

Sequence analyses of the Smolník creek stream sediments contaminated by acid mine drainage from abandoned mine (Western Carpathians, Slovakia)

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Abstract. Abandoned mine area has been taken as a model area to document the metal pollution of soil. The Smolník deposit was definitively closed and flooded in 1990-1994 (Jaško et al., 1996, 1998; Lintnerová 1996; Lintnerová et al., 1999). Acid mine drainage (AMD) generation could be presented as the main risk environmental problem related with this Cu-pyrite deposit. There are lots of other risks, like the mine heaps, works and mill tailing dumps stability related with a rate of infiltration, water saturation of waste and others combined with local hydrology and climate characteristics. It has been clearly documented, that AMD discharging from the flooded mine acidified and contaminated the Smolník creek with toxic concentration of elements, which have been transported to the river. All mineral and biological parts of the Smolník creek catchment are befallen and suffered due to AMD action. Stream sediments can accumulate metals, As, sulphates and others transported by AMD. Goal of this study is documented impact of AMD onto stream sediments in the vicinity of the creek bank. For stream sediments characterization we used acid dissolution and five-step sequence analyses. We observed a very good correlation between sequence analyses and acid dissolution of stream sediment.

Key words: stream sediments, mine waste, toxic metals, sequence analyses

Introduction

The old mine-district Smolník (in Eastern Slovakia) was definitively abandoned in 1991 and the mine was flooded up. However acid mine water enriched to iron and sulphates, Cu, Zn, As, Al and other elements discharged from underground in 1994 and heavily contaminated the creek water (Jaško et al., 1996; Lintnerová 1996; Lintnerová et al., 1999). Composition and amount of AMD discharged from mine was stabilized and decreased (e.g from TDS: 17 g/l to about 5g/l) from this time nevertheless AMD continually polluted the brook Smolník and river Hnilec water, stream sediments and some surrounding soil (Lintnerová et al., 2006; Rojkovič et al., 2003). Old mining waste dumps, which produce strongly acidic and mineralized AMD, are other serious source of pollution in this area (Tab. 1, Fig. 1). Tailing impoundment producing neutral water with high concentration of metals (especially Fe and As) and salts is the other important source of contamination in this region. All this sources add the contamination directly to the creek Smolník. Contamination is transported in the form of suspended solids (Tab. 2) for a long distance in water of the creek Smolník and river Hnilec and accumulates in stream sediments (Lintnerová et al., 2006).

This work aims to define the accumulation of the mine-derived elements (Cu, Zn, Al, As, Mn) in stream sediments and to characterize their relative mobility and potential bioavailability.

Tab. 1. Sources of contamination in Smolník mine area.

		SM-2	SM-OD	SM-3	SM-5	SM-Kar.
Al	mg/l	82.74	0.187	474	58.6	159.5
Fe (tot.)	mg/l	542.4	4.61	3229	321	1091
Fe (II+)	mg/l	356.8	1.81	421	166	222
Mn	mg/l	35.48	3.35	25.3	38727	170.5
Ca	mg/l	190.2	44.3	304	160	2538.5
Mg	mg/l	328	36.8	442	101	1003.5
SO ₄	mg/l	3642.4	253.75	14800	2220	9057.5
Zn	mg/l	9599	45	43000	7070	24405
Pb	mg/l	81.2	<4	156	18	42.5
As	mg/l	108.4	45.75	16800	140	13

(SM-2 – AMD from shaft Pech, SM-OD – water from tailing impoundment channel, SM-3 and SM-5 – AMD from old waste dump drainage channel, SM-Kar – AMD from mine Karitas; Rojkovič et al., 2003).

Tab. 2. Average chemical composition of suspended solids in Smolník brook and Hnilec river waste (Rojkovič et al., 2003).

		SM-1	SM-4	SM-6	SM-8	H-0	H-1
Fe	%	5.26	12.99	16.34	17.61	8.43	14.6
Al	%	1.96	7.96	8.68	6.36	3.71	3.76
As	mg/kg	112	142	251	135	124	103
Pb	mg/kg	196	171	163	166	150	106
Zn	mg/kg	1026	512	798	1235	1079	1979
Cu	mg/kg	592	1818	2157	2407	665	1856
Mg	mg/kg	6854	6261	4812	4738	18089	4778
Ca	mg/kg	16990	9531	12217	5306	33924	19101
K	mg/kg	11662	2638	1938	2366	8613	5942
Na	mg/kg	7997	2759	2755	2136	9549	8582
Mn	mg/kg	2536	940	769	819	5379	1439
number of samples		2	3	4	4	2	3

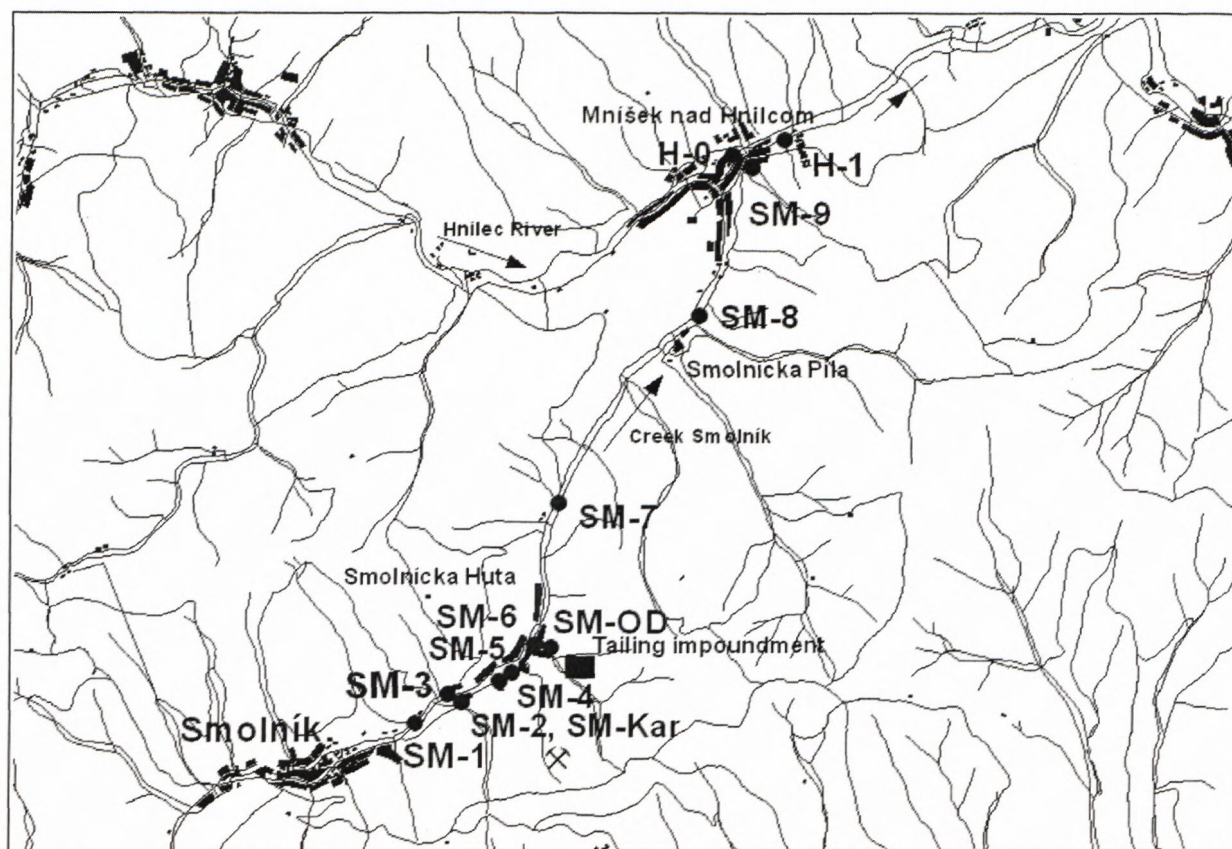


Fig. 1. Fe, As and Cu 5-step sequence analyses of stream sediment from Smolník stream. 1 - extraction in water, 2 - ion - exchangeable and carbonate phases, 3 - reducible – Fe and Mn oxide, 4 - oxidizable – organic mater, sulphides, 5 - aluminosilicate residue.

Methods

Eight samples of stream sediments were collected in June 2002 (Fig. 1). Samples of stream sediments were collected in the vicinity of the water monitoring sites. Sediments were dried (60 °C) and sieved on a < 1 mm screen. Part of homogenized sample was used to measure pH (active, exchangeable), Eh and conductivity in the soil paste. Active pH was measured in mixture of 5 g sample and 25 ml of distilled water and exchangeable pH in mixture of 5 g soils and 25 ml of 1M KCl. Exchangeable Al was determined in 1M KCl extract. 2 g of sample were mixed with 20 ml of 1M KCl and agitated 2 hours. Al was determined photometrically (MERC SQ300) in the filtrate. Water dissolved sulphates were analysed by the same device 1 g of fine sample was extracted 1 hour using the horizontal shaker. Sulphates were measured in filtrate.

Chemical analyses

Metals content (Fe, Mn, Al, Cu, Zn, Na, K, Ca, Mg, Pb, As) in stream sediments were determined by digestion of samples in concentrated HNO_3 for 2 hours at 85 °C. Insoluble residuum was dried at 105 °C and weighted. AAS and ICP AES methods were used to measure elemental concentrations. Concentrated nitric acid extracted all potentially mobile metals in suspended

solids or sediments. This method practically could supply the total analysis of sample (Pontér et al., 1992; Rhoton et al., 2002 and other).

Sequence extraction

Partitioning of metals among various geochemical phases is particularly interesting to assess mobility and ecotoxicity of metals in the catchment area. We used next sequence extraction scheme, developed in the Slovak GS laboratory (Mackových et al., 2003) on the basis of published schemes (Tessier et al., 1979; Rapin and Forstner, 1983; Rapin et al., 1986; Quevauviller et al., 1994). Five samples of stream sediments (SM1, SM4, SM7, SM8 and SM9) were selected and consequently extracted according this procedure. Seven elements - Fe, Si, Al, Cu, Zn, Mn and As were determined in the extracts.

Fraction 1: Extraction in water – inorganic salts, 1g of sample + 50 ml of distilled water, extraction/agitation – 16 hours, centrifugation, metals in supernatant were determined

Fraction 2: Ion - exchangeable and carbonate phases: residue from F1 + 40 ml 0,11M acetic acid (HOAc) 16 hours extraction/agitation, centrifugation – supernatant, metals determination.

Fraction 3: reducible – Fe and Mn oxide: residue from F2 + 40 ml 0.1 M NH_4OH HCl in 25 % HOAc, pH 2, 16

extraction, occasional agitation, centrifugation, metals determination in supernatant.

Fraction 4: oxidizable – organic matter, sulphides: residue from F3 + 2 x 10 ml 30 % H_2O_2 + HNO_3 , 85 °C, 50 ml NH_4OAc - extraction 16 hours, centrifugation, metals in supernatant.

Fraction 5: aluminosilicate residue: residue from F4 + HNO_3 + HF + HClO_4 .

Additional total chemical decomposition (HNO_3 + HF + HClO_4) of sediment samples and analyses of the same metals were performed to verify accuracy of analytical procedure. To compare accuracy of analyses the standard of river sediment CRM 601 (BCR) was used. AAS method with hydride generation was used for determination of As. Cu, Mn, Zn, Al, Fe were determined by ICP AES and Si was analysed by gravimetric method.

Results and discussion

Parameters of stream sediments are closely related to chemistry of stream water, but are not identical. The first step in our study was a basic characterization of stream sediments (Tab. 3). Stream sediment taken close from the place where AMD discharged from the mine (SM-4), directly to the stream Smolník, has low pH. High concentration of sulphide, iron and aluminium is typical for this sediment strongly affected with AMD. The pH of other stream sediments is significantly higher in the lower part of the stream. Higher acidity and content of sulphates were determined in pore solution of the sediment than in fluent water (Tab. 3).

Tab. 3. Basic characterization of stream sediments.

	SM-1	SM-4	SM-7	SM-8	SM-9
pH(water)	6.95	3.23	6.24	5.12	6.58
pH(KCl)	6.59	3.05	5.73	4.86	6.28
Eh	240	390	-150	190	-147
Al (mg/kg)KCl	1.12	228	1.2	2.48	0.8
$\text{SO}_4(\text{v H}_2\text{O})$	800	3550	650	1650	850
Fe (v H_2O)	0	154	12	3.5	7
TOC (%)	1.52	3.02	7.35	4.57	6.95

Negative value of Eh in the lower part of the stream (close to the Smolník stream and Hnilec river confluence) is very interesting especially by potential remobilization of metals adsorbed on Fe oxyhydroxides (samples SM-7 and SM-9). This fact should be supported by the higher concentration of organic matter in stream sediment from this part of the stream.

In the next step of the study we focused on decomposition of stream sediment in HNO_3 . This methodology was used to determine total concentration of available and mobile studied metals. We observed continuous accumulation of Fe in lower parts of the stream (Tab. 4). This phenomenon was found even though the amount of insoluble residuum was higher in this part of the stream. This fact indicates that percentage of Fe oxyhydroxides in soluble part of sediment is rising. High amount of Fe oxyhydroxides is transported in suspended solids and

sedimented in parts of stream with lower kinetic energy of flow (especially in monitoring point SM-8). Aluminium is evidently bounded on aluminosilicate minerals and tailing impoundment is a source of K and Ca.

Tab. 4. Dissolution of stream sediments in HNO_3 (in ppm, IR – insoluble residuum).

Element	SM-1	SM-4	SM-7	SM-8	SM-9
Fe	40800	49600	50800	122800	94800
Mn	676	254	612	484	552
Al	10540	10200	12540	11960	12080
Cu	348	308	254	308	356
Zn	226	130.2	228	184.2	54.8
Na	296	298	268	202	197.6
K	1514	1724	2434	1308	1554
Ca	87.6	32.2	123.8	51.8	234
Mg	6820	5940	4820	4420	4380
Pb	94	66	68	90	12
As	54.4	75.8	46.4	50	53.2
IR (%)	24.16	23.4	30.54	42.76	40

A sequence analysis of stream sediment was used to characterize the amount of metals bound in different phases. Sequential extraction procedures are connected with some problems, mainly partial selectivity, re-adsorption and release of metal during extraction steps, etc. The sufficient information about mineralogical and geochemical nature of stream sediments could eliminate these potential complications. It is well known that mobility of potentially toxic metals depends on their different binding or specific chemical forms and total concentration of metals is not the most important. Metal partitioning in all phases is very important in the case exchangeable or bioavailable phases to assess mobility and environmental risk.

The largest part of studied metals is bounded or adsorbed by oxides and by organic matter. The contents of exchangeable Fe, Cu, Zn, Mn increase mainly in the acidic condition in the sediments. Acid conditions and increased content of organic matter are two important factors, which change the mobility and bioavailability of metals. The most acid sediment is leached (SM-4) and the metals (Mn, Cu, Zn) content decreases. Leaching stops in the point SM-7 vicinity and the largest concentration of metals is in the point SM-8. The SM-7 sample is enriched in organic matter (TOC 7.35 % in comparison with SM-1: 3.5 %), and it could change redox condition and metal mobility in water and the ability of iron oxyhydroxides to attenuate metals.

Significant amount of Si and Al is bound on insoluble residuum (IR); (Tab. 5.). These results correlate with results obtained from acid dissolution of stream sediments. Ratio of Al content in IR and in available phases (sum of phases 1-4) is stable in the whole stream. On the other hand we can observe continuous rising of Al content in available phases downstream the Smolník stream. In samples taken above the mine the percentage of Al adsorbed on oxyhydroxides is only 1 % of total amount, in the lower part of stream about 7 %. It is caused by precipitation and sedimentation of Al in form of oxyhydroxides minerals.

Different situation we can observe in content of Fe. In part of the stream above the mine approximately 85 % of

Tab. 5. Sequence analyses of stream sediments in ppm (5 – insoluble residuum, 1-4 – sum of first 4 steps, available phases, Tot. – total amounts of studied elements).

Tot.	Fe	Al	Si	Mn	Cu	Zn	As
SM 1	61000	76500	297900	880	377	259	51.4
SM 4	69400	70000	292000	360	333	163	40.9
SM 7	72000	76600	240900	840	277	265	50.2
SM 8	139400	63300	230300	550	318	207	68.3
SM 9	122400	69000	217100	664	400	292	70.9
sum 1-4	Fe	Al	Si	Mn	Cu	Zn	As
SM 1	10440	3760	2921	529	274	158	11
SM 4	17750	6600	2000	38	243	69	9
SM 7	28230	8920	4300	603	237	193	12
SM 8	53790	8060	2824	296	236	105	1
SM 9	31110	10190	9800	415	343	198	1
5	Fe	Al	Si	Mn	Cu	Zn	As
SM 1	50560	72740	294979	351	103	101	40.7
SM 4	51650	63400	290000	322	90	94	32.3
SM 7	43770	67680	236600	237	40	72	38.4
SM 8	85610	55240	227460	254	82	102	66.9
SM 9	91290	58810	207300	249	57	94	69.5

Fe is bound on IR (stable aluminosilicate minerals), and 15 % is adsorbed on available phases (principally on oxyhydroxides Fe – 13 %); (Fig. 2). Rising of Fe oxyhydroxides in stream sediments we can observe in lower part of stream. Percentage of oxyhydroxides in stream sediment represented 31% in the sample SM-8 taken approximately 15 km from the mine (Fig. 1, Fig. 2). It is important if we know that in this part of stream are more reduced conditions in sediments (Tab. 3). The kinetic energy of flow is decreased in this part of the stream due to morphological condition and there are convenient conditions for sedimentation of suspended solids. This fact document increased ratio of Fe amount in available phases and in IR.

For contents of Zn, Cu and Mn there is typical, that amount of these elements adsorbed on available phases (phases 1-4) is higher than the amount bound on IR (Fig. 2). Binding of Cu on sulphides mineral phases (38-48 %) and oxyhydroxides (16-28 %) is dominant phenomena in stream sediments from Smolník stream. Only 25 % (in average) of Cu is bound on stable mineral forms (IR). Similar behavior we can indicate for Zn. Amount of Zn bound on IR is little bit higher (31-51 %), and main part of Zn is adsorbed on oxyhydroxides

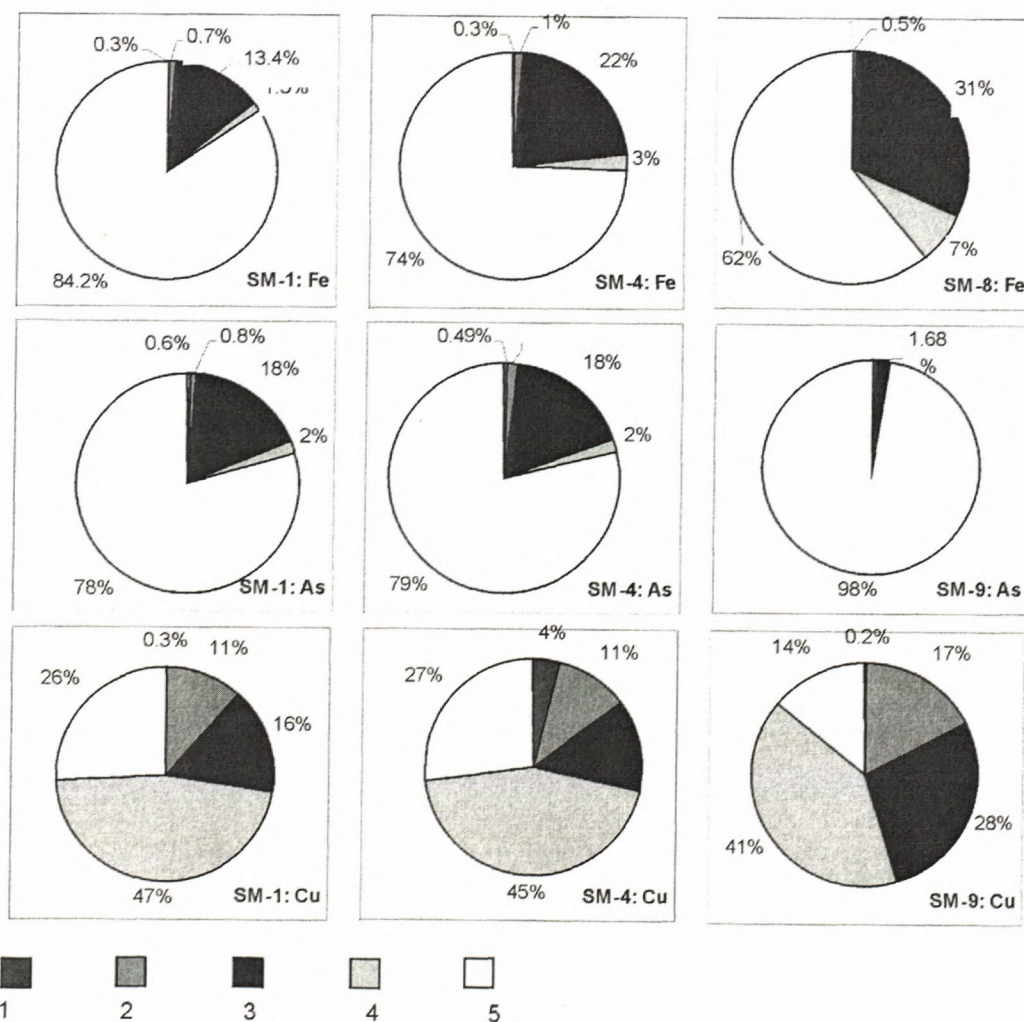


Fig. 2. Correlation of Fe and Cu in samples analysed by acid dissolution (HNO_3) and sequence analyses (SNV).

Explanatory notes: The content of elements in: 1 – water, 2 – exchangeable, 3 – reducible, 4 – oxidizable 5 – residual fractions.

(20-26 %) and on ion - exchangeable and carbonate phases (16-36 %). Amount of Zn occurred in oxidisable phases (organic matter and sulphides) represent 13-19 %.

Different results we obtained for As (Fig. 2). In samples taken close the mine and tailing impoundment we detected increased content of As adsorbed on oxyhydroxides (18-19 % from total amount of As in stream sediment). We can document that tailing impoundment is an important source of As in this area. Concentration of As in available phases is higher in sample SM-7 taken below the tailing impoundment, than in sample SM-4, taken below the mine. In the last two samples taken close to the confluence of Smolník stream with Hnilec river the whole As is bounded on residual mineral phases. This fact documents that Fe-oxyhydroxides precipitates with As are not transported in the form of suspended solids by stream.

If we compare results of sequence analyses and HNO_3 acid dissolution of stream sediments (Fig. 3) we can observed good correlation between these two methods, mainly for Fe, Cu, Zn and Mn. Values obtained by acid dissolution are little bit lower than total amount of studied elements obtained by sequence analyses. It is understandable, because acid dissolution by HNO_3 is not total dissolution, and some stable mineral forms stay in insoluble residuum. On the other hand, content of elements obtained by acid dissolution of stream sediments is little bit higher then content of elements from available phases obtained by sequence analyses. It is caused by partial dissolution of aluminosilicates by HNO_3 . This result indicates that for quick and rough characterization of stream there sediments is possible to use acid dissolution for determination of available amount of some

elements. Predictably for exact results and characterization of different phases is necessary to use sequence analyses.

For characterization of changes of stream sediments from Smolník stream we can use comparison of our results with results from 1996 (Jaško et al., 1996) realized by HNO_3 dissolution too (Fig. 3). The content of studied elements is approximately the same nowadays than 10 years ago; especially if we know that the samples were not taken from exactly identical places.

Conclusions

- mine derived contamination is transported in dissolved form and in suspended solids in the Smolník stream catchment
- contents of Fe, Cu and Zn in stream sediments continuously increase downstream the Smolník stream
- tailing impoundment is a permanent source of As contamination
- 30 % of Fe in the form of oxyhydroxides is in stream sediments
- HNO_3 extractions of stream sediments correlated with sequence analyses

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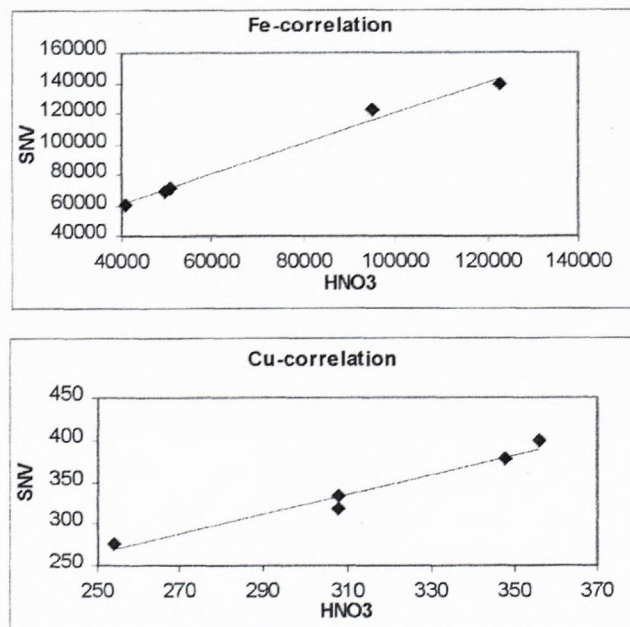


Fig. 3. Comparison of Fe and Cu amount extracted from stream sediments by different methods upper HNO_3 - acid dissolution (Tab. 4), SNV - sequence analyses total, lower SNV - sequence analyses available phases 1-4 (Tab. 5), 1995 - acid dissolution from Jaško et al., 1996).

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