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Inductively Coupled Plasma Mass Spectrometric (ICP/MS) Determination of Thallium in Soils and Winter Rapeseeds

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INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRIC (ICP/MS) DETERMINATION OF THALLIUM IN SOILS AND WINTER RAPESEEDS

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The ICP/MS method with lutetium, bismuth and indium as internal standards was used for the determination of thallium and other elements, i.e. Ti, V, Cr, Ni, Cu, Zn, Rb, Mo, Cd, As and Pb, in soils and rapeseeds. Samples were collected in two thallium highly pedogeochemically contaminated areas situated in South Bohemia and in Czech-Moravian Highlands, in two river alluvia, in two control sites with low levels of Tl and in one spot with anthropogenic contamination. Levels higher than 2.5 mg kg^{-1} have been found in rapeseeds in the highly polluted areas (c. 2.8 mg kg^{-1} in soils). High correlation coefficients, $r > 0.81$, between content of Tl in top- and sub-soils and rapeseeds were obtained. Thallium concentrations exceed twice of Pb content and by one order of magnitude of Cd amounts. This finding are very important because of the high toxicity of Tl and the absence of threshold limits for Tl in soils, agricultural products and foodstuffs in the Czech Republic.

Keywords: Thallium; Soils; Rapeseeds; ICP/MS; Atomic emission spectrometry; Mass spectrometry

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INTRODUCTION

Thallium is a rare and dispersed element that occurs mainly in sulphur containing ores and potassium minerals. Both, mono- and trivalent, thallium and their compounds are nonessential and they are toxic ^[1] to all organisms (plants, animals, humans). Thallium is more toxic than lead and it is relatively slowly removed from living organisms ^[2].

There is only little detailed information on the thallium status of soils ^[3,4]. The median 0.29 mg kg^{-1} and the maximum more than 50 mg kg^{-1} were found for $\text{HNO}_3/\text{H}_2\text{O}_2$ extracts of French soils ^[4,5]. The extremely high contents of thallium in several regions were explained by the pedogeochemical origin. Reports on the anthropogenic soil contamination are scarce [3]. Ores smelting, cement production, combustion of fossil fuels, etc. are the primary anthropogenic sources of thallium ^[2,3].

Thallium was found to be relatively mobile in soils ^[6]. The phytoavailability of the element depends on plant species ^[2,7,8]. Winter rape (*Brassica napus* L.), and in lesser extent turnip and garden cabbage accumulated Tl into the aerial parts (up to 20 mg kg^{-1} of dry weight). For the other plant species (carrot, French bean, potato, winter wheat), the amount of Tl taken up is lower and Tl is accumulated in roots. Relatively high Tl concentrations (up to 33 mg kg^{-1} of dry weight) were found in rape shoots and seeds ^[4]. The Tl content prompts questions on the potential of pedogeochemical Tl for food chains contamination. Garden cabbage, turnip and rape cattle cakes could be placed under control since high correlation coefficients between Tl content in soil and plants ($r > 0.6$) have been found.

Several analytical procedures can be used for the determination of thallium ^[9]. Flame atomic absorption spectrometry and inductively coupled plasma emission spectrometry are not very sensitive for the determination without pre-concentration ^[10]. Electrothermal atomic absorption spectrometry is more sensitive but Zeeman background correction and stabilized temperature platform furnace have to be used ^[4,11,12]. Extraction spectrophotometric determination of thallium in soils was also applied ^[13,14]. Inductively coupled plasma mass spectrometry (ICP/MS) was found to be very suitable method for the determination of thallium ^[15,16]. Both thallium isotopes, ^{203}Tl and ^{205}Tl , can be used for the determination.

Masson *et al.* ^[17] studied the soil extraction procedures suitable for the determination of thallium. Digestion by nitric acid and hydrogen peroxide proved to be the most suitable. Aqua regia soil extracts have been used for the determination of many potentially dangerous elements in soils and the extraction procedure has been internationally accepted ^[18–20], but

thallium has hardly been determined in aqua regia since HCl significantly worsen the detection limits, both in graphite furnace AAS as well as in stripping anodic voltammetry.

The main goal of the present work is to elaborate a suitable method for determination of thallium and other less commonly monitored elements in soil and plant materials (rapeseeds) from one single digestion solution and to compare their contents in sub- and top-soil and in winter rapeseed.

EXPERIMENTAL

Chemicals and apparatus

Thallium, rubidium, cadmium, lead and titanium single element standard stock solutions of 1000 mg l^{-1} and mixed standard solution containing 200 mg l^{-1} of V, 100 mg l^{-1} of Cr, 100 mg l^{-1} of Ni, 50 mg l^{-1} of Cu, 100 mg l^{-1} of Zn, 10 mg l^{-1} of Mo and 25 mg l^{-1} of As (Astapol, Analytika, Prague, Czech Republic) were used for preparation of calibrating standard solutions of appropriate concentrations. Lutetium solution of 1000 mg l^{-1} was prepared by dissolving 0.2843 g of lutetium oxide in 20 ml of 5 mol l^{-1} hydrochloric acid. After dissolution the volume was adjusted to 250 ml by water. Solutions of bismuth and indium of the same concentrations were used as internal standards. All other chemicals were from Fluka (Fluka Chemie AG, Buchs, Switzerland), Merck (Merck KGaG, Darmstadt, Germany) or Lachema (Pliva-Lachema Comp., Brno, Czech Republic). Reagents and standard solutions were prepared using Milli Q RG deionised water (Millipore, Bedford, MA, USA) further purified by sub-boiling distillation in a BSB 939-IR apparatus (Berghoef Laborprodukte GmbH, Eningen, Germany). Nitric and hydrochloric acids were purified by sub-boiling distillation in the same apparatus.

An Elan 6000 ICP/MS spectrometer (Perkin Elmer SCIEX, Norwalk, USA) with a cross flow nebulizer, a Scott's type spray chamber and a Gilson 212 peristaltic pump (see Table I for operational parameters) was used for elements determinations. A high-pressure microwave digestion system UniClever BM-lz (Plazmatronika, Wroclaw, Poland) with 110 ml Teflon vessels and maximal power of 150 W was used in three steps procedure (see Table II) for wet sample digestion in HNO_3 . An Apion Dry Mode Asher (Tessek Ltd., Prague, Czech Republic) was simultaneously used for digestion by dry ashing under superoxidative gas mixture in a heated block (max. 400°C) for comparison.

TABLE I Operational parameters of Elan 6000 ICP/MS spectrometer

<i>Parameter</i>	<i>Value</i>	<i>Parameter</i>	<i>Value</i>
RF power	1040 W	Sweeps/readings	10
Nebulizer gas flow	0.84 l min ⁻¹	Readings/replicate	1
Lens voltage	Rh 6, 9 V	Number of replicates	5
Detector	Dual mode	Measurement mode	Peak hopping
Solution flow rate	1.0 ml min ⁻¹		

Dwell time: 200 ms for Ni, Cd and As, 100 ms for Ti, Tl and Pb, 30 ms for Zn and 50 ms for all other elements (V, Cr, Cu, Rb, Mo).

TABLE II Operational parameters of high-pressure microwave digestion of rapeseeds using UniClever BM-lz

<i>Step</i>	<i>Time</i> min	<i>P_{min}</i> ^a atm	<i>P_{max}</i> ^b atm	<i>Power</i> ^c %
I.	3	17	20	70
II.	2	27	30	80
III.	5	42	45	100

^aminimum pressure in a vessel.

^bmaximum pressure in a vessel.

^cthe percentage of maximum power (150 W).

Sample collection

The ICP/MS method was applied for analyses of 39 rapeseed samples and 78 sub- and top-soils collected at the same spots. Samples were collected in two thallium highly pedogeochemically contaminated areas situated in South Bohemia and in Czech-Moravian Highlands, in two river alluvia, in two control sites with low levels of Tl and in one area with typical anthropogenic contamination. The places were selected on the basis of our previous results [16,19] taking into account the higher values of Tl in sub-and top-soils.

A mixed sample of rapeseeds from 7–10 places in the area 100 × 100 m was collected from each area. Soil samples (0–30 cm, sieved < 2 mm) were collected by the procedure described in our previous paper [16]. The samples from two horizons and two rapeseed digests were measured separately in triplicate and mean values were statistically treated. Both isotopes ²⁰³Tl and ²⁰⁵Tl were used to improve the precision of the measurements. Each series consisted of 17 samples (soils and/or rapeseeds), one internal reference standard and two blanks.

Rapeseed digestion

Usually 4 ml of concentrated nitric acid were added to 0.75 g (± 3 mg) of rapeseeds and the sample was mineralized under increasing pressure in

three steps (see Table II). Maximum temperature reached 180–190°C. After cooling, the sample digests were diluted with water up to 50 ml and analyzed by ICP/MS with Lu, Bi and In as internal standards. Several samples were simultaneously digested by dry ashing (14 h) under superoxidative gas mixture in a heated block (Apion) for comparison.

Soil extraction

Soil sample, 5.00 ± 0.005 g, was weighed into a digestion tube, 2 ml of water and 7 ml of concentrated nitric acid were added. After overnight standing, 20 ml of concentrated hydrochloric acid was added. The tubes were inserted into the block digester under the water coolers and after 30 min of standing at the laboratory temperature they were slowly heated up to 150°C and this temperature was kept for 120 min. After cooling the extracts were filtrated through the medium density filter paper into 100 ml volumetric flasks and made to the mark with water^[18,19] and diluted 1:10 with water just before measurement. Intensive cooling during the digestion was necessary to avoid possible thallium losses.

Calibration and data evaluation

Calibrating standard solutions at three different concentration levels were used (see Table III for the scheme). The concentration of the acids and lutetium, bismuth and indium in the standard calibrating solutions matched their concentrations in the sample solutions. Statistical evaluation was done by the software packages EXCEL 97 (Microsoft, Redmont, USA) and AXUM (MathSoft, UK).

TABLE III Calibration levels for construction of calibration curves

<i>Element</i> ^a	<i>St</i> ₂ ^b μg l ⁻¹	<i>St</i> ₃ μg l ⁻¹	<i>Element</i> ^a	<i>St</i> ₂ ^b μg l ⁻¹	<i>St</i> ₃ μg l ⁻¹	<i>Element</i> ^a	<i>St</i> ₂ ^b μg l ⁻¹	<i>St</i> ₃ μg l ⁻¹
⁴⁹ Ti	20	50	⁶⁵ Cu	25	50	¹¹¹ Cd	2	4
⁵¹ V	100	200	⁶⁷ Zn	50	100	⁷⁵ As	12.5	25
⁵³ Cr	50	100	⁸⁵ Rb	10	40	²⁰³ Tl	10	20
⁶² Ni	50	100	⁹⁵ Mo	5	10	²⁰⁵ Tl	10	20
⁶³ Cu	25	50	⁹⁷ Mo	5	10	²⁰⁸ Pb	10	10

^aisotope for which the calibration data were measured.

^bcalibration level 1 (blank) *St*₁ = 0.0.

RESULTS AND DISCUSSION

The optimized ¹⁶ ICP/MS method (see Table I for operational parameters) was verified using several soil samples with the reported aqua regia values from the WEPAL International Soil Exchange Programme ^[21], CRM URE 12-2-03 (*Lucerne alfalfa*, Institute of Radioecology, Košice, Slovakia, 50 mg g⁻¹ Tl) and artificial sample solutions prepared mixing four digests of rapeseed and diluting with water up to 200 ml and/or by spiking the samples with the known amounts of determined elements. Total amounts of Ti, V, Cr, Ni, Cu, Zn, Rb, Mo, Cd, As, Tl and Pb were determined in the mixed samples of rapeseed. Fortunately for thallium, at both masses in question, molecular bands from chlorides or fluorides hardly exist.

Concentration of the most elements was non-significantly affected by the digestion procedure (see Table IV for means, *n* = 3). Serious losses of Tl and As were observed when dry ashing in Apion apparatus was performed thus the microwave digestion was used in following experiments. Recovery was tested at two concentration levels by standard addition method and it was estimated to be 95–99% for Tl and 92–105% for other elements.

TABLE IV Comparison of element losses during high-pressure microwave digestion (MWD) and Apion dry ashing for the results on mixed rapeseeds samples (A, B and C)

Element	Digestion	A ^a		B ^a		C ^a	
		Concentration (mg kg ⁻¹)		Concentration (mg kg ⁻¹)		Concentration (mg kg ⁻¹)	
		Mean	SD	Mean	SD	Mean	SD
⁴⁹ Ti	MWD	0.196	0.009	0.186	0.012	0.179	0.007
	Apion	0.149	0.016	0.126	0.012	0.148	0.001
⁶² Ni	MWD	0.68	0.01	0.34	0.02	0.93	0.06
	Apion	0.62	0.01	0.40	0.04	0.96	0.03
⁶³ Cu	MWD	2.30	0.04	2.70	0.11	2.42	0.05
	Apion	3.15	0.11	3.82	0.14	3.47	0.35
⁶⁷ Zn	MWD	34.3	0.8	29.0	1.7	29.3	0.7
	Apion	30.4	2.2	26.8	1.6	26.7	1.1
⁸⁵ Rb	MWD	3.2	0.2	3.7	0.3	8.5	0.4
	Apion	3.2	0.1	3.5	0.1	8.4	0.4
⁹⁵ Mo	MWD	0.43	0.02	0.79	0.05	0.82	0.01
	Apion	0.43	0.02	0.78	0.03	0.83	0.02
¹¹¹ Cd	MWD	0.065	0.004	0.049	0.002	0.073	0.003
	Apion	0.068	0.005	0.049	0.002	0.088	0.002
⁷⁵ As	MWD	0.025	0.005	0.053	0.020	0.004	0.000
	Apion	0.014	0.006	0.034	0.004	0.007	0.000
²⁰⁵ Tl	MWD	0.083	0.003	0.077	0.004	1.123	0.014
	Apion	0.035	0.022	0.021	0.005	0.377	0.036

^aValues in bold marked the losses of element when dry ashing (Apion) was used, Ti was lost presumably as TiO₂ precipitate, As and Tl as their oxides (high vapour pressure).

The calibration curves were linear in the whole calibrating range with regression coefficients $r \geq 0.9999$. LOD (at 3S/N levels) for Tl was $0.0037 \text{ mg kg}^{-1}$ and RSD values for the complete analytical procedure were less than 8% for all elements except for As and Pb. The ICP OES and ASV analyses of five control samples confirmed the ICP/MS results accuracy for majority of the elements (see Table V).

The method was applied for analysis of 39 rapeseed samples and 78 sub- and top-soils collected at the same spots. The samples from two horizons and two rapeseed digests were measured separately in triplicate and mean values were statistically treated. The results for sub- and top-soils correlate very well with high correlation coefficient $r = 0.9791$ (see Fig. 1) that is in the agreement with our previous results obtained for larger set of data obtained during basal monitoring of soils in Czech Republic [16,18,19].

ICP/MS method was adapted for determination of thallium and other more or less commonly monitored elements in soils and rapeseeds (see Table VI). Zinc content was more stable in soils from river alluvia ($23\text{--}32 \text{ mg kg}^{-1}$) than in soils from the other spots ($19\text{--}40 \text{ mg kg}^{-1}$). Its levels differ in individual areas ($20\text{--}23 \text{ mg kg}^{-1}$ for locality 305, $31\text{--}38 \text{ mg kg}^{-1}$ for locality 306 and $21\text{--}24 \text{ mg kg}^{-1}$ for locality 702). Concentrations of copper are relatively constant in all areas except of locality 305 where significantly lower values were determined $1.8\text{--}2.0 \text{ mg kg}^{-1}$. Lead and molybdenum contents differ mainly in dependence on localities but Mo content varies more significantly in soils from river alluvia than in the other areas. Only scarce samples contained higher levels of chromium

TABLE V Comparison of results (in mg kg^{-1}) for rapeseed obtained by ICP/MS after high-pressure microwave digestion (bold values) and ICP-OES after dry ashing (normal font)

Sample	Concentration in mg kg^{-1}								
	As	Cd	Cr	Cu ^a	Mo	Ni	Pb	V	Zn
Re 4002 ^b	ND	0.03	0.02	2.15	0.42	0.37	0.03	ND	27.65
Re 4002	< 0.02	0.03	< 0.1	1.156	0.45	0.3	< 0.2	< 0.1	34.69
Re 5001 ^b	0.02	0.03	ND	2.44	0.65	0.29	0.04	0.01	24.63
Re 5001	< 0.02	0.02	< 0.1	2.335	0.6	0.29	< 0.2	< 0.1	28.41
Re 8008 ^b	0.01	0.07	0.12	2.77	0.40	0.57	0.08	0.01	27.79
Re 8008	< 0.02	0.06	< 0.1	1.925	0.37	0.51	< 0.2	< 0.1	29.98
Re 8010 ^b	ND	0.03	0.01	1.95	0.50	0.23	0.04	ND	19.34
Re 8010	< 0.02	0.02	< 0.1	1.585	0.50	< 0.2	< 0.2	< 0.1	24.24
Re 7904 ^b	0.01	0.04	0.01	2.56	0.44	1.03	0.03	0.01	26.95
Re 7904	< 0.02	0.04	< 0.1	1.435	0.55	0.82	< 0.2	< 0.1	29.16

Sample number: Re 4002 Staňkov, Re 5001 Žatec, Re 8008 Stará Bělá, Re 8010 Šenov u Nového Jičína,

^asystematically lower values for Cu were found by ICP-OES due to spectral interferences.

^bICP/MS, ND – values down to LODs, 0.11 mg kg^{-1} for samples 5001 and 8008, 0.02 mg kg^{-1} for 4002 and 0.08 mg kg^{-1} of Tl were found by ICP/MS in rapeseeds samples from uncontaminated areas.

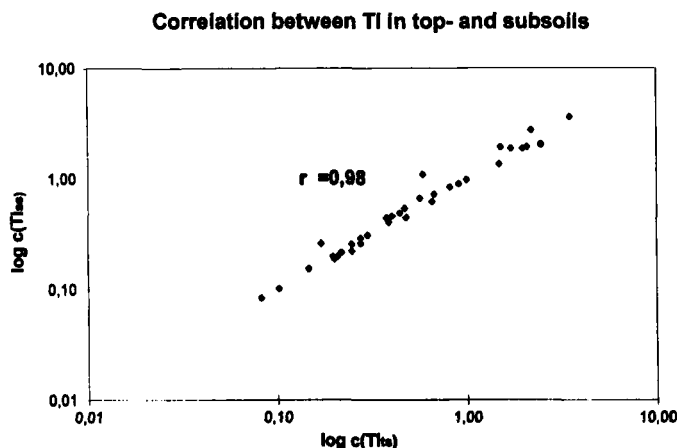


FIGURE 1 Correlation between thallium content in subsoil $\log c(\text{Tl}_{\text{ss}})$ and topsoil $\log c(\text{Tl}_{\text{ts}})$ determined by ICP/MS (experimental conditions see Table I).

TABLE VI Concentration ranges of different elements in rapeseeds collected from soils of alluvia of rivers and from TI pedogeochemically contaminated soils (in mg kg^{-1})

Isotope	Concentration in mg kg^{-1}			
	Alluvia of rivers		Contaminated soil	
	c_{min}	c_{max}	c_{min}	c_{max}
^{49}Ti	0.14	1.23	0.18	0.70
^{51}V	0.02	1.10	0.01	0.06
^{53}Cr	0.03	3.79	0.02	0.31
^{62}Ni	0.16	1.25	0.26	2.65
^{63}Cu	2.07	3.00	1.80	2.63
^{65}Cu	2.12	3.06	1.80	2.70
^{67}Zn	24.60	31.90	20.45	38.80
^{85}Rb	1.55	13.02	1.22	9.87
^{95}Mo	0.34	0.67	0.21	1.09
^{97}Mo	0.35	0.69	0.21	1.09
^{111}Cd	0.01	0.08	0.03	0.06
^{75}As	0.02	0.12	0.01	0.03
^{203}Tl	0.07	0.20	0.08	2.92
^{205}Tl	0.07	0.21	0.08	2.93
^{208}Pb	0.01	0.30	0.01	1.24
^{207}Pb	0.01	0.31	0.01	1.19

and lead while the mean values were around 0.1 and 0.05 mg kg^{-1} , respectively. Content of As was approximately twice higher in soils from river alluvia (0.04 mg kg^{-1}) than from the other soils (0.02 mg kg^{-1}). Concentrations of rubidium and vanadium were constant in all localities. Content of Rb

varied ($1.5\text{--}13\text{ mg kg}^{-1}$) or it was higher for vanadium in river alluvia soils. Surprisingly low and constant levels of Cd (0.04 mg kg^{-1}) were found. Titanium content from a single locality in river alluvia was much higher (0.82 mg kg^{-1}) than in all other places (mean 0.31 mg kg^{-1}).

More than 2.5 mg kg^{-1} of thallium have been found in the rapeseeds collected in highly polluted areas (c. 2.8 mg kg^{-1}) and Tl content depends seriously on locality (see Table VII). Generally, relatively low concentrations were found in river alluvia ($0.07\text{--}0.21\text{ mg kg}^{-1}$) while elevated values over 1 mg kg^{-1} were found in localities 702 and 305. Highly contaminated

TABLE VII Thallium concentration (for ^{203}Tl and/or ^{205}Tl) in sub-, topsoil and rapeseed in different pedogeochemically contaminated areas

Sample	Concentration of Tl (in mg kg^{-1})				
	Topsoil		Subsoil		Rapeseed
	^{203}Tl	^{205}Tl	^{203}Tl	^{205}Tl	^{205}Tl
601/01	0.204	0.208	0.196	0.198	0.07
601/02	0.218	0.218	0.214	0.216	0.08
601/03	0.242	0.248	0.250	0.256	0.19
601/05	0.244	0.248	0.216	0.222	0.09
207/01	0.166	0.170	0.258	0.260	0.07
207/02	0.294	0.300	0.300	0.306	0.11
207/03	0.266	0.276	0.254	0.260	0.09
207/04	0.098	0.102	0.100	0.102	0.10
207/05	0.194	0.198	0.194	0.198	0.10
207/06	0.148	0.146	0.152	0.152	0.08
207/07	0.080	0.082	0.080	0.084	0.09
207/08	0.144	0.146	0.148	0.154	0.20
207/09	0.268	0.278	0.282	0.288	0.10
207/10	0.196	0.200	0.182	0.188	0.09
703/11	0.560	0.564	0.656	0.662	0.15
703/13	0.652	0.654	0.604	0.616	0.19
703/14	0.466	0.488	0.524	0.536	0.21
703/18	0.658	0.670	0.712	0.720	0.21
703/21	0.582	0.586	1.078	1.090	0.25
703/29	0.370	0.378	0.438	0.440	0.08
702/13	1.932	1.964	1.854	1.882	1.12
702/14	3.462	3.512	3.668	3.666	2.18
702/25	2.446	2.474	2.048	2.046	1.50
306/21	1.486	1.502	1.938	1.938	0.16
306/23	0.480	0.478	0.438	0.444	0.17
306/24	0.904	0.908	0.880	0.894	0.17
306/26	0.810	0.814	0.822	0.836	0.16
306/27	0.444	0.440	0.482	0.486	0.15
306/29	0.384	0.390	0.396	0.402	0.17
306/30	0.398	0.402	0.448	0.456	0.16
305/11	2.082	2.076	1.936	1.944	2.54
305/12	2.202	2.186	2.738	2.770	2.93
305/16	1.466	1.474	1.354	1.360	2.58
305/17	1.712	1.706	1.894	1.888	2.58

rapeseeds sample (4.9 mg kg^{-1}) was found in the control spot with anthropogenic contamination of soils.

Highly positive correlation between Tl content in rapeseeds and in sub- and/or topsoil (see Figs. 2A, 2B) has been found. Correlation coefficients 0.815 and 0.825 were obtained for sub- and top-soils, respectively. Concentrations of Tl exceed twice the Pb content and by one order of

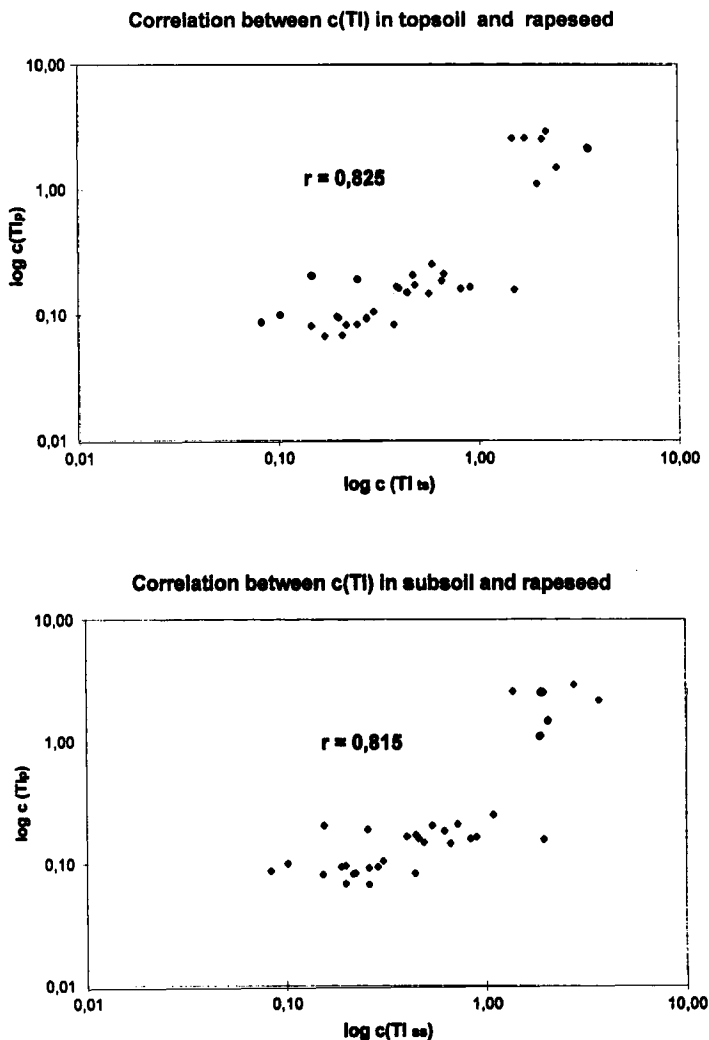


FIGURE 2 Correlation between thallium content in topsoil $\log c(\text{Tl}_{\text{ts}})$ and rapeseed $\log c(\text{Tl}_{\text{p}})$ (A) and in subsoil $\log c(\text{Tl}_{\text{ss}})$ and rapeseed $\log c(\text{Tl}_{\text{p}})$ samples (B) determined by ICP/MS (experimental conditions see Table I).

magnitude the Cd amounts. These are the very important findings because of the high toxicity of Tl and the absence of threshold limits for Tl in soils, agricultural products and foodstuffs in the Czech Republic. Partition coefficients between rapeseeds and soil (PC) up to 1.75 and 1.90 were found for top- and subsoils.

The influence of potassium content in soils on content of Tl and ratio of Rb in rapeseeds vs. soils was studied. Increasing content of potassium in soil decreases the ratio of rubidium concentrations in rapeseed vs. soils (see Fig. 3) while no correlation exists for thallium. Competitive transport of Rb^+ and K^+ due to similar ionic radii can explain the fact that an irreversible binding to $-\text{SH}$ functional groups leads to accumulation of thallium in plants containing elevated levels of sulphur without showing any remarkable toxicity symptoms and/or yield reduction and probably limits the competitive transport at the elevated amounts of K^+ .

The Tl : K proportion is geochemically feasible for total contents in minerals. Content of K in soils is enriched by fertilization and potassium ions are specifically retained by clay minerals and biomass. The $\text{HNO}_3/\text{H}_2\text{O}_2$ extract proposed [4,5,7], only marginally attacks Tl bound in acid silicates, where Tl^+ substitutes Rb^+ and K^+ , thus the influence of different extractants and Rb/K ratios were studied [20].

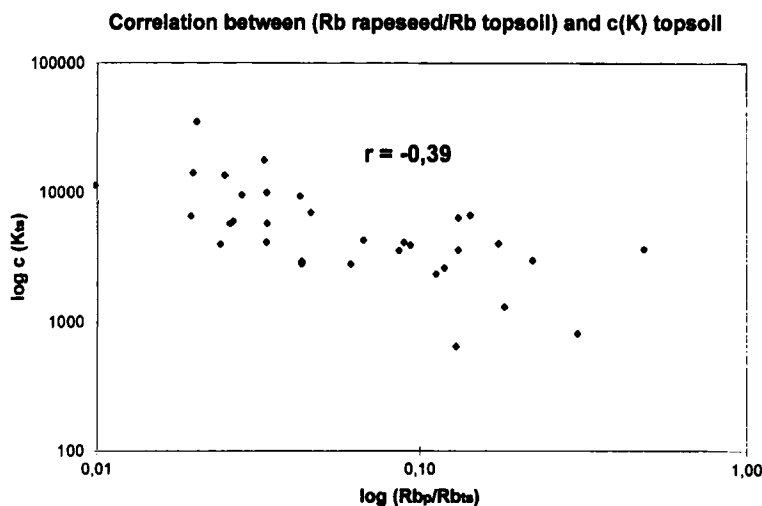


FIGURE 3 Correlation between rubidium content ratio in rapeseed and topsoil $\log c(\text{Rb}_p/\text{Rb}_{ts})$ and potassium in topsoil $\log c(\text{K}_{ts})$ (A) and in subsoil $\log c(\text{K}_{ss})$ samples (B) determined by ICP/MS (experimental conditions see Table I).

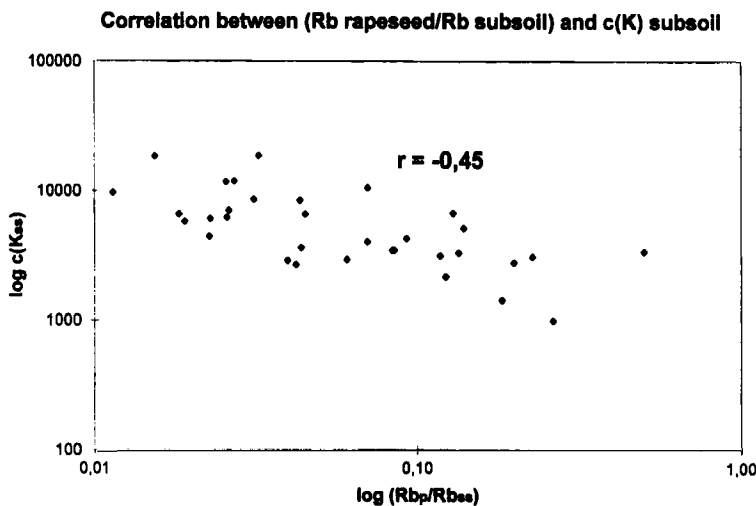


FIGURE 3A (Continued)

CONCLUSIONS

ICP/MS method was adapted for determination of thallium and other more or less commonly monitored elements in soils and rapeseeds. Thallium concentrations in rapeseeds can exceed twice the Pb content and the Cd amounts by one order of magnitude. Elevated levels of thallium without showing any remarkable toxicity symptoms and/or yield reduction were found in rapeseeds samples collected in two pedogeochemically contaminated areas. Irreversible binding to -SH functional groups leads to accumulation of thallium in plants containing elevated levels of sulphur (rapeseeds and some other plants are known to enrich thallium specifically). This is very important since it is considered as a great risk to human and animal nutrition and because of the high toxicity of Tl and the absence of threshold limits for Tl in soils, agricultural products and foodstuffs in the Czech Republic.

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