or leaves tissue to element concentrations in root tissue for a biomonitoring metal is typically >1.

Translocation factors for Ni in the *Rumex* plants were found in range of 1.4-3.8 (Fig. 5 and Table-3). The enrichment coefficient or bioaccumulation factor (EC) *i.e.*, the ratio of element concentration in aboveground tissue to element concentration in soil must also be higher than 1 for hyperaccumulated metal. The enrichment coefficient in studied samples was found lower than 1. Consequently, it can be concluded that *Rumex* leaves can be used biomonitoring, but not used for bioremediation.

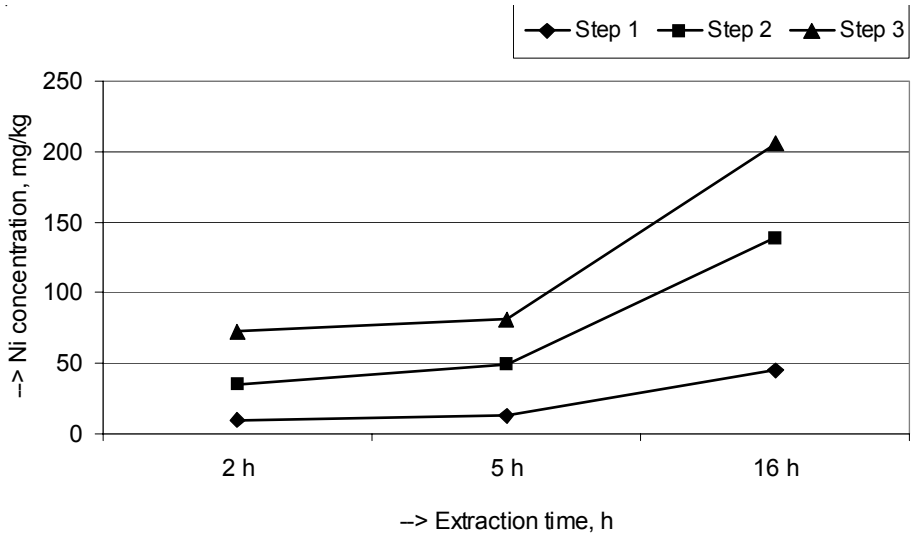

Fig. 4. Effect of extraction time on Ni concentration in soil sample by using sequential extraction

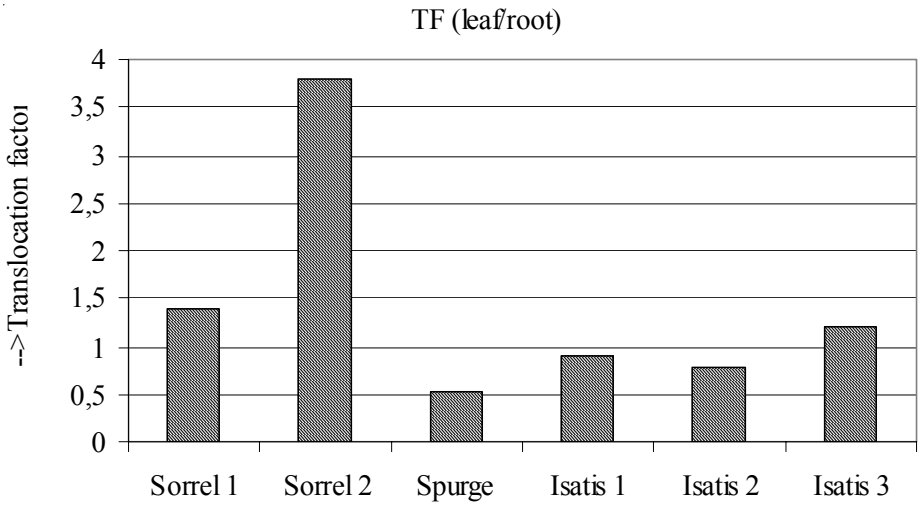

Fig. 5. Translocation factors for *Rumex* (Sorrel), *Euphorbia* (Spurge) and *Brassicasea* (Isatis)

Conclusion

The extraction procedure recommended by the Commission of the European Communities Bureau of Reference (BCR), was applied to different types of soil samples. The used sequential extraction procedure permits the evaluation of the different chemical forms present in soils. Therefore different selective chemical reagents and three sequential extraction procedure (BCR) used in this work were found useful to determine the mobility and chemical forms of Ni in soil samples. Ni concentrations in the hydroxylamine hydrochloride extracts were found higher compared to other extracts. From the Tables 2 and 3, it is observed that the results opbtained by using FAAS are in agreement with the results by using ICP-MS. It can be concluded that Rumex leaves can be used biomonitoring but not used for bioremediation.

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