Plant Uptake of Heavy Metals in Andong Serpentine Soil

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Abstract − **Serpentines soil have high values of magnesium and low values of calcium, and are usually deficient in N and P, but rich in iron, Ni, silicates. We investigated serpentine soil properties and measured the content of nutrient elements and heavy metals in shoots and root of plant species which were in common at serpentine and non-serpentine areas in Andong, Korea. The soils showed higher pH value above 6.9. The contents of Ni, Cr, Fe and Mg of serpentine soils exhibited 77, 27, 5.5 and 12.5 times more than in non-serpentine soils, respectively. The content of Na was almost same but K was two times higher in non-serpentine soil, compared with serpentine soil. The contents of nutrient element such as K, Ca, Na and P in serpentine plants did not show conspicuous differences with non-serpentine plants. On the other hand, the concentrations of Ni, Cr, Fe, Mg and Mg/Ca were very high in plant on serpentine area. The all plant species collected at the serpentine site were bodenvag plants, which are not restricted to a specific type of substrate. By the plant species and parts of plant tissues, the absorption levels and patterns showed high variation and were species-specific. *Carex lanceolata, Lysimachia clethroides* and *Cynanchum paniculatum* contained much chromium and *Eupatorium chinense* and *C. paniculatum* exhibited high contents of Ni. In leaf tissue, *C. lanceolata, Rubus parvifolius, Festuca ovina, Quercus serrata,* and *L. clethroides* took comparatively large amount of Cr in serpentine area. *E. chinense* contained large amount of Ni, Cr and Fe in a leaf tissue. The stem of *Galium verum, Juniperus rigida* included high amount of Cr, Ni and Fe. And *C. paniculatum* absorbed large amount of Ni and Cr in the stem.**

Key words : serpentine, heavy metals, plant species-metals relations, Andong

INTRODUCTION

Soil developed on serpentinites represents high concentrations of Mg, Cr, Ni, and Mg/Ca, but the paucity of essential macronutrients such as K (Kruckeberg 1984). They are often lacking in major plant nutrients such as nitrogen, phosphorus and potassium. These distinctive edaphic factors provide unique challenges to the vegetation of these areas. The presence of high levels of metals in soils exerts a pressure on plant species leading to the selection of a specific flora. Plants growing on metal-loaded soils respond by exclusion, indication or accumulation of metals (Baker 1981). Metal hyperaccumulator plants comprise species that accumulate above 10,000 mg kg^{-1} of Mn and Zn, 1,000 mg kg^{-1} of Cu, Co, Cr, Ni, and Pb or 50 mg kg^{-1} of Cd in their shoots (Baker and Brooks 1989; Wenzel and Jockwer 1999). These plants have attracted the interest of plant and soil scientists because of their role in the development of phytomining technologies for the treatment of metal-polluted soils, sediments and water resources (Wenzel *et al.* 1999), and the physiological effects of heavy

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metals on the plant growth, genetic adaptation or tolerance (Mengoni *et al.* 2003).

A large number of species have developed the ability to accumulate Zn, Cd, Ni, Co, Se, and Cu, and are usually endemic to various metalliferous soils (Baker *et al.* 1992). The greatest diversity of hyperacculumator species evolved in Ni-rich serpentine soil such as *Alyssum* genus (Baker *et al.* 1989)

The distribution of serpentine areas in Korea is locally restricted in Hongsung of Chungchungnam-do, and in Andong and Ulsan of Gyeongsang-do. Song *et al.* (1991), studying in Baekdong serpentine area, suggested that the element contents in soil were originated from properties of parent rock and the plant species collected at that sites exhibited different concentrations among metal elements. There was direct relationship between the concentration in plant and the concentration in soil. Kim *et al.* (1997) have reported a high absorption of Zn, Sc and Fe by *Gypsophila oldhamiana* at Hongseong serpentine area, and Mun *et al.* (1988) observed poor growth and a low biomass of *Miscanthus sinensis* in the serpentine gangue soils compared with that of a non-serpentine soil.

The objects of this study were to investigate the plant species which contained high concentration of heavy metals, and tried to find the species specific patterns of heavy metal uptake at naturally contaminated soil such as serpentine.

MATERIALS AND METHODS

1. Study site : Andong serpentine area

Andong serpentine area (E 128°26′ ~ 128°30′, N 36°31′ ~ 36°32′) is very conspicuous one because of largely exposed a basset. Andong serpentinite is the dunite originated from the upper mantle. Kim (1998) studied the vegetation and flora on Andong serpentine area. He reported that there was no endemic plants, *Pinus densiflora*, *P. rigida* and grass land was prevailing at that site. Also he showed that the growth of two pine species were retarded at serpentine soil, in contrast to the pine forest on adjacent non-serpentine terrain. But, currently, the serpentine area has been mined by Sinlim and Pungcheon mining company for the industrial use.

The climate of the study site is characterized by warm/humid summers and cold winters, and average annual air temperature and precipitation are 11.8°C and 1,050 mm, respectively (Korean meterological administration, www.kma.go.kr).

2. Soil analysis

Soil samples were taken at random in the location of plant sampling. Top soil was collected at a depth of approximately 10 cm and air-dried. For the analyses of soil properties, dry soil samples were sieved through a 2 mm stainless screen. Soil pH was determined using pH meter (Corning 530) after mixing 1 g of soil in 2.5 mL distilled water for about 30 min. Organic matter was determined by loss on ignition and the soil texture by hydrometer method. For element analysis, subsamples of soil (n=4) were prepared by using 5 mL HNO_3, 3 mL H_2O_2 and 5 mL HCl per 1 gram of sieved (< 1 mm) soil (Martin 1993). Concentrations of Ca, P, Na, K, Fe, Ni, Cr and Mg were analyzed by ICP-AES (inductively coupled plasma-atomic emission spectrometry, JY-ULTIMA2).

3. Plant analysis

17 plant species were sampled at serpentine in parallel with non-serpentine sites. By parts of plant tissue, each plant sample was washed in deionized water and dried at 60°C for 48 h. *Carex lanceolata* and *Festuca ovina*, because of a difficulty dividing leaf and stem part, were analyzed as the shoot. The roots of 8 plants among 17 plant species were researched for element contents, as well. Samples of each parts of plant tissues were digested by wet digestion method using 10 mL HNO_3 and 3 mL $HClO_4$ (Helrich 1990). The prepared plant samples were processed in the same way with soil samples. For plant element analysis, two replicates per each plant sample were used.

4. Statistical analysis

Four replicates were used for all measurements of soils and two determinations for element contents of plant samples. A one-way ANOVA was performed to determine differences between serpentine and non-serpentine soils for contents of heavy metal and nutrient elements using SPSS (Ver. 12.0.1, SPSS Inc.).

RESULTS AND DISCUSSION

1. Characteristics of serpentine soil

Eight elements (Ca, P, Na, K, Fe, Ni, Cr and Mg) were analyzed together with pH, C, N and soil organic matter (SOM) contents in soil samples collected on the serpentine and non-serpentine sites (Table 1 and 2). Serpentine soil showed a high pH value, SOM contents and low water capacity because of a low clay value. C and N contents did not show significant difference between both sites. The concentration of Ni, Cr, Fe and Mg in serpentine soil showed high values, comparing with non-serpentine soil, but relatively lower contents of heavy metals than serpentine soil at New Zealand and Europe continent (Proctor 1971; Brooks 1987; Lombini 1998). High Ni (1897.5 $\mu g\ g^{-1}$) and Cr (574.8 $\mu g\ g^{-1}$) concentrations and Mg/Ca (66.2) observed in serpentine sites showed the facts that our soil samples were derived from ultramafic rocks, which contains rich amount of Fe, Ni, Mg and Cr (Rabchevsky 1985). Potassium content showed a high value in non-serpentine soil, but Ca, Na and P concentrations were not significantly different between serpentine and non-serpentine soils.

2. Heavy metals and nutrient elements concentrations in plant tissue at serpentine soil

The heavy metals in serpentine soil are absorbed by plants growing on it, then affect growth of plants and various biological activities of the ecosystem. Heavy metal contents of plants investigated in Andong serpentine and non-serpentine areas showed relatively higher levels in serpentine plants than non-serpentine plants. Though there have been a deviation by plant species or plant individuals, high heavy metal contents of plants at serpentine sites have been reported in many works (Lyon *et al.* 1971; Kim *et al.* 1997; Song *et al.* 1999; Kataeva *et al.* 2004).

Table 3 summarizes the contents of the elements Ca, K, Na, P, Cr, Ni, Fe and Mg in samples of the plant species collected at random on the serpentine and non-serpentine areas. Most plant species from serpentine site exhibited a high Mg/Ca, low K and P contents. Among heavy metal elements, Nickel concentration showed a significant difference between serpentine and non-serpentine plant species, but chromium concentration, except a few species such as *C. lanceolata, L. clethroides* and *C. paniculatum*, did not show the apparent difference between serpentine and non-serpentine site for all part of plant tis-sues.

Ni contents in plant varied depending on the species and plant tissues, and the concentrations showed the ranges of 4.1 to 113.5 $\mu g\ g^{-1}$ in leaf tissues and from 4.6 to 108.8 $\mu g\ g^{-1}$ in stem. Leaves of *E. chinense* exhibited the highest concentration of Ni with 113.5 $\mu g\ g^{-1}$, and the stem of *C. paniculatum* with 108.8 $\mu g\ g^{-1}$. But leaf of *P. grandiflorum* from non-serpentine area with 4.4 $\mu g\ g^{-1}$ presented rather high Ni concentration, compared with 4.1 $\mu g\ g^{-1}$ in that

Table 1. Soil properties of serpentine soil and non-serpentine soil at Andong area

	pH	Soil texture (%)			C (%)	N (%)	C/N	Soil organic matter, SOM (%)
		Sand	Silt	Clay				
Non-serpentine	5.3~6.0	32.2~61.5	15.8~31.5	20.4~48.6	1.51 (±0.57)	0.13 (±0.05)	12.9 (±8.6)	5.9
Serpentine	6.9~7.4	57.7~70.8	19.6~29.1	9.1~17.7	1.28 (±0.3)	0.14 (±0.04)	9.6 (±3.4)	8.3

Table 2. Comparisons of some nutrient elements and heavy metals concentrations in serpentine and non-serpentine soils. Values are means ±S. D. (n=4)

	Ca ($\mu g\ g^{-1}$)	P ($\mu g\ g^{-1}$)	K ($\mu g\ g^{-1}$)	Na ($\mu g\ g^{-1}$)	Cr** ($\mu g\ g^{-1}$)	Ni** ($\mu g\ g^{-1}$)	Mg* ($mg\ g^{-1}$)	Fe*** ($mg\ g^{-1}$)	Mg/Ca**
Non-serpentine	1529 (±651)	174 (±60)	861 (±384)	147 (±20)	21.4 (±5.0)	24.2 (±8.2)	9.0 (±2.1)	25.7 (±4.7)	6.54
Serpentine	1852 (±384)	232 (±10)	419 (±79)	137 (±9)	574.8 (±128.8)	1897.5 (±638.7)	112.6 (±57.1)	143.3 (±22.3)	66.2

For each elements, the p value is associated with null hypothesis that the true mean is the same for all soil of two sites; statistical analyses were performed by t-test (*: $P<0.05$, **: $P<0.01$, ***: $P<0.001$).

Table 3. Nutrient and heavy metal elements in parts of plant tissue on non-serpentine and serpentine areas (N.S: non-serpentine site, S: serpentine site)

Species	Part	Site	Ca	K	Na	P	Cr	Ni	Fe	Mg
			μg g^{-1}							
Carex lanceolata	Shoot	N. S	3984	3935	1450	499	1.0	3.1	132	1054
		S	2874	7192	1668	422	4.3	42.0	509	4674
Festuca ovina	Shoot	N. S	2324	5746	1075	721	1.3	5.0	263	968
		S	1796	1971	941	758	2.5	12.5	294	1704
Thalictrum aquilegifolium	Leaf	N. S	13168	6771	1577	777	0.9	3.9	92	2111
		S	14928	2749	1482	916	1.3	22.3	111	8010
	Stem	N. S	3430	3270	1488	379	0.9	1.4	41	617
		S	2763	2135	1334	450	0.6	4.9	45	1460
Lysimachia clethroides	Leaf	N. S	8604	5680	1086	1266	0.1	2.5	294	6331
		S	5491	3420	1051	830	2.5	7.5	511	8366
	Stem	N. S	3843	7876	1229	1283	0.1	0.1	99	1945
		S	3340	3569	1015	459	2.5	6.3	436	5716
Cynanchum paniculatum	Leaf	N. S	27265	6798	1313	1578	0.1	2.5	238	5190
		S	9564	4761	1131	1043	2.5	57.5	278	16069
	Stem	N. S	4318	5201	1134	825	0.1	2.5	98	1375
		S	2815	3400	1085	565	2.5	108.8	120	6115
Rubus parvifolius	Leaf	N. S	12974	4649	399	916	1.3	5.0	364	5119
		S	8324	3398	345	1183	2.5	15.0	314	7589
	Stem	N. S	5769	3675	364	633	0.1	2.5	196	1698
		S	4829	4754	363	708	0.1	10.0	135	4054
Quercus serrata	Leaf	N. S	11598	1901	319	873	0.1	2.5	179	3765
		S	6409	1464	304	663	2.5	12.5	231	6409
	Stem	N. S	11145	1441	305	550	0.1	5.0	166	1414
		S	4209	1094	294	358	0.1	11.3	151	2160
Juniperus rigida	Leaf	N. S	19404	2600	343	785	1.3	3.6	280	1668
		S	6087	1649	263	819	2.0	45.3	344	3602
	Stem	N. S	18651	1292	298	486	1.9	4.4	592	771
		S	7399	1203	246	600	2.5	12.9	500	1929
Cocculus trilobus	Leaf	N. S	21214	7425	345	1330	0.9	1.3	255	1482
		S	6576	3661	326	1008	2.1	27.3	401	7070
	Stem	N. S	5536	2825	287	568	0.9	1.3	264	708
		S	2182	1749	246	560	1.9	13.4	309	1590
Platycodon grandiflorum	Leaf	N. S	17171	13496	304	1330	4.6	4.4	307	6072
		S	8060	7643	333	1095	1.0	4.1	250	8176
	Stem	N. S	3758	8631	306	791	1.4	2.3	90	1493
		S	2061	3482	273	386	1.1	4.6	128	2260
Eupatorium chinense var.	Leaf	N. S	17946	8918	330	1303	0.9	6.8	282	13740
		S	13262	4482	310	1298	3.3	113.5	694	22684
	Stem	N.	S3344	9774	341	613	0.8	2.9	94	2235
		S	2507	4924	318	562	1.1	22.3	162	6694
Zanthoxylum schinifolium	Leaf	N. S	14839	6935	380	1216	0.6	3.9	144	4025
		S	9637	2104	330	940	1.4	39.6	279	13382
	Stem	N. S	6835	6382	368	1076	0.8	2.5	102	1407
		S	3223	2213	302	651	1.0	21.1	192	2673
Lindera obtusiloba	Leaf	N. S	10132	6401	387	1030	0.6	3.9	133	2177
		S	4935	2291	339	704	0.9	13.3	141	5254
	Stem	N. S	5679	2393	294	658	0.9	2.4	74	782
		S	2087	954	275	367	0.5	5.3	51	1114
Pinus densiflora	Leaf	N. S	2973	3095	312	729	0.5	2.0	115	790
		S	1300	2242	279	665	0.6	7.8	97	1229
	Stem	N. S	5400	1271	297	360	1.1	1.8	298	706
		S	1520	1255	275	395	0.9	5.4	179	961

Table 3. Continued.

Species	Part	Site	Ca	K	Na	P	Cr	Ni	Fe	Mg
			μg g⁻¹							
Atractylodes japonica	Leaf	N. S	14932	10634	1095	807	1.1	3.0	196	5413
		S	5540	5689	1001	910	1.5	45.8	255	10644
	Stem	N. S	4235	6401	896	461	0.9	2.0	138	1413
		S	2820	1791	844	424	1.8	11.4	263	2230
Lespedeza cyrtobotrya	Leaf	N. S	18268	4434	1050	1902	0.8	4.0	204	2940
		S	8823	1869	845	880	1.0	15.9	236	3373
	Stem	N. S	4191	1771	840	667	0.5	3.8	48	556
		S	3052	2362	931	569	0.9	37.6	122	1322
Galium verum var.	Leaf	N. S	18225	6013	1022	870	3.3	3.1	244	3263
		S	12529	2339	995	872	2.3	43.9	365	4705
	Stem	N. S	9565	3120	1019	531	0.9	1.3	96	1430
		S	7661	4917	1006	513	3.3	30.0	631	2531

from serpentine area.

Cr concentration in *C. lanceolata* shoot from serpentine site was 4.3 $\mu g\ g^{-1}$, equibalent amount to the 0.7% Cr concentration of soil. The leaves of *E. chinense* (3.3 $\mu g\ g^{-1}$), *C. paniculatum* (2.5 $\mu g\ g^{-1}$) and *R. parvifolius* (2.5 $\mu g\ g^{-1}$) contained relatively high content of Cr at serpentine area. But, exceptionally, shoot of *P. grandiflorum* (4.6 $\mu g\ g^{-1}$) and leaf of *G. verum* (3.3 $\mu g\ g^{-1}$) on non-serpentine site showed very high values in Cr concentrations than that on serpentine site.

3. Species specific patterns of heavy metal uptake by the serpentine plants

Reeves *et al.* (1996) had classified plant species found on serpentine soils into two groups: (a) serpentine-tolerant or serpentine-facultative plants; (b) serpentinicolous, serpentine-endemic or serpentine-obligate plants. At Andong serpentine soils, serpentine-endemic species did not found (Kim 1998) but all of species were bodenvag species (Plant not restricted to a specific type of substrate) which also distributed at non-serpentine areas or serpentine-tolerant plants. In a New Zealand, *Myosotis monroi*, *Notothlaspi australe* and *Pimelea suterir* only presenting on serpentine soils have been reported to endemic plant species (Lyon *et al.* 1971). Also, *Cerastium nigrescens* in UK (Proctor and Woodell 1975), and *Quercus durata* and *Geonothus jepsonii* in US (Callizo 1992) have been reported as serpentine endemics. The presence of the endemic species are affected by the factors such as age of serpentine formation and size of land, so on (Kruckeberg 1984; Brookes 1987). Andong serpentine area, there are all bodenvag plants, had been influenced by severe disturbances by human activities such as collection of fire woods, or medicinal herbs and small size of land.

Each plant species absorbed heavy metals at different trends according to the kinds of element and plant tissue on serpentine area (Fig. 1). In leaf tissue, *C. lanceolata*, *R. parvifolius*, *F. ovina*, *Q. serrata*, and *L. clethroides* absorbed relatively small amount of Ni, but large amount of Cr, comparing with other common species in serpentine area. *E. chinense* in a very common species took large amount of Ni, Cr and Fe in a leaf tissue. In different ways with absorption of metals by leaf tissue, the stem of *G. verum*, *J. rigida* absorbed high amount of Cr, Ni and Fe. *C. paniculatum* absorbed large amount of Ni and Cr in the stem.

The ratio of Ni (0.1 ~ 1.11) and Cr contents (0 ~ 0.48) showed higher values in roots than in leaves and stems of most plant species. *E. chinense* have higher amount of Ni in leaf tissue than root (leaf/root of Ni; 1.11). *A. japonica* (0.91), *Q. serrata* (0.5), and *G. verum* (0.27) showed higher leaf/root of Ni than the stem/root (0.23, 0.45, 0.18, respectively). On the other hand, *C. panicum* and *P. glandflorum* showed higher stem/root of Ni than the leaf/root (Fig. 2).

The stem/root of Cr contents in *G. verum*, *P. grandiflorum* and *A. japonica* were comparatively higher (above 0.2) than leaf/root in their plants, and showed large ratio of stem/root than leaf/root. On the other hand, *E. chinense* and *Q. serrata* exhibited significantly large ratio of leaf/root of Cr than in stem/root.

The plant species on the naturally contaminated soil area, namely, serpentine area was investigated to screen the

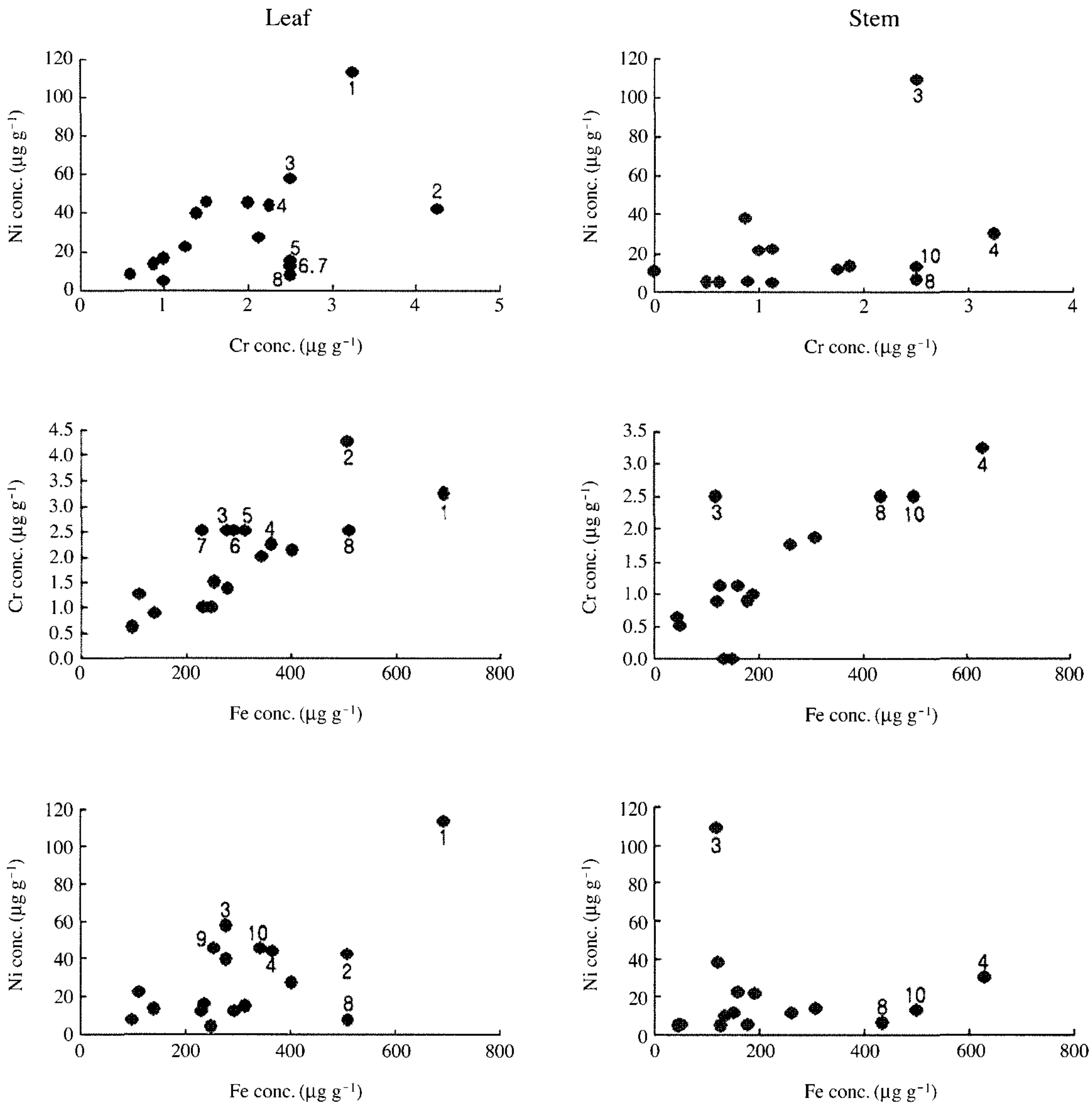

Fig. 1. Absorption patterns of Ni, Cr and Fe in leaf (n=17) and stem (n=15) tissues of each plant species in Andong serpentine area. There are species specific pattern of heavy metal absorption among plant tissues and plant species. 1: *E. chinense*, 2: *C. lanceolata*, 3: *C. paniculatum*, 4: *G. verum*, 5: *R. parvifolius*, 6: *F. ovina*, 7: *Q. serrata*, 8: *L. clethroides*, 9: *A. japonica*, 10: *J. rigida*.

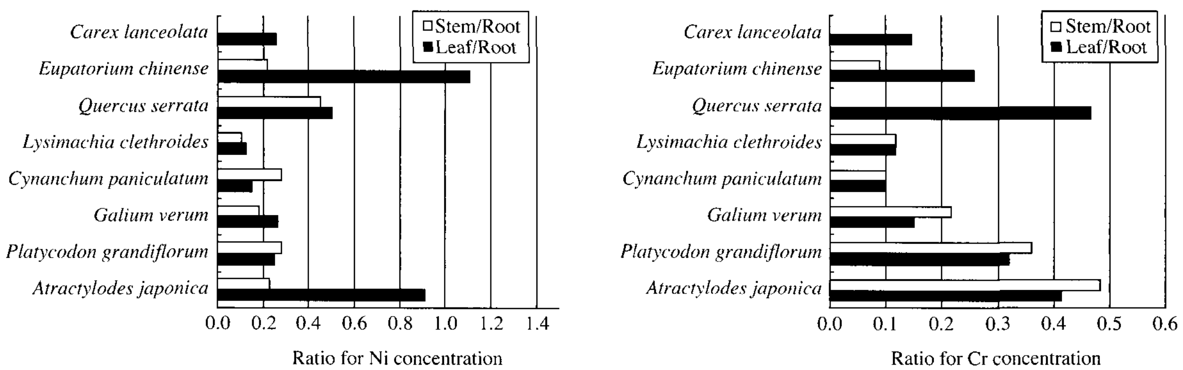

Fig. 2. The ratio of Ni and Cr content in root, leaf, and stem of plants collected from the serpentine site. (No bars: not detected or very low concentrations).

species which have tolerance and absorption of heavy metals, and experimented what kind of heavy metal was accumulated by plant part. This ecological study could make practical application of industrial use such as bioremediation with the study of heavy metal tolerance and accumulation of plants in the mine tails (Jung *et al.* 1993; Kim *et al.* 2002; Ok *et al.* 2003) and laboratory works (Lee and Lee 1996; Jeon and Choi 2006).

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