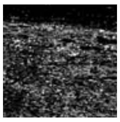
Fractionation of toxic trace elements in soils around Mo-Ni black shale-hosted mines, Zunyi region, southern China: Environmental implications

MICHAL POŇAVIČ, JAN PAŠAVA, ANNA VYMAZALOVÁ, BOHDAN KŘÍBEK, HAILIN DENG,
TAIJI LUO, CHAOYANG LI & MINGGUO ZENG



This paper examines the influence of Lower Cambrian metal-rich black shales and locally mined black shale-hosted Ni-Mo ore layers of southern China on the concentrations of selected toxic trace elements in soils. In order to better understand the mobility of toxic trace elements, and to evaluate the potential risk of environmental contamination, a sequential extraction analysis from soil horizons A, B, C_1 and C_2 in the area of the Jiepo-Ling Mo-Ni mine (Zunyi region) was carried out. Geochemical analyses confirmed significant enrichments of As, Mo, V and slightly lower proportions of Pb and Ni in the A-horizon relative to a local reference sample of uncontaminated soil. This contamination is anthropogenic, probably caused by the release of metal-rich black shale particles during mining operations. Conversely, the distribution of V and Cr in soils is controlled by the host rock. The results of sequential extraction analyses from individual soil horizons showed that almost all As, Ni, V, Cr and Zn are bound to the residual fraction. Some of the Mo (15.13–39.75%) was found to be associated with the organic matter/sulphide fraction. The distribution of Pb and Hg is erratic, indicating considerable mobility of these elements in the soil profile. In Hg-enriched horizons (B and C_1) most Hg (78.21–78.95% of the total content) occurs in the organic matter/sulphide fraction. The concentrations of Mo, Ni, Cr, V, Zn and Hg found in different parts of selected agricultural plants (e.g., tobacco leaves, corn grains, corn leaves, and corn stalks) exceed normal values given by Kabata-Pendias & Pendias (1984). We emphasise that long-term consumption of these products could result in serious health problems for the human population and domestic animals. Arsenic and lead concentrations were found to be within the range of normal values given for agricultural plants. • Key words: metals in soils, extraction analyses, metal-rich black shales, environmental implications, south China.

MICHAL POŇAVIČ, JAN PAŠAVA, ANNA VYMAZALOVÁ, BOHDAN KŘÍBEK, HAILIN DENG, TAIJI LUO, CHAOYANG LI & MINGGUO ZENG 2006. Fractionation of toxic trace elements in soils around Mo-Ni black shale-hosted mines, Zunyi region, southern China: Environmental implications. *Bulletin of Geosciences 81(3)*, 197–206 (2 figures, 5 tables). Czech Geological Survey, Prague. ISSN 1214-1119. Typescript received April 10, 2006; accepted in revised form September 15, 2006; issued September 30, 2006.

Michal Poňavič, Jan Pašava, Anna Vymazalová & Bohdan Kříbek, Czech Geological Survey, Klárov 131/3, 118 21 Praha 1, Czech Republic; ponavic@cgu.cz, pasava@cgu.cz • Hailin Deng, Taiji Luo & Chaoyang Li, Institute of Geochemistry, Open Laboratory of Ore Deposit Geochemistry, Chinese Academy of Science, Guanshui Road 73, Guiyang 550002, People's Republic of China; lcyolodg@sohu.com • Mingguo Zeng, Institute of Geology, Guizhou Bureau of Geology and Mineral Exploration and Development, Guiyang, Guizhou 550004, People's Republic of China

Weathering of sulphidic black shale can cause serious environmental harm by (1) the generation of sulphuric acid; (2) the release of toxic metals contained in the sulphides and other ore minerals; and (3) the leaching of metals from other minerals such as silicates and carbonates. Individual case studies have been reported 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 & Swain 1990), and other areas around the world. The Zunyi region in the Guizhou province of southwest China is well known because of its Mo-Ni-polyelement black shales that are locally mined and processed for Mo. It should be noted that this is an unusual type of ore, especially because of its high concentrations of Mo and Ni. Based on a preliminary study of the bulk distribution of metals in the rock-soil-plant system, Pašava *et al.* (2003) have shown that mining activities in the Zunyi region have resulted in serious agricultural contamination. In order to better understand the mobility of heavy metals and to evaluate their potential risk for contaminating the environment, the sequential extraction analysis of a soil profile from the area of the Jiepo-Ling Mo-Ni prospect (Zunyi region) was carried out. This site was selected because it represents a typical situation in which agricultural

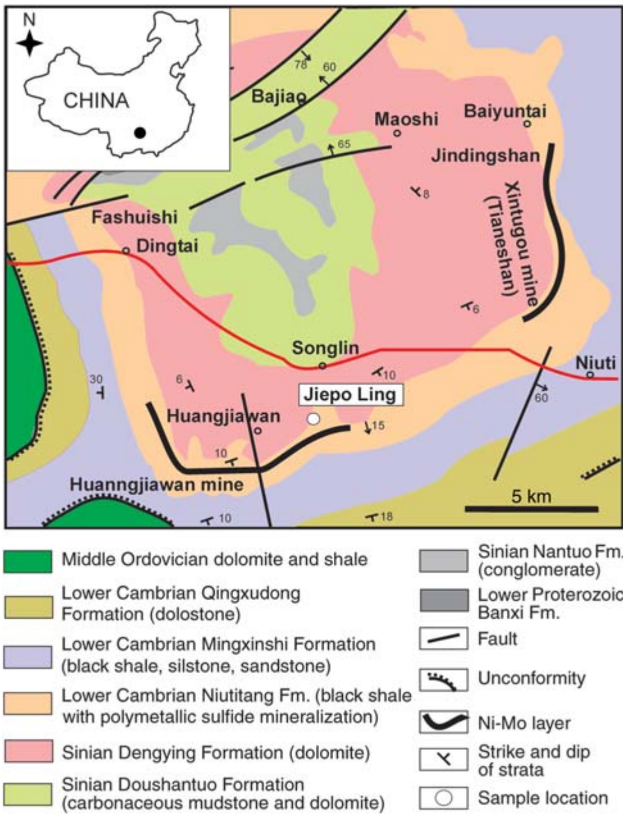


Figure 1. The location and geological position of the Jiepo-Ling Ni-Mo prospect in the Zunyi region in Guizhou province (southwest China), adapted from Mao *et al.* (2002).

land is developed on black shales in the vicinity of Mo-Ni waste dumps. The location and geology of the Jiepo-Ling Mo-Ni prospect in the Zunyi region in Guizhou province (southwest China) are shown in Fig. 1.

A similar technique has been used by other authors for a variety of contaminants. These include studying the behaviour of As in contaminated soils (Lumsdon *et al.* 2001), the speciation of base metals in tailings from closed metal mines in South Korea (Kim *et al.* 2001), and the study of contaminated soils in Indonesian rice fields (Quantin 2002).

Chinese metal-rich black shales

The Early Cambrian marine black shales of south and southwest China host Mo-Ni deposits that outcrop discontinuously throughout six provinces in a belt approximately 1600 km long. There is no volcanic activity directly associated with these deposits. The Mo-Ni 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). Pyrite is the only mineral that can be recognized macroscopically in ore samples. However, the major ore minerals of this shale are vaesite, bravoite and jordisite (Fan 1983). Minor ore minerals include arsenopyrite, chalcopyrite, covellite, sphalerite, millerite, polydymite, gersdorffite, sulvanite, pentlandite, tennantite, tiemannite, violarite, and native gold (Fan 1983, Coveney *et al.* 1993). Re/Os isotopic data from the Mo-Ni-PGE-rich sulphide layers suggest that most of the metal enrichment 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 the 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. A sedimentary origin has been suggested by Zeng (1998) and Mao *et al.* (2002).

Material

Altogether four reference samples of soil were collected from a representative soil profile in the Jiepo-Ling Ni-Mo mining region (Zunyi region: N 27° 41´ 39.6˝, E 106° 40´ 80.3˝, elevation: 1154 m). Four subsurface soil samples (dug holes) were taken from a horizon A, B, C_1 and C_2, from depths of 0–40, 60, 100 and 120 cm, respectively. One reference sample of representative uncontaminated soil was taken from a hilltop (N 27° 41´ 39.7˝, E 106° 40´ 69.1˝, elevation: 1217 m) in the Jiepo-Ling area. Yellow soil of an udic moisture regime (common in the lower slopes of steep canyons) is typical for the Zunyi region (Jiepo-Ling soil profile). A description of collected soil samples is given in Table 1.

The soil samples were disaggregated and sieved to 10 mesh (< 2mm), then quartered and pulverized in an agate ball mill to 200 mesh (< 80 μm).

Methods

A sequential extraction procedure adapted from Tessier *et al.* (1979) was used for the study of metals in individual soil samples (Table 2). Sequential methods progressively expose leaching reagents to the solid sample. Extraction methods are divided into several steps. The extraction phases involve determinations of exchangeable metallic ions, metals bound to carbonate, metals bound to oxyhydroxide Fe and Mn, metals bound to organic materials and sulphides, and metals bound to residue.

The only difference from the original procedure of Tessier (1979) was that we changed the volume of the

Table 1. Description of collected samples (Jiepo-Ling Ni-Mo prospect, Zunyi region).

Sample	Soil horizon	Thickness of horizon (cm)	Description	pH in distilled water	pH in 1 molar solution KCl
1	A	40	Light gray-brown soil with 10–20% of black shale fragments up to 1 cm in size and the presence of phosphate nodules; $C_{org.}$= 1.89%, $S_{tot.}$ = 0.062%, CO_2 = 0.03%	4.38	3.65
2	B	25–30	Soil colored by Fe oxohydroxides with the presence of black shale fragments; $C_{org.}$= 1.47%, $S_{tot.}$ = 0.047%, CO_2 = 0.03%	4.32	3.68
3	C_1	45	Highly weathered and fractured claystone, light gray color, Fe oxohydroxides along fractures; $C_{org.}$ = 0.47%, $S_{tot.}$ = 0.027%, CO_2 = 0.013%	4.46	3.74
4	C_2	30	Slightly weathered claystone, dark gray color; $C_{org.}$ = 0.14%, $S_{tot.}$ = 0.005%, CO_2 = 0.01%	4.85	3.95
Reference soil	A_1	5	$C_{org.}$ = 1.75%, S_{tot} = 0.026%, CO_2 = 0.09%, light gray-brown soil with 30–50% volume of fragments of parent rock (1–3 cm in size)	4.50	3.73

leaching reagent from 8 ml to 20 ml (step 1 and 2). This increase of the leaching reagents / solid phase ratio results in faster equilibration and increases the efficiency of the leaching reagents. Negative effects on the results of sequential extraction caused by the abundance of leaching reagents have not been noticed (Mihaljevič *et al.* 2003). One-gram sediment samples (dry weight) were used for the extractions. The extractions were conducted in centrifuge tubes (polypropylene, 50 ml) to minimize losses of solid material. Between each successive extraction step, centrifuging was used to separate the solid phases (4000 rpm, 20 min). The leachate was removed by pipette, and the residue was washed with 8 ml of deionized water (pH adjusted to pH of leached reagents). This second leachate was added to the first leachate and analyzed, using ICP-AES (Cr, V), ICP-MS (As, Mo, Ni, Pb, Zn,) and AAS (AMA 254 for Hg) techniques in the laboratories of Ecochem Company Ltd. in Prague. The limits of detection are given in Table 3. Analytical uncertainty corresponds to 95% of the reliability interval, which is given as an estimate of relative standard deviation in percents multiplied by the coefficient $k = 2$ (2σ). It is ± 20% for all parameters.

Results of sequential extraction analysis

The results of extraction analyses for individual elements in the distinct soil samples are summarized in Table 4 and graphically shown in Fig. 2. The distribution of selected metals in the studied soil samples, including the reference soil, is listed in Table 5.

Reference soil

The reference sample of uncontaminated soil taken from a hilltop above the Jiepo-Ling soil profile was analyzed only for selected major and trace elements, and the results are summarized in Table 5.

Discussion

In this section we discuss our results from the sequential extraction analysis of individual elements in terms of their behaviour in the rock-soil-plant system.

Vanadium

Vanadium concentrations in the black shales of the Zunyi region range from 1248 to 2536 mg/kg, with the maximum content determined in weathered black shale of the Jiepo-Ling Mo-Ni prospect (Pašava *et al.* 2003). These concentrations are in excess of the 250 mg/kg V given for average black shales by Yudovich & Ketris (1997).

Vanadium concentrations in surface soils from the Zunyi region range from 572 to 1221 mg/kg (Pašava *et al.* 2003). The average value of 816 mg/kg is more than nine times higher than world average for soils (90 mg/kg) reported by Bowen (1979). The sample of local reference soil contains an average of 243 mg/kg Cr (Table 5).

Only minor amounts of V were released from the studied samples during the first three steps of the sequential extraction analysis (Table 4, Fig. 2). More V (about 2% of the total V content) was liberated from the A and B soil horizons during the oxidation of organic matter and sulphides, while the C_1 and C_2 soil horizons yielded only 0.6% of the total V content. Mineral phases that contain V are more affected by oxidation-weathering processes than those in the deeper parts of the soil profile. Most of the V (96% of the total V content) is bound to primary V-minerals. An undetermined K-Mg-Al-silicate with varying contents of V (0.3–4.2 wt.%) and Cr (0.7–3.2 wt.%) was reported by Steiner *et al.* (2001) in Lower Cambrian black shales and cherts of southern China, the concentrations of which increase with depth (Fig. 2, Table 4). These results showed that the distribution of V in the soil profile at Jiepo-Ling is not affected by anthropogenic activities.

The range of V in the ash of most vegetables is from < 5 to 50 mg/kg (Shacklette *et al.* 1978). Vanadium phytotoxicity

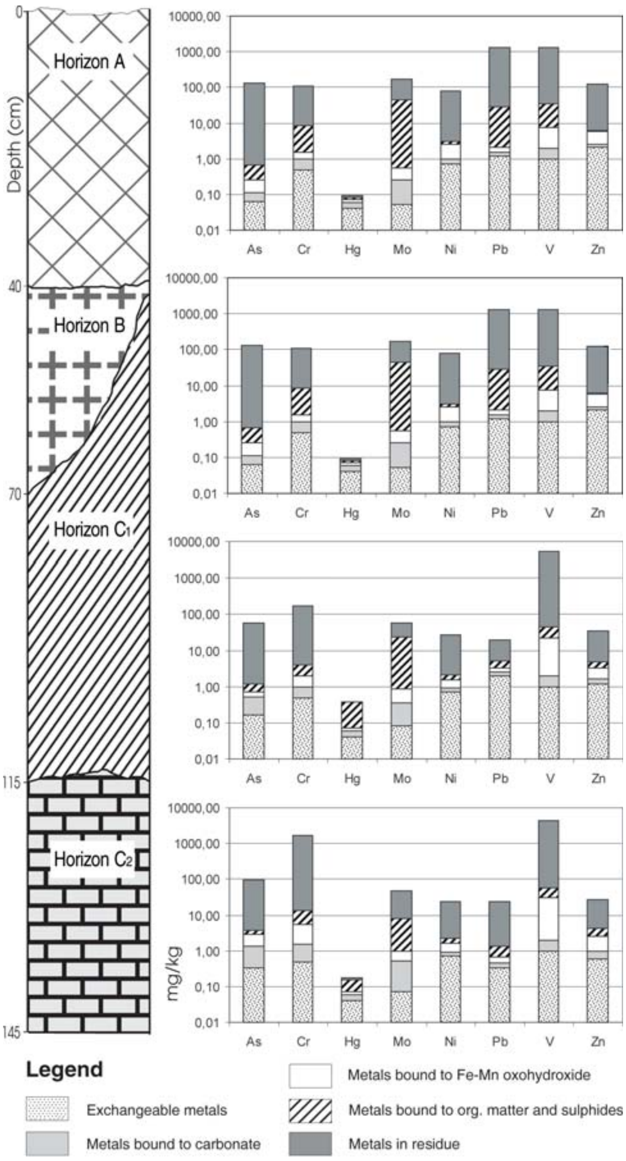


Figure 2. Distribution of studied metals (mg/kg) in soils from individual soils horizons collected from the Jiepo-Ling soil profile (Zunyi region, Guizhou province, southwest China).

Table 2. The sequential extraction procedure after Tessier *et al.* (1979).

Fraction	Leach reagents	Conditions	Equilibration time
Exchangeable	1M $MgCl_2$	pH = 7	1 hour
Metals bound to carbonate	1 M NaAc	pH = 5	2 hours
Bound to Fe-Mn oxohydroxide	0.04 M $NH_2OH.HCl$ in 25% HAc	90 °C	6 hours
Bound to sulphides and organics	30% H_2O_2 0.02 M HNO_3	pH = 2 85 °C	2 and 3 hours
Bound to silicates and residue oxides	$HClO_4$-HNO_3		

(chlorosis and dwarfing) may appear at concentration of about 2 mg/kg V (DW) in some plants (Davies *et al.* 1978). According to Pašava *et al.* (2003), V concentrations range from 0.25 to 70.17 mg/kg in the Zunyi region (the maximum was found in the bulb of a turnip growing near the Xiao-Zhu Mo-Ni prospect). Potentially phytotoxic concentrations at Jiepo-Ling were detected in tobacco leaves (V = 3.5 mg/kg) and corn leaves (V = 2.35 mg/kg).

Chromium

Chromium concentrations in fresh black shales from the Zunyi region range from 45 to 121 mg/kg, with an average of 89.9 mg/kg (Pašava *et al.* 2003), which is similar to the value of 86 mg/kg given for average black shale by Yudovich & Ketris (1997). A maximum Cr value of 1649 mg/kg was determined in weathered black shale of the Xiao-Zhu Mo-Ni prospect.

Chromium contents in surface soils from the Zunyi region range from 111 to 136 mg/kg (Pašava *et al.* 2003). The average value (124 mg/kg) is very close to the Cr concentration found in the local sample of reference soil (118 mg/kg – Table 5), and more than two times higher than world average for soils (60 mg/kg) given by Bowen (1979).

The distribution of Cr in individual fractions of the studied soil horizons from the Jiepo-Ling Mo-Ni prospect is very similar to that of V. Only a small amount of Cr was released into a leachate from the samples of the selected soil profile at the Jiepo-Ling Mo-Ni prospect (Table 4, Fig. 2). Most of the Cr remained bound to primary mineral phases in the residual fraction. The undetermined K-Mg-Al-silicate reported by Steiner *et al.* (2001) also contained Cr (0.7–3.2 wt.%). The relative amount of Cr released during the oxidation of organic matter and sulphides decreases with depth in the soil profile (sample 1, A-horizon: 7% of the total Cr content; sample 3, C_2-horizon: 0.5% of the total Cr content). This can be explained by the more intensive oxidation-weathering process of Cr-bearing minerals in the upper part of the soil profile, with the gradual destruction of primary minerals via oxidation effects of the leaching reagents. The Cr concentration increases with depth in the soil profile. The results show that the distribution of Cr in the studied soil horizons at Jiepo-Ling is not the result of anthropogenic contamination, but reflects its natural dispersion.

In the Zunyi region, the maximum Cr concentration (408 mg/kg) of all edible plants was detected in corn spike from the Xiao-Zhu Mo-Ni prospect. In the Jiepo-Ling area, 126 mg/kg of Cr was found in corn grains (Pašava *et al.* 2003), which is in excess of the average range (0.02–0.2 mg/kg) reported in plant material by Kabata-Pendias & Pendias (1984).

Molybdenum

Molybdenum concentrations in black shales from the Zunyi region range from 113 to 361 mg/kg, with the peak value determined in the weathered black shale of the Xiao-Zhu Mo-Ni prospect (Pašava *et al.* 2003). These values highly exceed the Mo concentration (29 mg/kg) given for average black shales by Yudovich & Ketris (1997).

For Asian paddy soils, a mean concentration of 2.9 mg/kg Mo was reported by Domingo & Kyuma (1983). In the Zunyi region, surface soils usually contain very high Mo concentrations (51–130 mg/kg) that clearly reflect a contribution from the Mo-Ni rich black shales (Pašava *et al.* 2003). The sample of reference soil from the Jiepo-Ling area contains an average of 6 mg/kg Mo (Table 5).

The distribution of Mo in individual fractions of the sequential extraction analysis from the studied samples of soil horizons at the Jiepo-Ling Mo-Ni prospect is similar (Table 4, Fig. 2). Only a very small amount of Mo was released into the leachate during the first step of the extraction analysis (leaching with $MgCl_2$), and most of the Mo was liberated during the decomposition of organic matter and sulphides. This indicates that Mo largely remained bound to primary mineral phases of the residual fraction. This is in agreement with the results of the detailed mineralogical studies by Kao *et al.* (2001), who identified jordisite (MoS_2), MoCS, and an un-named C/MoS_2 mixed-layer phase as principal Mo-carriers. The enrichment of Mo in the upper part of the soil profile (A and B horizons) at Jiepo-Ling can be explained either through the accumulation of Mo-organic complexes in the upper layer (rich in organic matter), in agreement with Fergusson (1990), and/or as a result of contamination by dust particles from the metalliferous black shales, which are widely dumped in the Jiepo-Ling area. Oxidizing conditions can then lead to the release of Mo, which is mostly present in the soil as MoO^{6+}, HMO^{4-}, in which form it is readily taken up by plants (Kabata-Pendias & Pendias 1984).

Among the micronutrients that are essential for plant growth, Mo is required in small amounts (Gupta & 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 0.07 to 1.75 mg/kg (DW), with legume vegetables being in the upper range and fruits being in the lower range (e.g., grains of sweet corn from the U.S. contain 0.18 mg/kg Mo on average, Kabata-Pendias & Pendias 1984. Rice and corn grains from the Zunyi region contain from 5 to 17 mg/kg and from 2 to 7 mg/kg Mo, respectively. At Jiepo-Ling, Pašava *et al.* (2003) found the highest Mo concentrations in corn leaves (21.5 mg/kg), tobacco leaves (7.4 mg/kg), and corn stalks (4.7 mg/kg). All these values are in excess of normal values for crop plants (0.07–1.75 mg/kg), reported by Kabata-Pendias & Pendias

Table 3. Limit of detection for studied metals (mg/kg).

Extraction steps	Exchangeable	Carbonate	Fe-Mn oxohydr.	Organics sulphides	Residue
V	< 2	< 2	< 2	< 2	< 2
Cr	< 1	< 1	< 1	< 1	< 1
Mo	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Ni	< 1.5	< 0.5	< 0.5	< 1.2	< 1.2
Zn	< 0.5	< 0.8	< 0.8	< 0.8	< 0.8
Hg	< 0.08	< 0.04	< 0.02	< 0.01	< 0.005
Pb	< 0.25	< 0.25	< 0.2	< 0.2	< 0.2
As	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03

(1984). Long-term exposure to increased Mo concentrations in foodstuff for animals may cause anemia, loss of hair, and other problems. Human beings can show indications of Mo-intoxication in the form of pneumoconiosis.

Nickel

Nickel concentrations in black shales from the Zunyi region range from 78 to 1142 mg/kg. The maximum value was determined in the weathered black shale of the Xiao-Zhu Mo-Ni prospect (Pašava *et al.* 2003), where the Ni concentration exceeds more than eighteen times the value of 63 mg/kg given for average black shales by Yudovich & Ketris (1997).

Nickel values in surface soils from the Zunyi region range from 64 to 199 mg/kg (Pašava *et al.* 2003). The average value (148 mg/kg) is almost four times higher than world average for soils (60 mg/kg) given by Bowen (1979). However, the sample of local reference soil from Jiepo-Ling shows Ni values (61 mg/kg – Table 5) that are almost identical to that of world soils.

The distribution of Ni in the samples of individual soil horizons from the Jiepo-Ling Mo-Ni prospect is highly uniform (Table 4, Fig. 2). The amount of released Ni during the first two steps of sequential extraction analysis was below the detection limit (Table 4). Only a small amount of Ni was liberated during the reduction of Fe-Mn oxohydroxides, which is in agreement with mineralogical data, as Ni occurs chiefly as more resistant sulphide minerals such as vaesite and bravoite, or as enrichments in base metal sulphides (Fan 1983, Coveney *et al.* 1993). It is important to emphasise that Ni bound to Fe-Mn oxohydroxides (usually co-precipitates of Ni) can be easily released into the host environment during abrupt changes of oxidation-reduction conditions. The fact that the total content of Ni decreases with depth in the studied soil profile (soil horizon A contains 75 mg/kg Ni, while C_2 contains 21 mg/kg Ni), can be explained as the result of contamination of the surface soil by particles from the metal-rich waste dumps of the Mo-Ni mining.

Table 4. Distribution of metals in individual extraction steps (%). * – below detection limit, calculated from ½ of the detection limit value.

Metals	Horizon	Exchangeable	Carbonate	Fe-Mn oxohydroxide	Organic matter – sulphide	Residue
V	A	0.07*	0.07*	0.40 ± 0.08	2.02 ± 0.4	97.43 ± 19
	B	0.09*	0.09*	1.14 ± 0.23	2.28 ± 0.46	96.41 ± 19
	C_1	0.02*	0.02*	0.39 ± 0.08	0.47 ± 0.09	99 ± 20
	C_2	0.02*	0.02*	0.66 ± 0.13	0.68 ± 0.14	99 ± 20
Cr	A	0.47*	0.47*	0.47*	6.6 ± 1.3	92 ± 18
	B	0.50*	0.50*	2.93 ± 0.59	5.2 ± 1	91 ± 18
	C_1	0.28*	0.28*	0.57 ± 0.11	1.21 ± 0.24	98 ± 20
	C_2	0.03*	0.06 ± 0.01	0.24 ± 0.05	0.44 ± 0.09	99 ± 20
Mo	A	0.03 ± 0.01	0.12 ± 0.02	0.17 ± 0.03	24.8 ± 5	75 ± 15
	B	0.35 ± 0.07	0.07 ± 0.01	0.26 ± 0.05	18.8 ± 3.8	81 ± 16
	C_1	0.14 ± 0.03	0.47 ± 0.09	0.88 ± 0.18	39.8 ± 7.9	59 ± 12
	C_2	0.15 ± 0.03	0.95 ± 0.19	0.87 ± 0.17	15.1 ± 3	83 ± 17
Ni	A	0.90*	0.39*	1.95 ± 0.39	0.78*	96 ± 19
	B|	1.27*	0.36*	2.73 ± 0.55	1.09*	95 ± 19
	C_1	2.68*	0.76*	2.41 ± 0.48	2.29*	92 ± 18
	C_2	3.01*	0.86*	3.10 ± 0.63	2.58*	90 ± 18
Zn	A	1.66 ± 0.33	0.32*	2.77 ± 0.56	0.32*	95 ± 19
	B	2.07 ± 0.41	0.41*	5.8 ± 1.2	2.89 ± 0.58	89 ± 18
	C_1	3.44 ± 0.68	1.15*	4.58 ± 0.91	4.87 ± 0.97	86 ± 17
	C_2	2.16 ± 0.43	1.47*	5.5 ± 1.1	6.6 ± 1.3	84 ± 16
Hg	A	43.48*	21.74*	10.87*	10.9 ± 2.2	13 ± 2.6
	B	11.17*	5.59*	2.79*	78 ± 16	2.23 ± 0.45
	C_1	10.53*	5.26*	2.63*	79 ± 16	2.63 ± 0.47
	C_2	23.53*	11.77*	5.88*	47 ± 9	11.8 ± 2.4
Pb	A	2.22 ± 0.44	0.63 ± 0.12	0.93 ± 0.19	50 ± 10	46.3 ± 9.3
	B	7.5 ± 1.4	2.06 ± 0.42	7.03 ± 1.43	8.4 ± 1.7	75 ± 15
	C_1	10.5 ± 2.1	2.78 ± 0.56	3.88 ± 0.78	9.4 ± 1.9	73 ± 15
	C_2	1.46 ± 0.29	0.53 ± 0.11	0.94 ± 0.19	2.87 ± 0.58	94 ± 19
As	A	0.05 ± 0.01	0.04 ± 0.007	0.11 ± 0.021	0.32 ± 0.064	99 ± 20
	B	0.07 ± 0.01	0.06 ± 0.012	0.08 ± 0.016	0.17 ± 0.034	100 ± 20
	C_1	0.27 ± 0.054	0.59 ± 0.12	0.34 ± 0.067	0.84 ± 0.17	98 ± 20
	C_2	0.34 ± 0.068	1.04 ± 0.21	1.47 ± 0.3	1 ± 0.2	96 ± 19

Nickel is readily and rapidly taken up from soils by plants, and until certain Ni concentrations in plant tissues are reached, the adsorption is positively correlated with the soil Ni concentrations (Kabata-Pendias & Pendias 1984). The Ni contents of foodstuffs such as cereal grains and pasture herbage growing on uncontaminated soils do not differ widely, and range from 0.1 to 3.7 mg/kg. The range of excessive or toxic amounts of Ni in most plant species varies from 10 to 100 mg/kg DW (Kabata-Pendias & Pendias 1984). In the Zunyi region, the maximum Ni concentration (60.7 mg/kg) in edible plants was detected by Pašava *et al.* (2003) in corn grains grown near the Jiepo-Ling Mo-Ni prospect, where toxic Ni concentrations were also detected in tobacco leaves (Ni = 10.64 mg/kg).

An increased probability of the occurrence of carcinogenic pneumonia diseases in populated areas with long-term exposure to Ni-sulphide dust was reported by Bencko et al. (1995). Such a risk clearly exists in the Zunyi region, where the Mo-Ni black shale-hosted ores are widely mined and processed.

Zinc

Zinc concentrations in black shales of the Zunyi region range from 53 to 836 mg/kg. The peak value was determined in the weathered black shales from the Xiao-Zhu Mo-Ni prospect (Pašava *et al.* 2003), where the Zn concentration is more than five times higher than the value of 160 mg/kg Zn given for average black shales by Yudovich & Ketris (1997). In the Jiepo-Ling Mo-Ni prospect the average Zn concentration in black shale is 34 mg/kg.

Table 5. Total concentrations of selected metals (mg/kg) in the studied samples (horizons A, B, C_1, C_2 and a reference soil).

Horizon	A	B	C_1	C_2	Reference soil
As	131 ± 26	82 ± 16	59 ± 12	98 ± 19	9 ± 0.1
Cr	106 ± 21	99 ± 20	174 ± 35	1710 ± 340	118 ± 2
Mo	174 ± 35	149 ± 30	58 ± 12	48 ± 9	6 ± 5
Ni	77 ± 15	55 ± 11	26 ± 5	23 ± 4	61 ± 5
Pb	54 ± 11	21 ± 4	19 ± 4	24 ± 5	37 ± 15
V	1330 ± 270	1140 ± 230	5150 ± 1030	4260 ± 850	243 ± 15
Zn	126 ± 25	97 ± 19	35 ± 7	27 ± 5	192 ± 2
Hg	0.1 ± 0.018	0.36 ± 0.07	0.38 ± 0.07	0.17 ± 0.04	0.1 ± 0.005

Zinc concentrations in surface soils of the Zunyi region vary from 139 to 270 mg/kg (average 212 mg/kg, Pašava *et al.* 2003). The value of 192 mg/kg found in the sample of reference soil from Jiepo-Ling (Table 5) is more than two times higher than world average for soils (90 mg/kg) given by Bowen (1979).

At the Jiepo-Ling Mo-Ni prospect, the distribution of Zn differs in individual fractions of the studied soil horizons (Table 4, Fig. 2). The samples representing the upper part of the soil profile (A and B horizons) are depleted in Zn relative to the samples from the C_1 and C_2 horizons (Table 4). The amount of Zn released during the oxidation of organic matter and sulphides from individual soil horizons increases with depth (Fig. 2). The upper part of the soil profile is characterized by higher Zn values than the lower soil horizons. This can be explained by contamination of the surface soil by particles of metal-rich black shales from the mining processes occurring in the Jiepo-Ling area.

Zinc concentrations in edible plants from uncontaminated soils usually range from 1.2 to 73 mg/kg (Kabata-Pendias & Pendias 1984). In the studied area, Zn contents in most of plants are within this range, with the exception of corn grains (134.7 mg/kg) and tobacco leaves (90.4 mg/kg) (Pašava *et al.* 2003).

Mercury

Mercury concentrations in black shales from the Zunyi region range from 0.49 to 1.74 mg/kg, with the peak value determined in the 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 (e.g., at Jiepo-Ling the average Hg value = 0.62 mg/kg – Pašava *et al.* 2003) than the Hg content of 0.22 mg/kg reported for average black shale by Yudovich & Ketris (1997).

Bowen (1979) reported 0.100 mg/kg of 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 mg/kg, with the maximum value determined in surface soil of the Xiao-Zhu Mo-Ni prospect, indicating a high degree of pollution (Pašava *et al.* 2003). The Hg content of the reference soil sample from Jiepo-Ling is 0.1 mg/kg (Table 5), which is well in the range of the values found in surface soils of the Zunyi region.

The amount of Hg released from individual horizons of the Jiepo-Ling soil during the first three stages of the sequential extraction analysis was negligible and below detection limit. Most of the Hg seems to be closely associated with organic matter/sulphide fraction (Table 4, Fig. 2). This finding is supported by the identification of traces of tiemannite (HgSe) from metal-rich black shales of the Zunyi region (Coveney *et al.* 1993).

Considerable differences in concentrations were observed for various plant species growing at the same location. This indicates that plant physiology plays an essential role in Hg uptake. Fergusson (1990) reported a range of 0.013–0.17 mg/kg Hg (DW) in edible plants, while Kabata-Pendias & 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 mg/kg (FW), respectively. In the Zunyi region, the maximum Hg concentration (0.130 mg/kg) was detected in tobacco leaves growing on yellow soil containing 0.210 mg/kg of Hg in the Xiao-Zhu Mo-Ni prospect. At the Jiepo-Ling area, Hg concentrations exceeding the normal values for crop plants given by Kabata-Pendias & Pendias (1984) were reported by Pašava *et al.* (2003) in corn stalks (Hg = 0.102 mg/kg) and tobacco leaves (Hg = 0.091 mg/kg). Roughly similar Hg concentrations (0.1 mg/kg) were found in lettuce leaves growing on contaminated soils in the vicinity of a chlor-alkali production plant in Canada (Temple & Linzon 1977). Low Hg contents in the organic matter-rich upper part of the soil profile at the Jiepo-Ling Mo-Ni prospect can be thus explained as Hg uptake by local plants.

Lead

Lead concentrations in the black shales of the Zunyi region range from 16 to 33 mg/kg, with the peak value detected in the weathered black shales of the Xiao-Zhu Mo-Ni prospect (Pašava *et al.* 2003). At the Xiao-Zhu and Jiepo-Ling mining areas, Pb values exceed the 17 mg/kg given for average black shale by Yudovich & Ketris (1997).

Lead concentrations in surface soils of the Zunyi region vary from 19 to 25 mg/kg (Pašava *et al.* 2003), which is below the world average for soil (35 mg/kg) given by Bowen (1979). The sample of reference soil from Jiepo-Ling has an average Pb value of 37 mg/kg (Table 5), which is comparable with the average for world soils.

In soils from the Jiepo-Ling Mo-Ni prospect, the sequential extraction analysis showed that most of the Pb (50% of the total Pb content) was released from the surface soil (sample 1: A-horizon, Table 4, Fig. 2) during the oxidation of organic matter and sulphides, while almost 46% of the total Pb remained in the residual fraction.

The distribution of Pb showed similar patterns in individual fractions of soil horizons B, C_1 and C_2 (Table 4, Fig. 3.7), with a slightly higher amount of Pb released during the first three stages of sequential extraction analysis, and again with the majority of the metal remaining in the final residual fraction. These results indicate the presence of more intense oxidation-weathering processes in the uppermost part of the soil profile were Pb^{2+} sulphates ($PbSO_4$) are generated, which are more mobile throughout the profile than are primary Pb-phases.

It is well known that small amounts of Pb can be taken into the edible portions of plants, and that larger amounts are found in the roots (Adriano 1986). Thus, Pb contents in plants growing in uncontaminated and unmineralised areas fall within the range from 0.1 to 10 mg/kg, with an average of 2 mg/kg (Kabata-Pendias & Pendias 1984). In the Zunyi region, the maximum Pb concentration (8.45 mg/kg) was found in tobacco leaves growing on yellow soil containing 21 mg/kg of Pb in the Xiao-Zhu Mo-Ni prospect. In the Jiepo-Ling Mo-Ni prospect, the maximum Pb concentrations were detected in corn leaves (6 mg/kg) and tobacco leaves (2.45 mg/kg) by Pašava *et al.* (2003). These values are within normal range of Pb concentrations in crop plants given by Kabata-Pendias & Pendias (1984).

Arsenic

Arsenic concentrations in black shales of the Zunyi region range from 133 to 308 mg/kg, with the maximum value detected in the weathered black shale of the Xiao-Zhu Mo-Ni prospect (Pašava *et al.* 2003). These values highly exceed the As content of 30 mg/kg given for average black shale by Yudovich & Ketris (1997).

Arsenic concentrations in surface soils from the Zunyi region range from 21 to 110 mg/kg, with the maximum value occurring in soil sampled close to the Tuan Shan Bao Mo-Ni prospect (Pašava *et al.* 2003). The average value (64 mg/kg) is lower than that of reference subsurface soil (115 mg/kg), and more than ten times higher than world average for soils (6 mg/kg) reported by Bowen (1979). The sample of reference soil from Jiepo-Ling has an average As value of 9.1 mg/kg (Table 5), which is comparable with that for world soils.

The distribution of As in the first three fractions of the sequential extraction analysis from the A and B soil horizons at the Jiepo-Ling Mo-Ni prospect is quite uniform. Less than 0.5% of the total As content was liberated during sequential extraction analysis, indicating that more than 99.5% of the As remains bound to resistant primary minerals in the residual fraction of the samples. The amount of As released during the first three stages of sequential extraction analysis is significantly higher for the samples representing the C_1 and C_2 soil horizons. These samples also show higher amounts of As released during the oxidation of organic matter and sulphides (Table 4). However, more than 96% of the total As content again remained in the residual fraction. These results show that most of As in the deeper part of the soil profile (C_1 and C_2 horizons) is closely associated with resistant mineral phases in a state of equilibrium between primary minerals and their oxidation products. The surface of primary minerals can be covered by readily dissolved oxidation products. Significant depletions of As in the leachate from the first two extraction steps (i.e. after $MgCl_2$ and NaAc reagents) from soil samples taken from the upper part of the soil profile (A and B horizons – see Table 4, Fig. 2) can be explained in terms of the gradual dissolution of oxidation products. Increased total As concentrations in the surface soil (130.7 mg/kg) could also result from contamination by particles of metal-rich black shales scattered from waste dumps located in the vicinity of the soil profile.

In the Zunyi region, the maximum concentration of As in all edible plants was found in a turnip bulb (9.31 mg/kg) in the Xiao-Zhu Mo-Ni prospect. At Jiepo-Ling, corn grains and tobacco leaves contain 0.4 mg/kg and 1.01 mg/kg As, respectively, which fits well into the normal value range in crop plants (Pašava *et al.* 2003).

Conclusions

The Early Cambrian marine black shales of south and southwest China host Mo-Ni deposits that have been locally processed for Mo. In addition to the very high contents of Mo and Ni, these black shales are also anomalously enriched in As, Cd, Cr, Hg, Pb, V, Zn, and other metals. Soils developed from these metal-rich black shales and/or located in the vicinity of ore processing sites tend to reflect this extreme geochemical composition. Detailed studies of the individual soil horizons in the area of the Jiepo-Ling Mo-Ni prospect confirmed the occurrence of both natural and anthropogenic enrichments.

In comparing the total values of the studied metals in the A-soil horizon and the sample of reference soil, it can be concluded that soil of the A-horizon at Jiepo-Ling is significantly enriched in As, Mo, V, and to a lesser extent in Pb and Ni. Conversely, Cr and Zn values are slightly lower in soil of A-horizon at Jiepo-Ling, and Hg concentrations are comparable in both soils.

When we compare the distribution of these metals within the individual soil horizons at Jiepo-Ling, it is apparent that the A-horizon is enriched in As, Mo, Ni, Pb and Zn. This enrichment is most likely related to anthropogenic contamination by particles of metal-rich black shales, which have been processed and dumped in the Jiepo-Ling area. Conversely, soils from deeper part of the soil profile (C_1 and C_2 horizons) show clear V and Cr enrichments, which very likely reflect the geochemical composition of local parent rock (black shale). Mercury shows an erratic distribution through the soil profile, with higher values in B and C_1 horizons.

The results of sequential extraction analyses from the individual soil horizons at Jiepo-Ling showed that most of the As (96.13–99.63% of the total content), Ni (90.44–95.98% of the total content), V (96.41–99.11% of the total content), Cr (90.82–99.23% of the total content) and Zn (84.28–94.94% of the total content) is bound to the residual fraction. Most of the Mo (58.76–82.89% of the total content) is also bound to residual fraction, however, 15.13–39.75% of it is associated with organic matter/sulphide fraction. A similar situation applies to Pb, of which 46.26–94.21% of the total content is bound to the residual fraction. Only the A-horizon contains 49.96% of the total Pb content in its organic matter/sulphide fraction. In the Hg-enriched horizons (B and C_1), most of the Hg (78.21–78.95% of the total content) occurs in the organic matter/sulphide fraction. In the A-horizon, most of Hg (43.48% of the total content) occurs among easily exchangeable metals.

At Jiepo-Ling, the concentrations of Mo, Ni, Cr, V, Zn and Hg found in selected agricultural plants (e.g., tobacco leaves, corn grains, corn leaves, corn stalks) exceed normal values given by Kabata-Pendias & Pendias (1984). It is important to emphasise that the long-term consumption of these products could result in serious health problems to the population of humans and domestic animals. Conversely, As and Pb were found to be within the range of normal values given for agricultural plants. More studies are needed to evaluate the real impact of the consumption of these contaminated agricultural products on the health of the local communities.

Acknowledgements

This project was funded by the grant 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 454 "Medical Geology". Reviews of two anonymous reviewers helped significantly to improve the quality of this paper.

References

Adriano, D.C. 1986. *Trace elements in the terrestrial environment*. 533 pp. Springer-Verlag, New York.

Bencko, V., Cikert, M. & Lener, J. 1995. *Toxické kovy v životním a pracovním prostředí člověka*. 288 pp. Grada, Prague (in Czech).

Borovec, Z. 1994. Distribution of toxic metals in stream sediment. *Acta Universitatis Carolinae, Geologica 38*, 91–103.

Bowen, H.J.M. 1979. *Environmental chemistry of the elements*. 316 pp. Academic Press, London.

Coveney, R.M., Grauch, R.I. & Murowchick, J.B. 1993. Ore mineralogy of nickel-molybdenum beds hosted by black shales of south China, 369–375. *In* Reddy, R.G. & Weizenbach, R.N. (eds) *The minerals, metals and materials society, Proceedings of the Paul E. Queneau International Symposium "Extractive Metallurgy of Copper, Nickel and Cobalt"*.

Chon, H.T., Cho, C.H., Kim, K.W. & Moon, H.S. 1996. The occurrence and dispersion of potentially toxic elements in areas covered by black shales and slates in Korea. *Applied Geochemistry 11*, 69–76.

Davies, R., Beckett, P.H.T. & Wollan, E. 1978. Critical levels of twenty potentially toxic elements in young spring barley. *Plant Soil 49*, 395–408.

Domingo, L.E. & Kyuma, K. 1983. Trace elements in tropical Asian paddy soils. *Soil Science Plant Nutrition 29*, 439–452.

Fan, D. 1983. Polyelements in the Lower Cambrian black shale series in southern China, 447–474. *In* Augustithis, S.S. (ed.) *The significance of trace metals in solving petrogenetic problems and controversies*. Theophrastus Publications S.A., Athens.

Fergusson, J.E. 1990. *The heavy elements: Chemistry, environmental impact and health effects*. 614 pp. Pergamon Press, Oxford.

Gupta, U.C. & Lipsett, J. 1981. Molybdenum in soils, plants and animals. *Advances in Agronomy 34*, 73–115.

Horan, M.F., Morgan, J.B., Grauch, R.I., Coveney, R.M. Jr., Murowchick, J.B. & Hulbert, L.J. 1994. Rhenium and osmium isotopes in black shales and Ni-Mo-PGE-rich sulfide layers, Yukon Territory, Canada, and Hunan and Guizhou Provinces, China. *Geochimica et Cosmochimica Acta 58*, 257–265.

Kabata-Pendias, A. & Pendias, H. 1984. *Trace elements in soils and plants*. 315 pp. CRC Press, Boca Raton, Florida.

Kao, L.S., Peacor, D.R., Coveney, R.M. Jr., Zhao, G., Dungey, K.E., Curtis, M.D. & Penner-Hahn, J.E. 2001. A C/MoS_2 mixed-layer phase (MoSC) occurring in metalliferous black shales from southern China, and new data on jordisite. *American Mineralogist 86*, 852–861.

Kim, K.K., Kim, K.W., Kim, J.Y., Kim, I.S., Cheong, Y.W. & Min, J.S. 2001. Characteristics of tailings from the closed metal mines as potential contamination source in South Korea. *Environmental Geology 41*, 358–364.

LOTT, D.A., COVENEY, R.M. JR., MUROWCHICK, J.B. & GRAUCH, R.I. 1999. Sedimentary exhalative nickel molybdenum ores in south China. *Economic Geology 94*, 1051–1066.

LOUKOLA-RUSKEENIEMI, K., KANTOLA, M., HENTTONEN, P. & HALONEN, T. 1999. Migration of elements from black shales to aquatic ecosystems and local residents: a pilot study in Finland, 30–31. *In* PAŠAVA, J. (ed.) *Organics in major environmental issues, Proceedings of the IGCP 429 Inaugural Meeting*. Czech Geological Survey, Special Publication, Prague.

LUMSDON, D.G., MEEUSSEM, J.C.L., PATERSON, E., GARDEN, L.M. & ANDERSON, P. 2001. Use of solid phase characterisation and chemical modelling for assessing the behaviour of arsenic in contaminated soils. *Applied Geochemistry 16*, 571–581.

MAO, J., LEHMANN, B., ANDAO, D., GUANGDI, Z., DONGSHENG, M., YITIAN, W., MINGGUO, Z. & KERRICH, R. 2002. Re-Os dating of polymetallic Ni-Mo-PGE-Au mineralization in Lower Cambrian black shales of South China and its geological significance. *Economic Geology 17*, 1535–1547.

MIHALJEVIČ, M., POŇAVIČ, M., ETTLER, V. & ŠEBEK, O. 2003. A comparison of sequential extraction techniques for determining arsenic fractionation in synthetic mineral mixtures. *Analytical and Bioanalytical Chemistry 377*, 723–729.

PAŠAVA, J., GABRIEL, Z. & KOVALOVÁ, M. 1993. Proterozoic normal and metal-rich black shales from the Bohemian Massif, Czech Republic: industrial and environmental aspects, 209–212. *In* FENOLL HACH-ALI, P., TORRES-RUIZ, J. & GERVILLA, F. (eds) *Current Research in Geology Applied to Ore Deposits*. University of Granada, Granada.

PAŠAVA, J., KŘÍBEK, B., ŽÁK, K., LI, C., DENG, H., LIU, J., GAO, Z., LUO, T. & ZENG, M. 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. *Bulletin of Geosciences 78(3)*, 251–260.

PRESSER, T.S. & SWAIN, W.C. 1990. Geochemical evidence for Se mobilization by weathering of pyritic shales, San Joaquin Valley, California, USA. *Applied Geochemistry 5*, 703–717.

QUANTIN, C., BECQUER, T., ROUILLER, J.H. & BERTHELIN, J. 2002. Redistribution of metals in a New Caledonia ferrasol after microbial weathering. *Soil Science Society of America Journal 66(6)*, 1797–1804.

REICHENBACH, I. 1992. *Black shales as an environmental hazard: a database on black shales in Canada*. Internal Report, Geological Survey of Canada, Ottawa, 1–69.

SHACKLETTE, H.T., ERDMAN, J.A. & HARMS, T.F. 1978. Trace elements in foodstuffs, 25. *In* OEHME, F.W. (ed.) *Toxicity of heavy metals in environment, Part I.* Marcel Decker, New York.

STEINER, M., WALLIS, E., ERDTMANN, B.D., ZHAO, Y. & YANG, R. 2001. Submarine-hydrothermal exhalative ore layers in black shales from South China and associated fossils – insight into a Lower Cambrian facies and bio-evolution. *Palaeogeography, Palaeoclimatology, Palaeoecology 169(3–4)*, 165–191.

TEMPLE, P.J. & LINZON, S.N. 1977. Contamination of vegetation, soil, snow and garden crops by atmospheric deposition of mercury from a chlor-alkali plant, 389–398. *In* HEMPHILL, D.D. (ed.) *11th Annual Conference on Trace substances in environmental health.* University of Missouri Press, Columbia, Mo.

TESSIER, A., CAMPBELL, P.G.C. & BOSSON, M. 1979. Sequential extraction procedure for speciation of particulate trace metals. *Analytical Chemistry 51*, 844–851.

ZENG, M. 1998. Geological feature of the Huangjiawan Ni-Mo deposit in Zunyi of Guizhou and its prospect for development. *Guizhou Geology 15*, 305–310 (in Chinese with English abstract).

YUDOVICH, Y.E. & KETRIS, M.P. 1997. *Geochemistry of black shales*. 211 pp. Prolog Publisher, Syktyvkar.