Bulletin of Geosciences, Vol. 78, No. 3, 251–260, 2003

Environmental impacts of mining of Ni-Mo black shale-hosted deposits in the Zunyi region, southern China: Preliminary results of the study of toxic metals in the system rock–soil–plant

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Abstract: The Zunyi region in Guizhou province (southern China) is well known by the occurrences of Mo-Ni-polyelement black shales that are locally mined and processed for Mo. The preliminary results of our environmentally oriented study covering the vicinity of the Xiao-Zhu mine, Jiepo-Ling and Tuan Shan Bao Mo-Ni prospects can be summarized as follows: [1] The studied surface soil samples from all three Ni-Mo prospects are characterized by increased Mo, Ni, As, Cd, Zn and Cu concentrations and lower Pb values when compared to the worldwide averages for normal soil (Bowen 1979). [2] Maximum Mo concentration was found in rice stalk and maximum As and V concentrations in the bulb of turnip close to the Xiao-Zhu Mo-Ni mine. Peak Ni, Zn and Hg concentrations were detected in corn grain of the Jiepo-Ling area. Cd accumulates preferentially in tobacco leaves where it reaches maximum values. [3] Rice grains from the Xiao-Zhu area contain anomalous concentrations of Cd and rice grains from the Tuan Shan Bao area contain anomalous concentrations of Cd, Cu and Zn. [4] Corn grains from the Jiepo-Ling area bear anomalous concentrations of Zn, Cd, Cu, Mo and Ni.

Key words: environmental impacts, mining, Mo-Ni ores, black shale, soil, crop plants, southern China

Introduction

Weathering of sulfidic black shale may cause serious environmental harm due to the (1) generation of sulfuric acid; (2) release of toxic metals contained in sulfides and other ore minerals and (3) leaching of metals from other minerals such as silicates and carbonates. Individual case studies come from Canada (Reichenbach 1992), the Czech Republic (Pašava et al. 1993), Finland (Loukola-Ruskeeniemi et al. 1999), South Korea (Chon et al. 1996), U.S.A. (Presser and Swain 1990), and other regions of the world. The Zunyi region in Guizhou province (southwest China) is well known by the occurrences of Ni-Mo-polyelement black shales that are locally mined and processed for Mo. It should be noted that this ore type is quite unique in the world especially in its anomalous concentrations of Mo and Ni. Metal mining is an important point source of trace elements in the environment. Mining, processing and disposal of tailings, along with mine wastewater, provide obvious sources of contamination (Adriano 1986). Thus, elevated levels of heavy metals from metalliferous mines are found in and around the mines due to the discharge and dispersion of mine-waste materials into the ecosystem. As a result, large areas of agricultural land may get contaminated. The main goal of this study was to evaluate environmental impacts of mining through characterization of variations in the distribution of selected trace elements in the system of rock – soils – crop plants. The preliminary results of our joint study covering the vicinity of the Xiao-Zhu mine (part of the Huangjiawan Mo-Ni deposit), Jiepo-Ling and Tuan Shan Bao Ni-Mo prospects are summarized in the following text. The location and geological position of the Xiao-Zhu, Jiepo-Ling and Tuan Shan Bao prospects are shown in Fig. 1.

Chinese metal-rich black shales

The Early Cambrian marine black shales of southern and southwestern China host Ni-Mo deposits that outcrop discontinuously throughout six provinces in a belt approximately 1600 km long. There is no volcanic activity directly

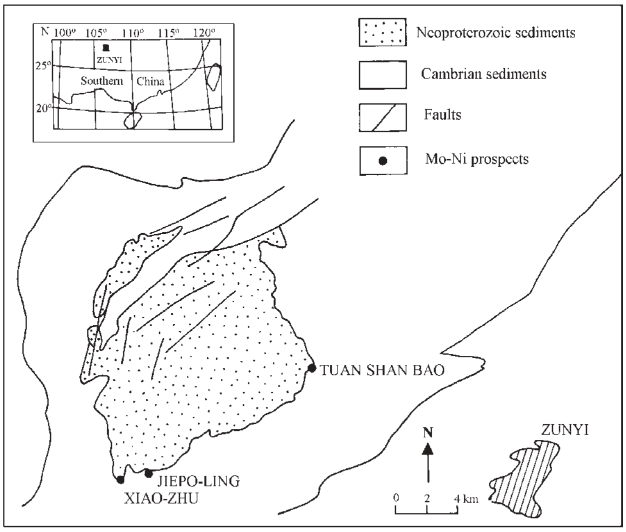

Fig. 1. Simplified geological map of the Zunyi region with locations of the Ni–Mo sampling sites in the northern part of the Guizhou province, south China.

Tab. 1. Distribution of selected trace elements in soils and crop plants and the values of biological absorption coefficients (BAC) in the Xiao-Zhu Mo-Ni prospect (Zunyi region, Guizhou province) – concentrations are in ppm and in plants they refer to dry weight

	As	As_{BAC}	Cd	Cd_{BAC}	Cu	Cu_{BAC}	Hg	Hg_{BAC}	Mo	Mo_{BAC}	Ni	Ni_{BAC}	Pb	Pb_{BAC}	Zn	Zn_{BAC}	V	V_{BAC}
Corn grain	0.55	0.026	0.03	0.027	1.79	0.024	0.015	0.071	2.04	0.04	0.69	0.004	0.30	0.014	19.76	0.087	0.59	0.001
Rice stalk	3.78	0.18	0.503	0.457	3.69	0.049	0.027	0.129	58.14	1.14	1.85	0.010	0.92	0.044	20.98	0.092	1.34	0.002
Rice grain	0.85	0.04	0.35	0.318	2.9	0.039	0.018	0.086	16.81	0.330	0.70	0.004	0.30	0.014	15.78	0.069	1.17	0.002
Turnip bulb	9.31	0.443	1.746	1.587	27.46	0.366	0.048	0.229	30.00	0.588	33.56	0.186	4.07	0.193	44.07	0.195	70.17	0.123
Tobacco stalk	0.78	0.037	1.25	1.136	14.80	0.197	0.012	0.057	2.56	0.050	4.46	0.025	0.3	0.014	32.26	0.143	18.71	0.033
Tobacco leaf	1.08	0.051	12.64	11.490	46.2	0.616	0.13	0.619	14.08	0.276	9.48	0.052	8.45	0.402	121.97	0.540	4.30	0.008
Average black shale (n = 5)	139 (38)				99.2 (13.1)				332 (66.9)		428 (201)						521 (393)	
Strongly weathered black shale (n = 1)	308		2.7		422		0.496		361		1142		33		836		1248	
Yellow surface soil*	21		1.1		75		0.21		51		181		21		226		572	
Average subsurface soil**	114.8 (24.2)		< 0.8		43.8 (7.2)		0.340 (0.188)		177.5 (48.2)		91 (72.9)		26 (9.6)		136.8 (11.8)		2594 (1615.6)	
Normal soil***	6		0.35		30		0.1		1.2		50		35		90		90	
Permissible level in soil****	20		3		100				5		100		100		300			
Normal value in crop plants*****	0.009 – 1.5		0.05 – 0.2 (0.06)		5 – 30 (2.3)		0.002 – 0.086		0.07 – 1.75		0.1 – 3.7		5 – 10 (0.44)		27 – 150 (16.6)		0.006 – 0.28	

* representative sample of surface yellow soil from the tobacco field (total of 5 sub-samples) – for more detailed description see chapter Materials and methods; ** background value of C-horizon (average of 4 samples) from the Jiepo-Ling area with standard deviation given in parentheses; *** data from Bowen (1979); **** data from Kloke (1979); ***** ranges for crop plants from Kabata-Pendias and Pendias (1984) and average values for rice grain from Yoo et al. (1992), given in parentheses

associated with these deposits. The Ni-Mo ore contains more than 4 wt% Mo, at least 2 wt% Ni, up to 2 wt% Zn, 2.5 wt% As and 1–2 g/t of precious metals, primarily Au, Pt, Pd, and Os (Fan 1983). The results of our analyses of weathered black shales from both natural outcrops and mine waste sites in the Xiao-Zhu, Jiepo-Ling and Tuan Shan Bao Mo–Ni prospects are listed in Tabs 1, 2 and 3. Macroscopically, only pyrite can be recognized in ore samples (Fig. 2). However, major ore minerals are vaesite, bravoite and jordisite (Fan 1983, Kao et al. 2001). Minor ore minerals include arsenopyrite, chalcopyrite, covellite, sphalerite, millerite, polydymite, gersdorffite, sulvanite, pentlandite, tennantite, tiemannite, violarite, and native gold (Fan 1983, Grauch et al. 1991). Re/Os isotopic data of the Ni-Mo-PGE-rich sulfide layers suggest that most of the metal enrichment of the sulfide layers occurred soon after sediment deposition, probably during diagenesis (Horan et al. 1994). A sedimentary exhalative depositional model involving submarine hydrothermal vents in shallow waters (< 250 m) with maximum temperatures near 266 °C was suggested by Lott et al. (1999) and Steiner et al (2001). These authors also indicated a possibility that some ore constituents (i.e., precious metals) were derived from a deeply circulating hydrothermal system that penetrated the Precambrian basement and interacted with mafic and ultramafic rocks. Sedimentary origin was suggested by Zeng (1998) and Mao et al. (2002).

The Huangjiawan Ni-Mo orebody is located about 25 km W of Zunyi and occurs in the form of lenses with average thickness of 0.05–0.5 m, locally up to 2 m. The ore contains 10–15 wt% of Mo + Ni in the form of various Ni-Mo sulfides.

Material and methods

Altogether 28 samples (16 rocks and soil samples, 12 samples of various parts of crop plants) were collected in the vicinity of the Huangjiawan Mo-Ni deposit (Xiao-Zhu mine) and Jiepo-Ling and Tuan Shan Bao Mo-Ni prospects in the Zunyi region.

Five samples of fresh black shale were taken in the footwall and hanging wall of the Mo-Ni ore layer in the adit No. 1 in the Xiao-Zhu Mo-Ni prospect. Two other samples of slightly weathered black shale were taken from natural outcrops at the Jiepo-Ling Mo-Ni prospect. Three samples of strongly weathered black shale come from waste dumps after Mo-Ni mining – one from the Xiao-Zhu (about 30 m below the adit No. 1), one from the Jiepo-Ling (below reference samples of subsurface soil – deeply weathered sulfide black shale) and one from the Tuan Shan Bao (about 40 m below the adit), prospects.

Three representative samples of surface soil were taken at agricultural sites (tobacco field at Xiao-Zhu, rice field at Tuan Shan Bao and cornfield at Jiepo-Ling prospects). Each sample comprised a composite of 5 sub-samples taken in center and at a distance of 1 m to the north, south, east and west from the central point. At Jiepo-Ling, four subsurface soil samples were taken from a natural outcrop from a depth of 45 cm (yellowish-brownish clayey C-horizon with average C_{tot} = 0.57 at std = 0.2 and CO_2 = 0.03 at std = 0.004). Considering similar geological situation at all three studied Mo-Ni prospects, an average of these samples was taken as a reference background value for all studied regions.

Random samples of crop plants were taken from different agricultural sites in the Xiao-Zhu, Jiepo-Ling and Tuan Ban Shao prospects. They included corn grain, leaf, stalk and spike (*Zea mays* L.), rice grain and stalk (*Oriza sativa* L.), tobacco leaves and stalk (*Nicotina tabacum* L.) and turnip bulb (*Brassica napus* L.).

Soil and rock samples were air-dried, pulverized and analyzed in the laboratories of the Czech Geological Survey in Prague. Crop plants were thoroughly washed by distilled water and dried in a clean room at room temperature for 7 days. The dried samples were pulverized in agate mortar and heated at a temperature of 500 °C. Trace elements were determined in ash (AW) and then recalculated to the original dry weight (DW). TOC (total organic carbon) and S_{tot} (total sulfur) of rock and soil samples were determined by IR C, S analyzer (Eltra) and carbonate CO_2 on a Coulomat 7012 Strohlein instrument. Ni, Cu, Zn, Mo, Pb and V were measured by flameless AAS (FAAS) on a Perkin Elmer 503 instrument with graphite cell, Cd and As by HGAAS and Hg on a mercury analyser AMA 254 in the laboratories of the Czech Geological Survey in Prague (Vítková et al. analysts).

Values of biological absorption coefficient (BAC) were calculated (BAC = Cp/Cs where Cp = element concentration in plants and Cs = element concentration in soils) and presented in Tabs 1–3.

Results

Xiao-Zhu Mine Area

Sampling of surface soil and crop plants was carried out in a shallow valley about 40 m below the adit No. 1 with waste damp located in front of the adit.

The distribution of selected trace elements in rocks, soils and crop plants compared to the values in local reference soil sample, world normal soil and crop plant is presented in Tab. 1. Surface soil in the Xiao-Zhu area is enriched in Cd, Ni, Zn and slightly also in Cu, and depleted in As, Hg, Mo and V relative to local reference soil sample. Concentrations of Mo and Ni are 10× and 1.8× higher than their permissible levels in normal soil suggested by Kloke (1979).

Fig. 2. Sample of Lower Cambrian black shale hosting Mo-Ni-PGE ores (Xiao-Zhu Mo-Ni mine, Guizhou province, south China). Macroscopically, only pyrite can be recognized.

The highest Mo concentration (58.14 ppm) was detected in rice stalk. Biological absorption coefficient (BAC = Cp/Cs where Cp = element concentration in plants and Cs = element concentration in soils) for Mo is 0.59. The highest Ni (33.56 ppm), As (9.31 ppm) and V (70.17 ppm) concentrations and also the highest values of biological absorption coefficients (Ni_{BAC} = 0.186, As_{BAC} = 0.443, V_{BAC} = 0.123) were found in the bulb of turnip (Tab. 1). Peak Cd (12.64 ppm), Cu (46.2 ppm), Pb (8.45 ppm), Zn (121.97 ppm) and Hg (0.13 ppm) concentrations and also the values of biological absorption coefficients (Cd_{BAC} = 11.49, Cu_{BAC} = 0.616, Pb_{BAC} = 0.402, Zn_{BAC} = 0.540, Hg_{BAC} = 0.619) were detected in tobacco leaves (Tab. 1).

The values of Ni/Mo, Mo/As and Ni/As ratios in surface soil and various crop plants from the Xiao-Zhu area are presented in Tab. 4. It is apparent that Mo is compared to Ni and As preferentially concentrated in rice and corn grains, rice stalk and tobacco leaf. Concentrations of Ni, Mo and As in tobacco stalk and turnip bulb reflect their distribution in surface soil.

Jiepo-Ling Mo-Ni prospect

Sampling of soil, tobacco and corn was carried out above the Mo-Ni working (Fig. 3). The distribution of selected trace elements in soils and crop plants compared to the values in local reference soil, normal soil of Bowen (1979) and crop plant is given in Tab. 2.

Surface soil from the Jiepo-Ling area shows a very close distribution of Cd, Cu, Ni, Pb, Zn and lower As, Hg, Mo and V concentrations when compared to the local reference subsurface soil sample. Concentrations of Mo and As are 15× and 3× higher than their permissible levels in normal soil suggested by Kloke (1979).

Tab. 2. Distribution of selected trace elements in soils and crop plants and the values of biological absorption coefficients (BAC) in the Jiepo-Ling Mo-Ni prospect (Zunyi region, Guizhou province) – concentrations are in ppm and in plants they refer to dry weight

	As	As_{BAC}	Cd	Cd_{BAC}	Cu	Cu_{BAC}	Hg	Hg_{BAC}	Mo	Mo_{BAC}	Ni	Ni_{BAC}	Pb	Pb_{BAC}	Zn	Zn_{BAC}	V	V_{BAC}
Corn spike	0.33	0.005	0.279	0.698	2.67	0.043	0.009	0.056	1.44	0.019	2.75	0.043	0.3	0.012	27.35	0.198	0.25	0.0002
Corn leaf	1.08	0.017	0.535	1.338	9.85	0.159	0.044	0.275	21.45	0.290	9.19	0.144	6.06	0.242	31.36	0.226	2.35	0.002
Corn stalk	0.55	0.009	0.323	0.808	4.36	0.070	0.102	0.638	4.73	0.064	2.42	0.038	0.65	0.026	20.93	0.151	1.25	0.001
Corn grain	0.40	0.006	0.161	0.403	13.11	0.211	0.005	0.031	7.40	0.100	60.66	0.948	0.3	0.012	134.69	0.969	0.25	0.0002
Corn grain	1.01	0.016	9.99	24.975	27.45	0.443	0.091	0.569	3.62	0.049	10.64	0.166	2.45	0.098	90.44	0.651	3.51	0.003
Black shale (n = 2)	72.7 (85.8)		< 0.8		10.5 (3.5)		0.62 (0.086)		162 (52.3)		73 (7)		21 (4.2)		34.5 (26.2)		3258 (1020)	
Strongly weathered black shale (n = 1)	70.6		< 0.8		24		0.199		79		118		25		158		7019	
Yellow surface soil*	62		0.4		62		0.16		74		64		25		139		1221	
Average subsurface soil**	114.8 (24.2)		< 0.8		43.8 (7.2)		0.340 (0.188)		177.5 (48.2)		91 (72.9)		26 (9.6)		136.8 (11.8)		2594 (1615.6)	
Normal soil***	6		0.35		30		0.1		1.2		50		35		90		90	
Permissible level in soil****	20		3		100				5		100		100		300			
Normal value in crop plants*****	0.009 – 1.5		0.05–0.2 (0.06)		5 – 30 (2.3)		0.002 – 0.086		0.07 – 1.75		0.1 – 3.7		5 – 10 (0.44)		27 – 150 (16.6)		0.006 – 0.28	

* representative sample of surface yellow soil from the tobacco field (total of 5 sub-samples) – for more detailed description see chapter Materials and methods; ** background value of C-horizon (average of 4 samples) from the Jiepo-Ling area with standard deviation given in parentheses; *** data from Bowen (1979); **** data from Kloke (1979); ***** ranges for crop plants from Kabata-Pendias and Pendias (1984) and average values for rice grain from Yoo et al. (1992), given in parentheses

The highest Mo (21.45 ppm), As (1.08 ppm) and Pb (6.06 ppm) concentrations and biological absorption coefficients (Mo_{BAC} = 0.290, As_{BAC} = 0.017, Pb_{BAC} = 0.242) of all studied crop plants were detected in corn leaves (Tab. 2). The peak Ni (60.66 ppm) and Zn (134.69 ppm) concentrations and biological absorption coefficients (Ni_{BAC} = 0.948, Zn_{BAC} = 0.969) were found in corn grains (Tab. 2). The highest Cd (9.99 ppm), Cu (27.45 ppm) and V (3.51 ppm) concentrations and biological absorption coefficients (Cd_{BAC} = 24.975, Cu_{BAC} = 0.443, V_{BAC} = 0.003) were detected in tobacco leaves (Tab. 2). The maximum Hg concentration and the value of biological absorption coefficient were encountered in corn stalks (Hg = 0.102 ppm, Hg_{BAC} = 0.64).

The values of Ni/Mo, Mo/As and Ni/As ratios in surface soils and rice grains from the Jiepo-Ling area are presented in Tab. 4. Clearly, concentrations of Mo, Ni and As in corn stalks and leaves are well comparable with their distribution in surface soil while Ni is preferentially taken up by corn spikes and grains and tobacco leaf.

Tuan Shan Bao Mo-Ni prospect

Sampling of soil and rice was carried out in a valley about 30 m downstream of the abandoned mine adit. The distribution of selected trace elements in soils and rice grains compared to the values in local reference subsurface soil sample, normal soil of Bowen (1979) and crop plant is given in Tab. 3.

It is apparent that surface soil from the Tuan Shan Bao rice field is enriched in Cd, Cu, Hg, Ni and Zn and depleted in Mo and Pb relative to the reference subsurface soil. The concentrations of Mo, As and Ni are 26×, 5.5× and 2× higher than their permissible levels in normal soil suggested by Kloke (1979). The following biological absorption coefficients were calculated for yellow soil/rice grains: Mo_{BAC} = 0.04, Ni_{BAC} = 0.04, As_{BAC} = 0.005, Cd_{BAC} = 0.87, Cu_{BAC} = 0.04, Zn_{BAC} = 0.09, V_{BAC} = 0.004 and Hg_{BAC} = 0.03. The concentrations of Cd, Cu, and Zn in rice grains are 20×, 1.8× and 1.5× higher that those for rice grains given by Yoo et al. (1992). Pb concentration in rice grains is lower than normal value given by Yoo et al. (1992).

The values of Ni/Mo, Mo/As and Ni/As ratios presented in Tab. 4 indicate similar distribution of these metals in surface soil and rice grains at this locality.

Fig. 3. Jiepo-Ling Mo-Ni workings (Zunyi region, Guizhou province, south China).

Discussion

In this part we discuss the distribution and behavior of individual elements in the system rock–soil–plant.

Arsenic. Arsenic concentrations in black shales of the Zunyi region are from 133 to 308 ppm with the maximum value detected in weathered black shale of the Xiao-Zhu Mo-Ni prospect. These values highly exceed the average As content of 30 ppm given for average black shale by Yudovich and Ketris (1997).

Arsenic concentrations in surface soils from the Zunyi region range from 21 to 110 ppm with the maximum value in soil sampled close to the Tuan Shan Bao Mo-Ni prospect. The average value (64 ppm) is lower than its average in the reference subsurface soil (115 ppm) and more than ten times higher than world average for soils (6 ppm) reported by Bowen (1979).

Fergusson (1990) reported average range of As in edible plants from 0.01 to 1.5 ppm (DW). The concentration of As in plants grown on uncontaminated soils vary from 0.009 to 1.5 ppm DW, with grains of brown rice containing 0.01–0.02 ppm As and grains of sweet corn containing 0.03–0.4 ppm (Kabata-Pendias and Pendias 1984). Excessive levels of As in brown rice grains (maximum 1.2 ppm) grown at a contaminated site were reported from Japan (Iimura et al. 1977). In the Zunyi region, the maximum concentration of As of all edible plants was found in a bulb of turnip (9.31 ppm) in the Xiao-Zhu Mo-Ni prospect. Rice grains and corn grains contain 0.68 ppm and 0.48 ppm As, respectively.

Cadmium. Cadmium concentrations in black shales of the Zunyi region vary from 0.4 to 2.7 ppm with maximum values detected in weathered black shales of the Xiao-Zhu Mo-Ni prospect. In all the studied Mo-Ni prospects these values are below the average Cd content of 5.3 ppm reported for average black shale by Yudovich and Ketris (1997).

The range of Cd concentrations (0.4–1.4 ppm) in surface soils of the Zunyi region is well comparable with that of polluted soils (0.6–1.9 ppm derived from metalliferous black shales of the Chung-Joo area, Okchon zone, Korea; Chon 1997). The average value of Cd (0.97 ppm) in our Chinese samples also exceeds the world average Cd content of soils (0.35 ppm), reported by Bowen (1979) and is also lower than the average value of Cd in local reference subsurface soil (< 0.8 ppm).

Based on the studies of metal contents in plants and soils in areas underlain by black shales of the Okchon zone in Korea, Chon (1997) concluded that mean concentration of Cd in crop plants is higher than those of Cu, Pb, and Zn and that the concentration of Cd in plant species decreased in the order of chinese cabbage > red pepper > soybean =

Tab. 3. Distribution of selected trace elements in soils and crop plants and the values of biological absorption coefficients in the Tuan Shan Bao Mo-Ni prospect (Zunyi region, Guizhou province) – concentrations are in ppm and in plants they refer to dry weight

	As	As_{BAC}	Cd	Cd_{BAC}	Cu	Cu_{BAC}	Hg	Hg_{BAC}	Mo	Mo_{BAC}	Ni	Ni_{BAC}	Pb	Pb_{BAC}	Zn	Zn_{BAC}	V	V_{BAC}
Rice grain	0.51	0.005	1.22	0.871	4.06	0.041	0.016	0.027	5.05	0.039	7.18	0.036	0.3	0.016	24.84	0.092	2.93	0.004
Yellow soil*	110		1.4		99		0.60		130		199		19		270		655	
Average subsurface soil**	114.8 (24.2)		< 0.8		43.8 (7.2)		0.340 (0.188)		177.5 (48.2)		91 (72.9)		26 (9.6)		136.8 (11.8)		2594 (1615.6)	
Strongly weathered black shale	184		0.4		59		1.74		113		100		16		182		1489	
Normal soil***	6		0.35		30		0.1		1.2		50		35		90		90	
Permissible level in soil****	20		3		100				5		100		100		300			
Normal value in crop plants*****	0.009–1.5		0.05 – 0.2 (0.06)		5 – 30 (2.3)		0.002 – 0.086		0.07 – 1.75		0.1 – 3.7		5 – 10 (0.44)		27 – 150 (16.6)		0.006 – 0.28	

* representative sample of surface yellow soil from the tobacco field (total of 5 sub-samples) – for more detailed description see chapter Materials and methods
** background value of C-horizon (average of 4 samples) from the Jiepo-Ling area with standard deviation given in parentheses
*** data from Bowen (1979)
**** data from Kloke (1979)
***** ranges for crop plants from Kabata-Pendias and Pendias (1984) and average values for rice grain from Yoo et al. (1992), given in parentheses

sesame > rice stalk > corn > rice grain. In our samples, Cd values decrease in the order of tobacco leaf > bulb of turnip > corn leaf > tobacco stalk > rice stalk = corn leaf > rice grain > corn grain. This is in agreement with the results of various case studies that tobacco leaf is an accumulator of heavy metals, especially Cd (Murty et al. 1986, Kim and Thornton 1993, Chon 1997 and others). Chon (1997) also reported that the biological absorption coefficients (BAC) in plants are in the order of Cd (0.08–0.244) > Zn = Cu > Pb, which suggests that Cd is more bioavailable to plants than Cu, Pb and Zn. The highest degree of bioavailability for Cd was also confirmed in crop plants of the Zunyi region (Cd_{BAC} ranges from 0.35 to 24.98) with maximum concentration (12.64 ppm) and biological absorption coefficient (11.49) in tobacco leaf. Tobacco leaf also accumulated the highest concentration of Cu, Hg, Pb and Zn. The average Cd concentration in tobacco sampled in the Zunyi region is 11.3 ppm, which is higher than that of tobacco grown on Korean alluvial soils (average 6.08 ppm) – Jung and Thornton (1996). Friberg et al. (1974) suggested that smoking of 20 cigarettes per day will cause the inhalation of 2 to 4 ppm of cadmium. Following the calculation by Friberg et al. (1974), it is estimated that a pack of 20 cigarettes from tobacco of the Zunyi region would give a total intake of 32.3 ppm.

Also concentrations of Cd determined in rice grains in the Zunyi region (0.35–1.22 ppm, average 0.625 ppm) are higher than those in rice grains from the Chung-Joo (0.10–0.22 ppm), Geum-Kwan (0.18–0.31 ppm) and Bo-Eun (0.12–0.25 ppm) areas of the Okchon zone in Korea (Chon 1997). Higher Cd and lower Pb, Cu and Zn values of biological absorption coefficients are typical for rice grains and stalks from the Zunyi region when compared to similar plants from the Okchon zone in Korea (Fig. 4).

The Cd concentration (0.35 ppm) in rice grain in the Xiao Zhu Mo-Ni prospect is very similar to that of the Chinese rice standard (0.4 ppm) reported by Ko et al. (1972). However, the Cd concentration (1.22 ppm) in rice grains of the Tuan Shan Bao Mo-Ni prospect significantly exceeds this standard value.

Higher values of Cd than normal values in crop plants (0.05–0.2 ppm, Kabata-Pendias and Pendias 1984) were also found in the rice stalk and bulb of turnip from the Xiao-Zhu Mo-Ni prospect and in corn leaf and stalk from the Jiepo-Ling Mo-Ni prospect.

Copper. Copper concentrations in black shales of the Zunyi region vary from 13 to 422 ppm with maximum value detected in weathered black shale of the Xiao-Zhu Mo-Ni prospect. Only at the Xiao-Zhu Mo-Ni prospect the Cu value exceeds more than four times the average Cu concentration of 100 ppm given for average black shale by Yudovich and Ketris (1997).

Copper concentrations in surface soils of the Zunyi region range from 62 to 99 ppm (average 79 ppm) that is higher than world average for soils (30 ppm) reported by Bowen (1979) and local reference subsurface soil sample (44 ppm).

Copper levels in plants grown on uncontaminated soils do not exceed 20 ppm, and this metal appears to be present

Tab. 4. Metal ratios in various crop plants from the Zunyi region

Locality	Xiao-Zhu			Jiepo-Ling			Tuan Shan Bao		
	Ni/Mo	Ni/As	Mo/As	Ni/Mo	Ni/As	Mo/As	Ni/Mo	Ni/As	Mo/As
Corn grain	0.3	1.3	3.7	8.2	151.7	18.5	–	–	–
Corn leaf	–	–	–	0.4	8.5	19.9	–	–	–
Corn spike	–	–	–	1.9	8.3	4.4	–	–	–
Corn stalk	–	–	–	0.5	4.4	8.6	–	–	–
Rice grain	0.04	0.8	19.8	–	–	–	1.4	14.1	9.9
Rice stalk	0.03	0.5	15.4	–	–	–	–	–	–
Tobacco leaf	0.7	8.8	13.0	2.9	10.5	3.6	–	–	–
Tobacco stalk	1.7	5.7	3.3	–	–	–	–	–	–
Turnip bulb	1.1	3.6	3.2	–	–	–	–	–	–
Yellow surface soil*	3.5	8.6	2.4	0.9	1.0	1.2	1.5	1.8	1.2

* representative sample of surface yellow soil from the tobacco field (total of 5 sub-samples) – for more detailed description see chapter Materials and methods

in similar concentrations in both root and leaf tissues (Kabata-Pendias and Pendias 1984). In the study area, average Cu contents in most of plants are lower than 20 ppm with the exception of tobacco leaves, which contain 36.8 ppm on average, and a bulb of turnip, which contains 27.5 ppm Cu.

Lead. Lead concentrations in black shales of the Zunyi region range from 16 to 33 ppm with peak value detected in weathered black shales of the Xiao-Zhu Mo-Ni prospect. At the Xiao-Zhu and Jiepo-Ling prospects, Pb values exceed the average Pb value of 17 ppm given for average black shale by Yudovich and Ketris (1997).

Lead concentrations in surface soils of the Zunyi region vary from 19 to 25 ppm, which is below the world average for soil (35 ppm), given by Bowen (1979) and well comparable with the local reference subsurface soil sample (26 ppm).

It is well known that small amounts of Pb can be taken up into edible portion of plants and larger amounts are found in the plant roots (Adriano 1986). Thus, Pb contents in plants growing in uncontaminated and unmineralized areas fall within the range from 0.1 to 10 ppm, with an average of 2 ppm (Kabata-Pendias and Pendias 1984). In our samples the maximum Pb concentration (8.45 ppm) was found in tobacco leaves growing on yellow soil containing 21 ppm of Pb in the Xiao-Zhu Mo-Ni prospect. Thus, our data fall well within the range suggested by Kabata-Pendias and Pendias (1984).

Mercury. Mercury concentrations in black shales from the Zunyi region range from 0.49 to 1.74 ppm with peak value determined in weathered black shale of the Tuan Shan Bao Mo-Ni prospect. In all the studied Mo-Ni prospects, Hg values in black shales are significantly higher than the average Hg content of 0.22 ppm reported for average black shale by Yudovich and Ketris (1997).

In well-drained forest soils of northern Québec, Lucotte et al. (1999) reported Hg values in the range from 0.1 to 0.35 ppm. Bowen (1979) reported 0.100 ppm Hg as a world average soil content. In the samples of surface soil from the Zunyi region, the Hg values range from 0.16 to 0.60 ppm with the maximum value of 0.6 ppm determined in surface soil of the Xiao-Zhu Mo-Ni prospect, indicating a high degree of pollution. The average value of Hg in local reference subsurface soil is 0.34 ppm, which is well in the range of values found in surface soils.

Considerable differences in the concentrations were observed for various plant species growing at the same location. This observation indicates that the plant physiology plays an essential role in its Hg uptake. For example, most of the macrophytes (e.g., *Alisma* spp., *Carex* spp., *Cassandra* spp., *Myrique* spp. and others) frequently exhibit maximum Hg concentrations in their root system. Conversely, *Nuphar variegatum* accumulates as much Hg in its leaves as in its roots, and much less than any plant species growing nearby (Lucotte et al. 1999).

Fergusson (1990) reported a range of 0.013–0.17 ppm Hg (DW) in edible plants while Kabata-Pendias and Pendias (1984) listed background levels of Hg in vegetables and fruits varying from 0.002 to 0.086 and from 0.006 to 0.07 ppm (FW). In our samples, maximum Hg concentration (0.130 ppm) was detected in a tobacco leaf growing on yellow soil containing 0.210 ppm of Hg in the Xiao-Zhu Mo-Ni prospect. Roughly similar concentration of Hg (0.1 ppm) was found in lettuce leaves growing on contaminated soils in the vicinity of chlor-alkali plant in Canada (Temple and Linzon 1977). In corn and rice grains of the Zunyi region, Hg concentrations range from 0.005 to 0.015 ppm and from 0.016 to 0.018 ppm, respectively.

Molybdenum. Molybdenum concentrations in black shales from the Zunyi region range from 113 to 361 ppm with peak value determined in weathered black shale of the Xiao-Zhu Mo-Ni prospect. These values highly exceed the average concentration of Mo (29 ppm) given for average black shale by Yudovich and Ketris (1997).

For Asian paddy soils, a mean concentration of 2.9 ppm Mo was reported by Domingo and Kyuma (1983). Our surface soils contain very high Mo concentrations (51–130 ppm) and clearly reflect the contribution from Mo–Ni-rich black shales (average sample of local reference subsurface soil contains 178 ppm Mo).

Among the micronutrients that are essential for plant growth, Mo is required in small amounts (Gupta and Lipsett 1981). Molybdenum is freely taken up, and apparently normal plants may exhibit a considerable range of contents. Plant foodstuffs contain variable amounts of Mo within the range of 0.0018 to 1.23 ppm (FW), 0.07 to 1.75 ppm (DW) and 0.53 to 30 ppm (AW) with legume vegetables being in the upper range and fruits being in the lower range (e.g., grains of sweet corn from U.S. contain 0.18 ppm Mo on average; Kabata-Pendias and Pendias 1984). Molybdenum concentrations in rice, tobacco, red pepper and lettuce in the Deog-Pyoung uraniferous black shale area are in the range of 0.9–16 ppm and are not associated with obvious phytotoxicity (Kim and Thornton 1993). Rice grains and corn grains from the Zunyi region contain 5 to 17 ppm and 2 to 7 ppm Mo, respectively.

The toxicity of any level of dietary Mo is affected by the ratio of the dietary Cu to dietary Mo. The critical Cu:Mo ratio, with respect to the incidence of hypocuprosis in animal feeds from western Canada, was 2 (Miltimore and Mason 1971) whereas on some English pastures the ratio was reported as closer to 4 (Alloway 1973). Animals are quite sensitive to a forage ration with high Mo, and ratios of Cu : Mo < 4 can be expected to result in Mo-induced Cu deficiency. Evidence of disturbed Cu metabolism in ruminant animals is often related to a low Cu : Mo ratio in pasture plants. The low Cu : Mo ratio of rice stalks (0.06) and corn leaves and stalks (0.45 and 0.92, respectively) that are also consumed by animals (e.g., oxen and buffalo) in the Zunyi region can possibly result in disturbed Cu metabolism.

Nickel. Nickel concentrations in sampled black shales from the Zunyi region range from 78 to 1142 ppm with the maximum value determined in weathered black shale of the Xiao-Zhu Mo-Ni prospect. In the Xiao-Zhu Mo-Ni prospect, the Ni concentration exceeds more than eighteen times the average value of 63 ppm given for average black shale by Yudovich and Ketris (1997).

Nickel values in surface soils from the Zunyi region range from 64 to 199 ppm with maxium value in soil from the Tuan Shan Bao Mo-Ni prospect. The average value (148 ppm) is almost four times higher than the world average for soils (60 ppm) given by Bowen (1979) and also higher than Ni concentration in the average local reference subsurface soil sample (91 ppm).

Nickel is readily and rapidly taken up by plants from soils, and until certain Ni concentrations in plant tissues are reached, the adsorption is positively correlated with the soil Ni concentrations (Kabata-Pendias and Pendias 1984). The Ni contents in certain foodstuffs, cereal grains and pasture herbage growing on uncontaminated soils do not differ widely and range from 0.1 to 3.7 ppm and generally, the range of excessive or toxic amounts of Ni in most plant species varies from 10 to 100 ppm DW (Kabata-Pendias and Kabata 1984). In the Zunyi region, the maximum Ni concentration (60.7 ppm) of all edible plants was detected in corn grain of the Jiepo-Ling Mo-Ni prospect where also toxic Ni concentration was detected in tobacco leaves (Ni = 10.64 ppm). Clear Ni contamination was also evidenced in a bulb of turnip from the Xiao-Zhu Mo-Ni prospect (Ni = 33.6 ppm) and rice grains from the Tuan Shan Bao Mo-Ni prospect, containing 7.18 ppm Ni.

Vanadium. Vanadium concentrations in black shales of the Zunyi region range from 1248 to 2536 ppm with maximum content determined in weathered black shale of the Jiepo-Ling Mo-Ni prospect. These values are in excess of the average value of 250 ppm V, given for the average black shale by Yudovich and Ketris (1997).

Vanadium concentrations in surface soils from the Zunyi region range from 572 to 1221 ppm. The average value of 816 ppm is more than nine times higher than world average for soils (90 ppm) reported by Bowen (1979) and significantly lower that vanadium value in the local average reference subsurface soil sample (2594 ppm). The range of V in ash of most vegetables is from < 5 to 50 ppm (Shacklette et al. 1978). Phytotoxicity of V (chlorosis and dwarfing) may appear at about 2 ppm V (DW) in some plants (Davies et al. 1978). In the Zunyi region, V concentrations range from 0.25 to 70.17 ppm (maximum in a bulb of turnip in the Xiao-Zhu Mo-Ni prospect). Potentially phytotoxic concentrations were also found in a tobacco stalk (18.71 ppm V) and tobacco leaves (3.5–4.3 ppm V).

Zinc. Zinc concentrations in black shales of the Zunyi region range from 53 to 836 ppm with peak value determined in weathered black shales from the Xiao-Zhu Mo-Ni prospect. In the Xiao-Zhu Mo-Ni prospect the Zn concentration is more than five times higher than the average value of 160 ppm Zn, given for average black shale by Yudovich and Ketris (1997).

Zinc concentrations in surface soils of the Zunyi region vary from 139 to 270 ppm. The average value of 212 ppm is more than two times higher than the world average for soils (90 ppm) given by Bowen (1979) and slightly lower than

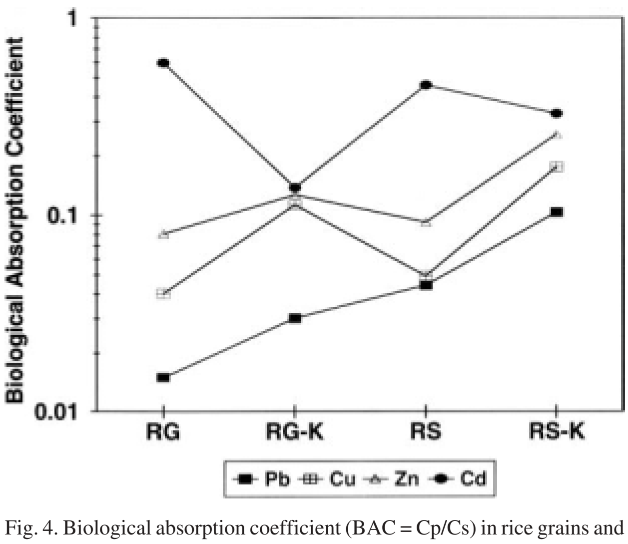

Fig. 4. Biological absorption coefficient (BAC = Cp/Cs) in rice grains and stalks from the Zunyi region, southern China (RG, RS) compared to the Okchon zone in Korea (RG-K, RS-K). Data for Korean samples are from Chon (1997). Cp = metal concentration in plant, Cs = metal concentration in soil. Higher values of biological absorption coefficients for Pb, Cu, and Zn in rice grains and stalks from the Okchon zone (Korea) are directly associated with higher absolute concentrations of these metals in rice grains and stalks when compared to rice grains and stalks from the Zunyi region (southern China).

Zn value in the local average reference subsurface soil sample (139 ppm).

Zinc concentrations in edible plants from uncontaminated soils usually range from 1.2 to 73 ppm (Kabata-Pendias and Pendias 1984). In the study area, Zn contents in most plants are within this range with the exception of tobacco leaves (average 106.2 ppm).

Conclusions

1. Black shales cropping out in the area of the Xiao-Zhu Mo-Ni prospect are characterized by anomalous concentrations of As, Cu, Hg, Mo, Ni, V, Pb and Zn compared to the average black shale of Yudovich and Ketris (1997). Black shales from the Jiepo-Ling Mo-Ni prospect have the highest V content and black shales from Tuan Shan Bao revealed the highest Hg concentration of all the studied black shales from the Zunyi region.
2. The studied surface soil samples from all three Ni-Mo prospects are characterized by increased Mo, Ni, As, Cd, Zn, and Cu concentrations and lower Pb values compared to the worldwide averages for normal soil. Generally, surface soil samples from Xiao-Zhu and Tuan Shan Bao show an enrichment in Cd, Ni, Zn (Cu, Hg) when compared to the local reference subsurface soil sample, indicating addition of these metals through weathering of sulfide material and its washout downstream from mine waste dumps to agricultural sites. In contrast, surface soil from Jiepo-Ling is characterized by a similar distribution of metals as in the local reference subsurface soil sample and reflects most likely only a natural enrichment from the underlying metal-rich black shales. Mo, As and Ni values in our surface soil samples are very often above permissible levels suggested by Kloke (1979).
3. The study of Ni/Mo, Mo/As and Ni/As ratios in surface soils and various crop plants showed that the concentrations of Ni, Mo and As in tobacco stalk and leaves and in turnip bulb at Xiao-Zhu and that the concentrations of Ni, Mo and As in rice grains at Tuan Shan Bao reflect the concentrations of these elements in surface soil. At Jiepo-Ling, concentrations of Ni, Mo and As reflect concentrations of these elements only in corn stalk and leaves. At this locality, Ni is preferentially concentrated in tobacco leaves, corn spike and corn grains.
4. The maximum Mo concentration was found in rice stalk and the maximum As and V concentrations were found in a bulb of turnip sampled below the Xiao-Zhu Mo-Ni mine. Peak Ni, Zn and Hg concentrations were detected in corn grains of the Jiepo-Ling Mo-Ni prospect. Cd shows the highest degree of bioavailability of all the elements and preferentially accumulates in tobacco leaves where it reaches maximum values. This mechanism is also supported by extremely high biological absorption ratios between Cd and tobacco leaves in both Xiao-Zhu and Jiepo-Ling areas (Cd_{BAC} = 11.49 and 24.98, respectively).
5. Rice grains from the Xiao-Zhu area contain anomalous concentrations of Cd, and rice grains from the Tuan Shan Bao area contain anomalous concentrations of Cd, Cu and Zn.
6. Corn grains from the Jiepo-Ling area are characterized by anomalous concentrations of Zn, Cd, Cu, Mo and Ni.
7. The long-term regular consumption of these metal-contaminated crop plants may cause a potential health problem.

Acknowledgements: This study was funded through the grant project ME 444 (KONTAKT) of the Ministry of Education of the Czech Republic (to Jan Pašava) and a grant from the Ministry of Science and Technology of the People's Republic of China (to Hailin Deng). This is also a contribution to the IGCP 429 "Organics in major environmental issues".

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Handling editor: Martin Novák