Distribution of Thallium in Soil and Plants Growing in the Keban Mining District of Turkey and Determined by ICP-MS

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ABSTRACT

In this study, we examined the Tl concentrations in soil and plants taken from an abandoned Pb-Zn-Cu mining area (Keban, Turkey). This region contains Pb, Zn, and Ag sulphide mineralizations that have been mined for 6000 years. For this purpose, soil and plant parts (including roots and shoots) were taken from 20 points in that area and the Tl concentrations determined by ICP-MS. The plants *Euphorbia macroclada*, *Verbascum cheiranthifolium Boiss*, and *Astragalus gummifer* were examined. The Tl levels in the soils ranged from 3.0–27.6 mg kg^{-1} which is 3–27 times higher than in uncontaminated soils (1.0 mg kg^{-1}). The observed Tl levels in plant parts ranged from 0.05–4.62 mg kg^{-1} which is up to 92-times higher than the allowable levels (0.05 mg kg^{-1}) proposed in the literature. It was also observed that high concentrations of metals such as Mo, Cu, Pb, Zn, Ag, and As inhibit the Tl uptake by plant roots and shoots.

INTRODUCTION

With respect to degree of toxicity, Tl ranks alongside Pb, Hg, and Cd. Thallium is emitted into the environment due to lead, zinc, and similar mining activities. Studies with regard to Tl concentrations in environmental and plant samples are relatively new and rare (1). Plants may also serve as biomonitors of anthropogenic contaminants. Since Tl is a highly toxic element, it has caused a number of outbreaks of poisoning around the world, even resulting in high mortalities (2–3). Therefore, all data relating to Tl concentrations in the environment are of significant importance. To this effect, a detailed environmental Health Criteria monograph on Tl was published by the World Health Organization - International Program on Chemical Safety in 1996 (4).

Thallium is present in the environment as a result of natural processes and from anthropogenic sources. It is emitted into the environment from the mining processes of sulphide ores containing heavy metals (in particular lead, zinc, and copper) as well as from industrial sources such as coal-burning power plants, brick works and cement plants, combustion of fossil fuels, oil refining, and metal smelting (4).

Thallium is also used in small quantities in the electronics industry, the production of certain glasses and crystals, and in the manufacture of medical diagnostics tools such as scintigraphy. In the past, Tl has commonly been used as a rodenticide, but its use for this purpose has been banned in many countries (4–7).

The concentration of thallium (5) in plants (shoots and roots) from the calamine waste heap was found 100–1000 times higher than the level normally found in plants [0.05 mg/kg Tl dry wt (8)]. Furthermore, an average concentration of thallium of geological origin of 1.54 mg/kg dry wt (with a maximum value of 55 mg/kg) has been reported for soil (6). Tremel et al. found that rape seeds (*Brassica napus*) contained the largest amounts of thallium, up to 33 mg/kg dry wt (shoots, up to 20 mg/kg dry wt) (7).

In China (2004), thallium contents ranged from 40 to 124 mg/kg in soils originating from the Tl–Hg–As mineralized area; from 20 to 28 mg/kg in slope wash materials; from 14 to 62 mg/kg in alluvial deposits downstream; from 1.5 to 6.9 mg/kg in undisturbed natural soils; and from <0.2 to 0.5 mg/kg Tl in soils in the background area (9). In 1981, emissions from a cement plant in Germany led to high Tl concentrations in soils, river sediments, brooks, and in garden vegetables (10). Several recent studies report on the relationship between Tl concentrations in environmental samples such as soil, water and plant, and their possible health effects (5,11–13). These studies also point out that more research is required to investigate the accurate concentration of Tl in all environmental and biological samples.

Thallium concentrations in uncontaminated areas have been found to range from 0.01 to 1.0 mg kg^{-1} (ppm) for soil, less than 1 ng mL^{-1} (ppb) for water, and below 0.1 mg kg^{-1} for plants (dry weight) (14). Concentrations exceeding 1 mg kg^{-1} in soil (basis on dry weight) are usually indicative of an anthropogenic source. On the other hand, much higher values have been found in the vicinity of some metallic ore deposits, metal works, and a surrounding cement plant (5,9–10,15–17). Thallium occurrence and its effects

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on plants were reviewed in detail by Heim et al. (18). They found that the median top-soil content is 0.5 mg/kg in the area investigated, and the moss Pleurozium schreberi grown in this area contains 0.04–0.13 mg/kg and the moss Polytrichum formosum between 0.01 and 0.05 mg/kg T1.

The most common techniques for the determination of Tl at very low levels are flameless atomic absorption spectroscopy (flameless AAS) (5–7), inductively coupled plasma optical emission spectroscopy (ICP-OES) (18), inductively coupled plasma mass spectrometry (ICP-MS) (15,19), voltammetry (20), and X-Ray fluorimetry (21).

In this study, Tl concentrations were determined by ICP-MS in top-soil samples, the roots and shoots of the plants, including *Euphorbia macroclada*, *Verbascum cheiranthifolium Boiss*, and *Astragalus gummife*, all found in the Keban mining area. The results were compared in order to investigate the correlation between the soil and the root and shoots of the plants growing there.

EXPERIMENTAL

Instrumentation

A PerkinElmer SCIEX ELAN® 9000 inductively coupled plasma mass spectrometer was used for the determination of uranium and thallium (PerkinElmer SCIEX, Concord, Ontario, Canada). The operating conditions as recommended by the manufacturers (23) are given in Table I.

The Study Area

In this study, the plants and associated soil samples were collected from an area consisting of granitic-syenitic rocks in the Keban mining district (Elazig, Eastern Turkey) (Figure 1). This area has a Pb-Zn mining history going back 6000 years and is heavily contaminated with toxic metals such as Pb and As due to ancient and modern mining activities.

Plant Samples

The vegetation in the investigated area is very poor and only a few annual and biannual plant species are scattered on an otherwise barren rocky landscape. The plant species found in the Keban region are able to grow in severe climate conditions because of their massive and deep-reaching root systems and their ability to live in areas not enriched with organic material. Briefly, *Euphorbia macroclada Boiss* (local name: Sütlegen), *Verbascum cheiranthifolium Boiss* (local name: Sigir Kuyrugu), and *Astragalus gummifer* (local name: Keven) are among the plant species examined for this study. Their ability to live in heavily contaminated areas and their deep-reaching root systems were the criteria for choosing the plants.

TABLE I
Operating Conditions for ICP-MS

Inductively coupled plasma	PerkinElmer SCIEX ELAN 9000 ICP-MS
Nebulizer	Cross-flow
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

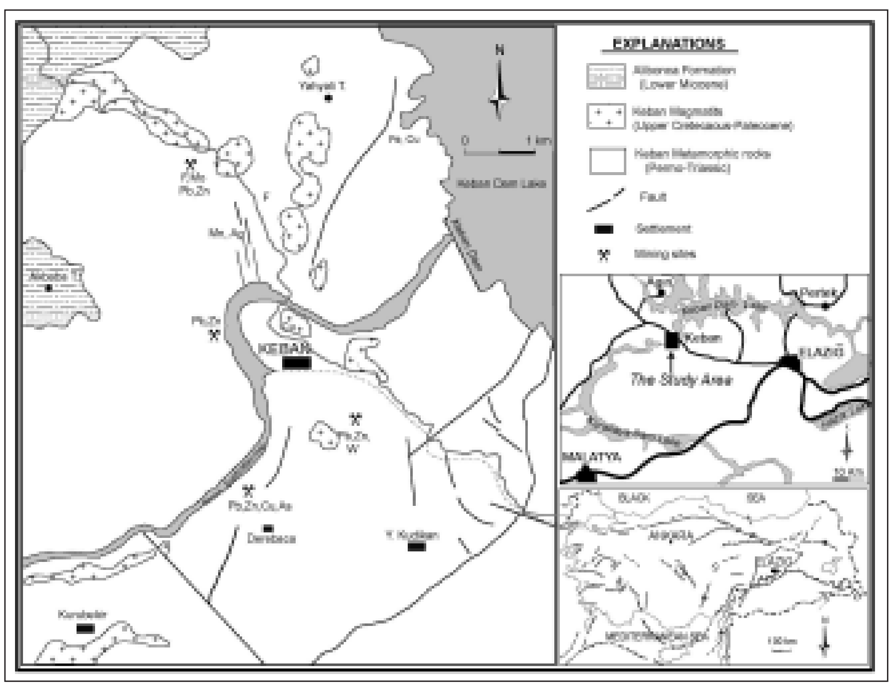

Fig. 1. Geological map of the study area (simplified from Akgul (23).

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Preparation of Samples

The plant samples (including the root) and surrounding soil were taken from 20 sites of the Keban mining area in Elazig, Turkey.

Plant Samples

The plant samples were collected randomly, and the collection sites selected represented the whole of the Keban mining area. Triplicate shoot and root samples were taken from each sampling site. The root samples were taken from a depth of 30–40 cm. The shoot and root samples of the studied plants were thoroughly washed with tap water followed by distilled water and dried at 100 °C in an oven for 30 minutes, then at 60 °C for 24 hours. The plant samples were ashed by heating in a furnace at 250 °C for about 30 minutes; then the heat was gradually increased to 500 °C for 2 hours. These ashed samples (1.00–3.00 g) were ground with hand mortars, then labeled, and analyzed by ICP-MS at ACME Analytical Labs in Canada using the parameters listed in Table I.

For digestion of the ashed samples, concentrated HNO_3 was added (2 mL was used for 1.0 g) to each sample and heated on a hot plate below 95 °C for one hour. The mixture of HCl–HNO_3–H_2O (1/1/1) was then added and further heated on a hot plate for one hour at 95 °C by stirring occasionally (6 mL of the mixture at a ratio of 1/1/1 was used for 1.0 g). The ratio of the ashed Tl samples to dry samples was found to be as follows: *Euphorbia*: 42%, *Verbascum*: 44%, *Astragalus*: 44 % at the studied conditions described below. Thus, the metal concentrations on a dried-weight basis were calculated from the concentrations on ashed-weight basis.

Soil Samples

Triplicate soil samples (1.0 g) were collected from 30–40 cm depths in the area surrounding the roots. For digestion of the soil samples, HCl–HNO_3–H_2O was added (6 mL of the mixture at a ratio of 1/1/1 for 1.0 g) and heated on a hot plate for one hour at 95 °C. Thus, all sample constituents, except the silicates, were digested.

RESULTS AND DISCUSSION

Accuracy of the method was studied by examining the shoots of various samples found in the area, including EU-21, VR-25, and AS-28, and the soil samples associated with these samples by an independent analytical method. The instrument used was a PerkinElmer Model 3100 Optima DV inductively coupled plasma optical emission spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) following the parameters as described in the manufacturer's manual. It was observed that the recoveries were at least 90% for all studied samples.

With respect to degree of toxicity, Tl ranks with Pb, Hg, and Cd, but Tl is even more toxic than these metals (2,3,5,24). It is known that the Tl content in soils depends on their geological composition and the anthropogenic contaminants. Tremel et al. (6–7) studied the uptake of Tl and its accumulation in several species of crop plants grown in soils with high Tl levels of geochemical origin. They found that *Brassica napus* (rape seeds) contained the largest amounts of Tl up to 20 mg kg^{-1} dry weight for shoots (6–7).

Our study revealed that the largest amount of Tl was accumulated in *Euphorbia*, but this accumulation depends on the other metal concentrations in the soil and root. The obtained results for all studied soil samples were found to be 3–27 times greater (Table II – see next page) than the Tl concentrations in uncontaminated soils as reported by Smith and Carson (13). This can be attributed to the presence in that area of sulphide ores containing lead, zinc, silver, and CaF_2. The correlation between the levels of other elements and Tl are given in Table III. It can be seen that there are significant positive correlations between Tl and Mo, Cu, Pb, Zn, Ag, and As. In addition, Tl concentrations of the studied plants were found to be 143 times (14.3 mg kg^{-1}) greater than the Tl concentrations (0.1 mg kg^{-1}) of plants grown in uncontaminated areas.

Tl in *Euphorbia*

The number such as –44, –21, –25, –28 in Table II signifies the point where plant and soil samples were collected. For example EU-44 means that the Euphorbia plant was taken from the point number –44.

Table II (see next page) shows that the Tl concentrations in both shoot and root of one Euphorbia plant (EU-44) were 143 times greater (14.3 mg kg^{-1}) than the normal levels reported in dry plant tissue (0.1 mg kg^{-1}). Lower Tl concentrations were found in the root and shoot of EU-29 despite higher Tl levels in the EU-29 soil sample. It is interesting to note that the Cu and Zn concentrations (5412 and 18,042 mg kg^{-1}, respectively) in the EU-29 soil sample were 30 and 16 times greater than in those of the EU-44 soil sample (145 and 1585 mg kg^{-1},

TABLE III
Correlation Relationships Between Tl and Other Metals in Soils of the Keban Mining Area

	Mo	Cu	Pb	Zn	Ag	As
Tl	0.85	0.83	0.85	0.84	0.86	0.85

TABLE II
Thallium and Other Metal Content in Soil With Roots and Shoots of the Studied Samples:
Euphorbia m., *Verbascum c.*, **and** *Astragalus g.*

Sample No.	In Plants (in mg kg^{-1}) Tl in root	Tl(*) in shoot	Mo in root	Mo in shoot	Cu in root	Cu in shoot	Pb in root	Pb in shoot	Zn in root	Zn in shoot	Ag in root	Ag in shoot	As in root	As in shoot	In Soil (in mg kg^{-1}) Tl (*)	Mo	Cu	Pb	Zn	Ag	As
EU-21	1.17	1.72(1.56)	85	43	12	3.2	243	13	104	95	0.246	0.173	35	2.6	12.6(11.4)	136	27	654	188	0.66	111
EU-24	0.29	0.47	78	137	15	4.9	152	16	100	100	0.207	0.053	21	2.8	6.7	127	57	687	292	1.15	130
EU-26	0.45	0.49	55	23	30	9	242	14	126	53	0.189	0.039	42	5.2	8.3	313	49	773	449	0.75	380
EU-29	1.46	0.11	686	124	949	33	1985	68	3600	190	3.124	0.124	332	10.2	27.6	2636	5412	7089	18042	24.1	1806
EU-31	0.75	0.46	68	260	15	10	211	32	180	70	0.18	0.113	13	2.9	7.1	423	135	1353	631	1.93	117
EU-34	0.31	0.05	60	68	13	6.3	277	76	269	92	0.247	0.097	20	5.9	4.2	94	35	815	821	0.88	75
EU-41	1.36	0.27	171	39	26	4.8	557	21	186	83	0.308	0.052	39	2.9	10.8	466	61	1600	412	1.46	185
EU-44	4.62	0.05	273	75	44	4.5	1179	49	436	155	1.457	0.142	63	3.7	16.1	578	145	2802	1585	4.48	279
EU-45	0.22	0.05	11	3	19	4.7	338	13	81	15	0.254	0.034	29	1.3	3	22	65	1301	305	1.15	96
VR-25	0.41	0.3(0.28)	81	80	61	27	16	295	194	254	0.104	0.365	3	63.5	11.6(10.5)	115	41	550	593	0.56	423
VR -25Y	0.15	0.23	26	28	40	22	79	140	238	202	0.122	0.215	24	35.8	11.6	115	41	550	593	0.56	423
VR-27	0.68	0.47	9	13	9	10	27	40	26	42	0.055	0.079	24	28.1	4.3	16	3	26	24	0.08	56
VR-35	0.08	0.13	16	16	25	20	138	195	147	237	0.2	0.317	11	22.7	4.2	94	35	815	820	0.88	75
VR-47	0.23	0.18	23	13	18	12	240	218	222	224	0.202	0.291	18	18.6	3	48	33	651	671	0.67	69
AS-22		0.1		95		13		156		102		0.263		18.3	8	114	80	1206	529	2.15	164
AS-28		0.42(0.38)		26		4.7		47		70		0.07		32	14.3(13)	22	5	57	307	0.11	95
AS-32		0.16		402		27		395		208		0.433		25	7	411	127	1365	681	1.88	104
AS-36		0.2		362		30		419		241		0.541		27.1	12.9	1243	240	3640	1190	14.4	129
AS-40		0.58		375		20		552		108		0.308		39.2	12	589	76	1843	407	1.21	142
AS-42		0.67		303		28		528		171		0.394		45.4	13.4	342	96	1713	670	1.5	220

(*): The results in parenthesis represent the values obtained by using ICP-OES.

respectively). Similarly, the Mo and Pb concentrations (2636 and 7089 mg kg^{-1}, respectively) of the EU-29 soil sample were 5 and 3 times greater than those in the EU-44 soil samples (578 and 2802 mg kg^{-1}, respectively).

In addition, Ag and As concentrations of the EU-29 soil samples were greater by 5–6 times than the concentrations of EU-44. As a result, it may be said that these six metals have antagonistic effects on Tl absorption of *Euphorbia* due to their high concentrations (particularly Cu and Zn) in the EU-29 soil sample and their similar chemical properties. The proportion of Tl concentration in shoot to root for EU-29 was found exceedingly lower (0.011) than for EU-44 (0.075). This result proves the antagonistic effect described above, particularly in the Tl uptake from root to shoot. In addition, higher concentrations (Table II) of the metals Mo, Cu, Pb, Zn, Ag, and As in EU-29 in comparison to both EU-44 and other EU-plant parts (especially in root) also prove the antagonistic effects of these metals on Tl uptake by the plant. Distributions of Tl between the studied soil and plant parts are given in Figures 2 and 3. As can be seen, antagonistic effects from the elements can be observed in the plants grown in Cu-, Zn-, Mo-, Pb-, Ag-, and As-rich soils, resulting in lower amounts of Tl taken up by the roots and shoots of the plants.

Tl in *Verbascum*

As can be seen from Table II, the Tl concentrations in both root and shoot of the VR-27 *Verbascum* plant were higher than in the other *Verbascum* samples despite the higher Tl concentrations in the soil samples around these plants. The Mo, Cu, Pb, Zn, Ag, and As concentrations in the soil samples with number VR-25 and VR-25Y were 7–25 times higher than in the soil sample with number VR-27. Thus, it can be said that Mo, Cu, Pb, Zn, Ag, and As also inhibit the Tl uptake by the VR-25 and VR-25Y *Verbascum* plant from the soil. On the other hand, Tl levels in both root and shoot of the VR-35 *Verbascum* plant and VR-47 *Verbascum* plant were significantly lower than in those of the VR-27 *Verbascum* plant, although the Tl levels of those three soil samples around these three plants were close to each other. These results may also be attributed to the antagonistic effects of Mo, Cu, Pb, Zn, and Ag due to their higher concentrations given in Table II for the VR-35 and VR-47 *Verbascum* soils, which were found higher, that is at least five times than that of VR-27 *Verbascum* soil. Distributions of the Tl concentrations found between the studied soil and plant parts are given in Figures 2 and 4. Antagonistic effects of these elements on Tl uptake and their reflection of Tl content in the root and shoot samples were found to be very similar to the VR-27 *Verbascum* plant.

Tl in *Astragalus*

As can be seen from Table II, the antagonistic effects of Mo, Cu, Pb, Zn, and Ag on the Tl uptake of the *Astragalus* samples (AS-36 and AS-40 *Astragalus* plants) were similar to those described above for the *Euphorbia* and *Verbascum* plants. Although the Tl concentrations in the AS-36 and AS-40 soil samples were very close to each other, the Tl levels in the AS-36 shoots were three times lower than those in the AS-40 shoots. The Mo, Cu, Pb, Zn, and Ag concentrations in the AS-36 soil samples were higher than in the AS-40 soil sample. The Cu, Zn, and Ag concentrations in the AS-36 shoots were also greater than those in the AS-40 shoots. Distributions of the Tl concentrations between the studied soil and the plant parts are given in Figures 2 and 5. These figures show that an increase in Tl concentration in the soil caused the increase in plant Tl concentrations.

From Figure 2 it can be seen that the Tl levels in the all Euphorbia roots linearly change with the Tl levels in the soil, except for the EU-44 sample. The corresponding values for VR and AS do not change linearly with Tl in the soil samples. In addition, any clear positive correlation between Tl concentrations in the shoot and the soil samples for the three studied plant species was not observed (Figures 3, 4, and 5). These results can be attributed to the mechanism of Tl uptake by plants from the soil and the Tl transfer to shoots, as well as the other metal levels present in the soil and root samples.

The transfer of toxic metals from soil to plant parts is significantly important because of their subsequent uptake by humans with deleterious consequences. The aim of this study was to determine the relation between Tl concentrations in plant parts and the corresponding soil samples. It can be seen that the transfer of Tl from soil to plant depends on the matrix element concentrations. Scheckel et al. (22) reported higher thallium levels in the leaves of *Iberis intermedia* than in its roots when Tl was added to the soil. In this study, the Tl concentrations of only some shoot samples were found to be higher than in their roots.

CONCLUSION

Most of the observed Tl levels in the *Euphorbia*, *Verbascum*, and *Astragalus* plant samples (including leaves, roots, and surrounding soil) from the Keban mining area of Elazig, Turkey, were found to be higher than the Tl concentrations of uncontaminated soil (higher than 1.0 mg kg^{-1}) and allowable levels for plants (0.05 mg kg^{-1}). It was concluded that such high Tl-containing lands are not suitable agriculture soils because the plants grown in such areas can uptake high and ultimately toxic levels of

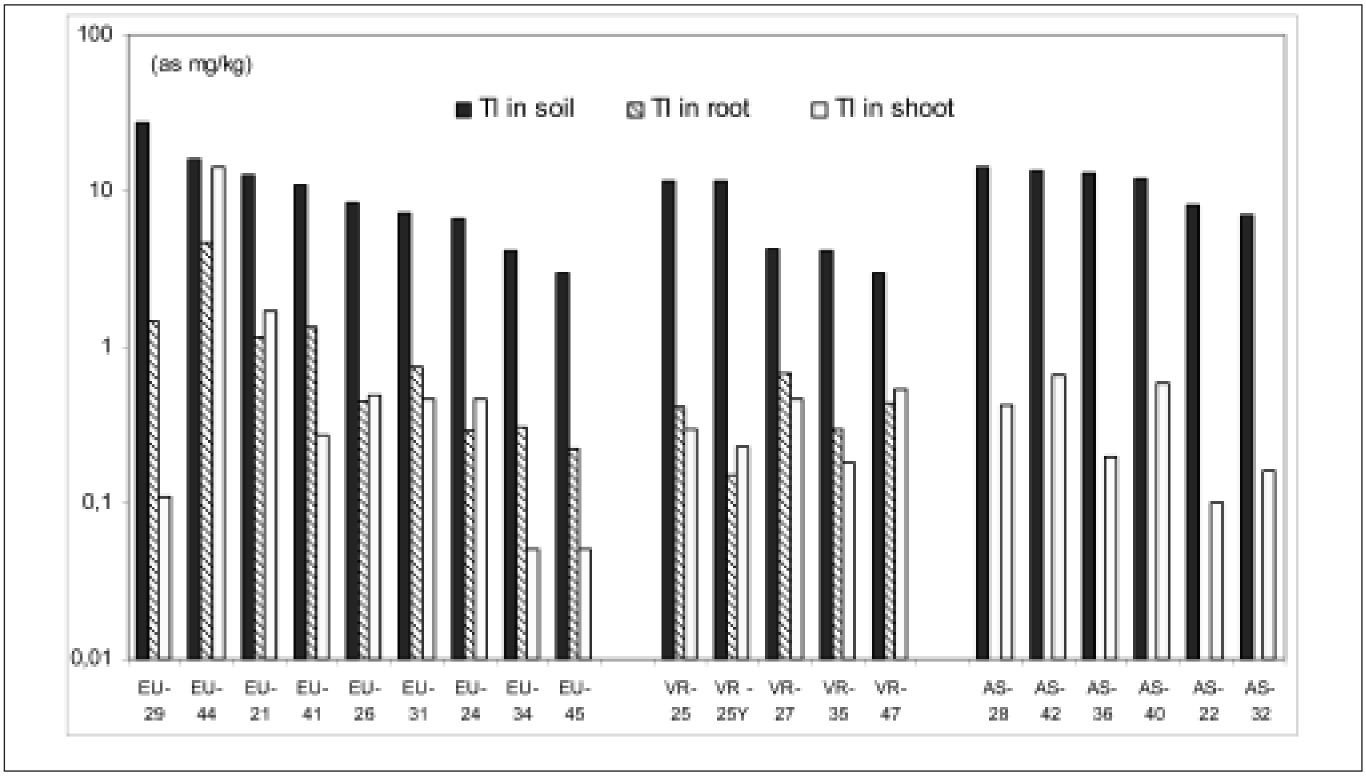

Fig. 2. Histograms for Tl contents of soil, root and shoot samples (EU: Euphorbia, VR: Verbascum, AG: Astragalus) in the Keban mining area.

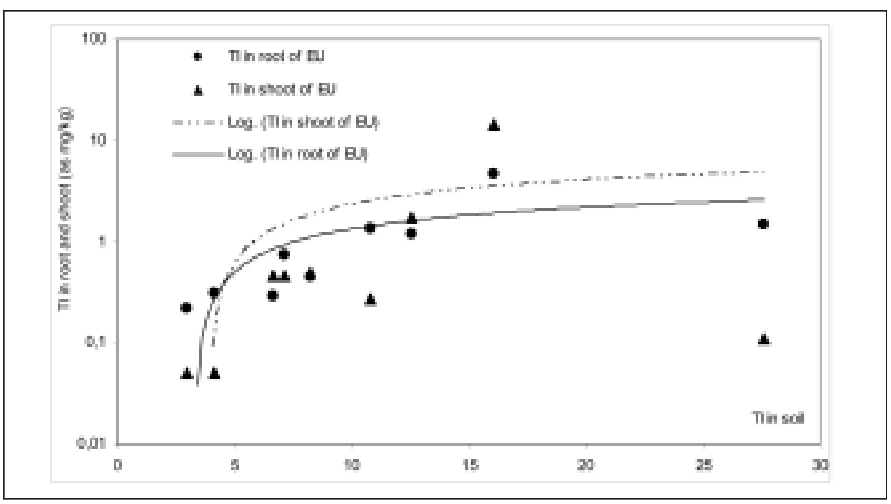

Fig. 3. Correlation relationships for Tl between root and shoot of Euphorbia with soil in Keban mining area.

Tl concentrations. It was also observed that Mo, Cu, Pb, Zn, As, and Ag inhibit the Tl uptake by plant root from soil and by plant shoot from root. It can, therefore, be said that these antagonistic effects can benefit in controlling the Tl uptake abilities of plants.

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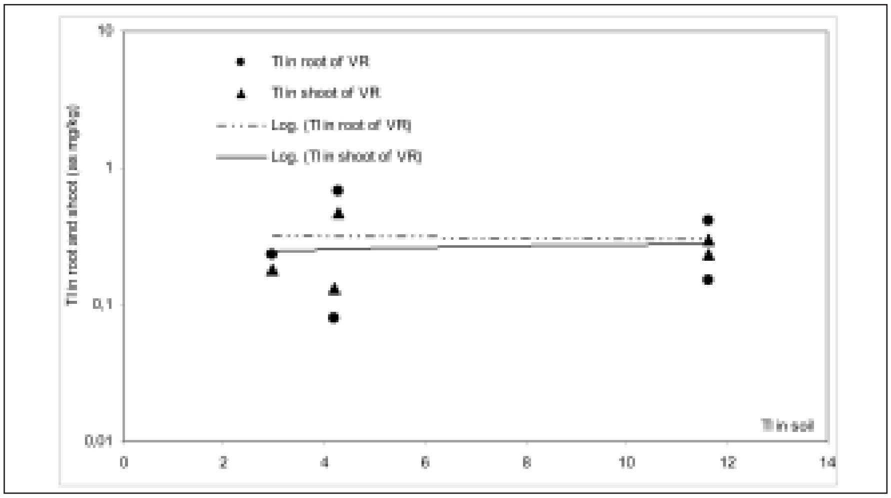

Fig. 4. Correlation relationships for Tl between root-shoot of Verbascum with soil in the Keban mining area.

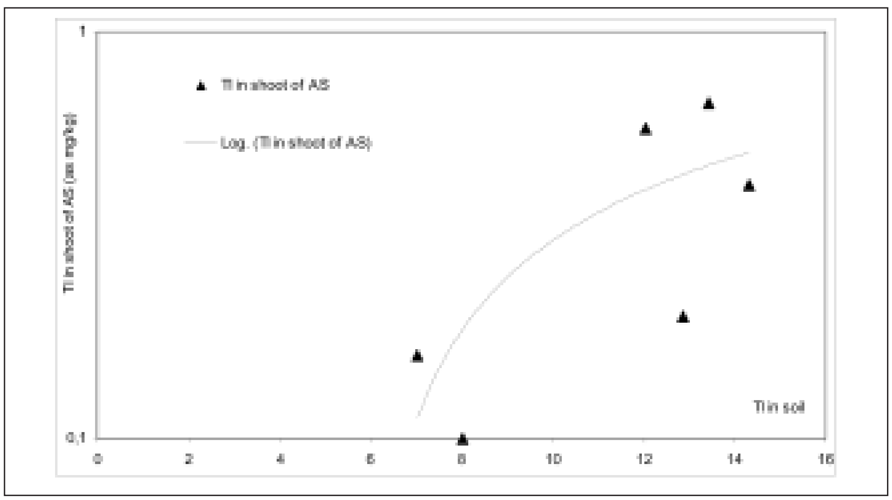

Fig. 5. Correlation relationships for Tl between shoots of Astragalus with soil in the Keban mining area.

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