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SUMMARY

In early 2000, two major mining-related accidents occurred in the Maramureş County in Romania which caused the release of large amounts of cyanide and heavy metals into the rivers Szamos and Tisza (a major tributary of the Danube). The high concentrations of cyanides killed almost immediately more than 1,000 t of fish on the Hungarian side. Cyanides pose a short-term threat to the environment due to their degradability. In contrast, heavy metals deposit in the river catchment area and can accumulate in the food web due to their lack of degradability, which results in a long-term threat to the ecosystem and to humans.

To assess the contamination, sediments were sampled along Szamos and Tisza in Hungary from 2000 to 2005. The aqua-regia soluble element contents and the bonding forms of selected elements were analyzed in the grain size fraction $< 20 \mu\text{m}$.

Heavy metal concentrations in sediments were initially high at the Szamos ($\leq 3,000 \text{ mg/kg Zn}$) and decreased with increasing distance from the mining accident (ca. $500 \mu\text{g/g Zn}$ in the middle section of the Tisza). In 2005, the trace element concentrations in the Szamos have decreased to a level slightly higher than in the Tisza. The concentration decline is probably caused by dilution with “uncontaminated” sediment, transport of contaminated substrate further downriver as well as transport out off the river onto the floodplains. Most of the sediment profiles do not reflect the mining accidents of the year 2000, which indicates a long history of heavy metal contamination in the Tisza catchment. Cluster analysis discriminates three sections of the research area: (1) Szamos, (2) middle Tisza and (3) lower Tisza. This pattern is based on the contamination level ranking from high to low. Over the observed years the element pattern changed only marginally: (1) Cd–Pb–Zn, (2) As–Cu, (3) Cr and (4) Co–Ni.

Although the decrease of the sedimentary heavy metal concentration gives a positive impression regarding the sediment quality, potential sinks of the contaminants should be determined. Therefore further research is needed to assess the effect on floodplains, because they are due to their agricultural use integrated in the human food web.

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1. Introduction

1.1 Motivation

In January and March 2000, major accidental mining spills contaminated rivers in the Tisza River basin with large amounts of cyanides and heavy metals. The first ecological consequences were clearly visible and initiated a large number of investigations at the river system. While the cyanide caused a high mortality of fish and other life forms in the rivers (ca. 1,242 t fish killed in Hungary; WWF, 2002), the consequences and the fate of the heavy metals in the river system were not clear. The Centre for Environmental Research Leipzig-Halle (UFZ) sampled sediments and water along the rivers Szamos and Tisza in Hungary in cooperation with the ELTE University (e.g. Óvári et al., 2004) and the Technical University Braunschweig (e.g. Kraft et al., 2003a) starting in 2000.

To monitor the inorganic contamination, sampling campaigns were undertaken in 2000 to 2005. The investigations comprised the analysis of aqua regia soluble element contents and the analysis of the potential mobility of the contaminants by means of sequential extraction schemes (Jakob et al., 1990; Pueyo et al., 2001).

1.2 The accidents

Following a period of heavy rainfall (30 L/m²) and snowmelt, a dam breach occurred on January 30, 2000 at the Aurul S. A. gold processing plant in Baia Mare (Maramureş County, Romania) releasing ca. 100,000 m³ tailings waters. The water contained ca. 1,000 t cyanides and 1,000 t heavy metals. The polluted waters flowed over small rivers from the dam into the Szamos, which enters the Tisza at Vasárosnamény in Hungary. As a countermeasure, the Hungarian authorities closed the outflow sluices and the reservoir at Kisköre (Tisza Lake).

Shortly after the Baia Mare accident (March 10, 2000), another accidental spill occurred at the Novat tailing dam¹ near Baia Borsa (Maramureş County, Romania) again triggered by heavy rainfall (37 L/m²) and snowmelt. Polluted water flowed through the Vaser River into the Upper Tisza. The total load was estimated at 40,000 t² solid waste (containing heavy metals, e.g. Cu, Pb, Zn) and 100,000 m³ water.

Table lists mining accidents of the last years in the Tisza River basin, which demonstrates the persistent ecological threat in this area. Flooding in this region occurs relatively regularly. Based on mathematical/statistical assessment of floods, it is estimated that significant floods occur every five to six years and great floods every ten to twelve years (EUR/02/5036813).

1.3 (Potential) Sources of pollution

The Maramureş County in Romania's northwest has a long history of mining for Au, Cu, Pb, Zn, Ag, Mn and salt. This region is also called *Transylvania's Golden Quadrilateral*, where mining is documented since the pre-roman times (BGR, 1977). The county has high levels of persistent contamination of soil, water and air with many pollutants. These were released during the decades of industrial activity that used environmentally unsound technologies, including an old lead smelter, copper smelter, sulphuric acid plant, the operations of the national mining company REMIN and Aurul S.A., a joint venture between REMIN and Esmeralda Exploration Ltd. Australia. Wastes from mining operations are stored in 243 deposits of mining waste rocks (3.5 Mt) and 20 tailing dams (12 abandoned, 7 active and 1 damaged; 113 Mt; 443.3 ha).

¹ at the Preparation Enterprise for processing complex ores of Pb and Zn

² other sources: 20,000 t of mineral waste

Strong activity of mining and metallurgical industries in Romania takes place along the Szamos and its tributaries as well as in the area of the Bihor Massif (tributaries of Körös and Maros). The ore grades of the mined metals in the Maramureş County Cu, Pb and Zn are generally low (Cu: 0.35 %; Pb: 0.6–1.2 %; Zn: 0.4–1.0 %). The mineralizations of Pb and Zn are associated with Cu, Sb, Bi, Cd, Au and Hg. The ores are processed (smelting and refining) at Baia Mare, Zlatna and Copsa Mica. The metal recovery lies between 50 and 75 %, leaving relatively high contaminated slag behind (UNECE Committee, 2001).

Gold is processed at Transylvania's Golden Quadrilateral and further south at *e.g.* Baia de Aries. Other elements which are mined in Romania are Al (bauxite) and U (pechblende and associated sulfide mineralizations; Carpathians, The Apuseni, Banat Mts.; UNECE Committee, 2001).

The environmental impact of this intensive mining includes the release of heavy metals by acid mine drainage (AMD). AMD is caused by the oxidation of sulfide ores³ leading to a low pH, which leaches heavy metals from the tailings and introduces them into the river systems. A risk assessment in north western Romania revealed 11 risky tailings deposits. Other risks are the leakage from pipelines, air pollution and dam safety (UNECE Committee, 2001).



Fig. 1-1: Location of the accidental spills (Baia Mare and Baia Borsa) in the catchment area of the Danube (modified after BMTF, 2000)

Although this study concentrates itself on the effects of the accidental mining spills in Romania on the Hungarian rivers Tisza and Szamos, other regions are also affected by mining-related heavy metal contamination. A drastic example is the mining spill of Aznalcóllar in south western Spain on April 25, 1998. 5 M m³ of acid waste from pyrite processing were released into the Guadalquivir River. The waste also reached the world heritage and national park Coto Doñana.

Other examples of catastrophic environmental impacts to large rivers are the chemical spill at the Sandoz factory near Basel (Switzerland) on Nov. 1, 1986 (pesticides, insecticides, Hg) and the very

³ mainly pyrite and marcasite, which are not removed during the ore processing

recent spills affecting amongst others the drinking water supply of China and Russia (Nov., 2005: Songhua River; benzene, nitrobenzene).

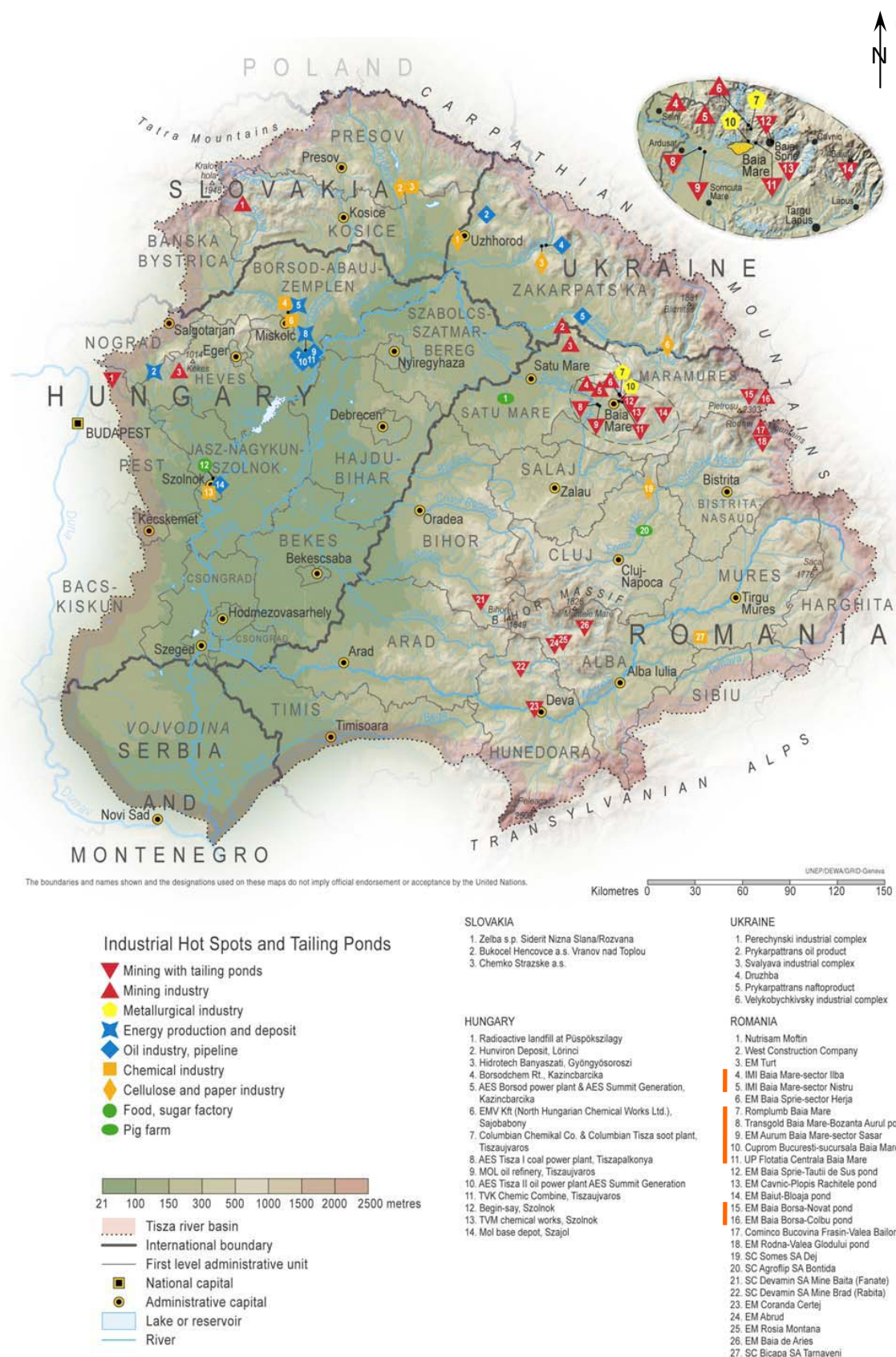


Fig. 1-2: Potential accident risk spots in the Tisza River Basin, with zoom in the Maramureş mining region (taken from UNEP-Report 2004; mining industries at Baia Mare and Baia Borsa are highlighted)

Table 1-1: History of mining related accidents in the Tisza River Basin

Date	Locality/ Enterprise	River	Description	Source
30.01.2000	Baia Mare/ Aurul S.A. (gold recovery from old tailings)	Sasar (–Lapus– Szamos–Tisza)	tailings dam crest failure after overflow caused from heavy rain and melting snow; 100,000 m ³ of cyanide-contaminated liquid; killing tonnes of fish and poisoning the drinking water of more than 2 million people in Hungary	http://www.wise-uranium.org/mdaf.html
06.02.2000	Bozinta Mare (close to Baia Mare)/ REMIN S.A.	Lapus	1,500 m ³ of waste water (cyanide: 7 mg/L) ; malfunction of a neutralisation device and careless handling	http://www.ukar.org/danube/dd01-big-romanian-spills.html
10.03.2000	Baia Borsa/ REMIN S.A.	Vaser (–Tisza)	tailings dam failure after heavy rain; 18,000–22,000 t of heavy-metal contaminated tailings (Zn, Pb, Cu);	http://www.wise-uranium.org/mdaf.html
15.03.2000	Baia Borsa/ REMIN S.A.	Vaser (–Tisza)	Novat settling pond; dam failure for 2–3 hours; Zn, Pb, Cu, Al	http://www.ukar.org/danube/dd01-big-romanian-spills.html
15.07.2000	Herja/ Pb mine	Tisza	broken pipeline; polluted water; sludge (Zn, Pb)	http://www.ukar.org/danube/dd01-big-romanian-spills.html
05.09.2004	Baia Borsa	Cisla (–Vişeu–Tisza)	sludge (Zn, Pb, Cu); water supplies in Ukraine cut off	http://www.ukar.org/danube/dd01-big-romanian-spills.html
14.09.2004	Rosia Poieni (Rosia Montana)/ Cuprumin Abrud Ltd	Aries (–Maros–Tisza)	tailing pond accident	
27.11.2005	Baia Borsa	Vişeu (–Tisza)	cyanide; 30 kg fish died	

2. Investigation area

The Hungarian sections of the Tisza River and the Szamos River form the investigation area. The Tisza basin is the largest sub-basin (157,186 km²) of the Danube basin (801,463 km²). Samples of sediment and water were taken starting shortly after the eastern border to Romania at Csenger and ending at Szeged in the south of Hungary close to the Serbian border (Fig. 3-1).

The Tisza and three of its tributaries (Szamos, Körös, Maros) were investigated. The Szamos and the Maros can be seen as its most polluted tributaries due to the influence of industrial and domestic sewage from towns at the end of the Carpathian Mountains. As a result the water quality decreased drastically (WWF, 2002).

2.1 Tisza River

The Tisza River is the largest tributary of the Danube. It has a total length of 966 km. During high water periods agriculturally used land becomes flooded. Barrages have been constructed in the river at Tiszalök (rkm 523⁴), Szolnok (rkm 332) and Szeged (rkm 180).

Most of the Tisza's course can be characterized as a lowland river (exception: upper section). Its hydrological regime fluctuates extremely and is determined by the discharge from middle-mountain tributaries. Periods of high discharge and water levels lie in spring, when large floods occur regularly. Low water levels characterize the summer. The Tisza transports large amounts of sediments (10–11 M t/a; Gatescu, 1990).

Due to drainage measures, which were undertaken in the 18th and 19th centuries the river course was shortened by 40 % (Dobrosi et al., 1993; Varga, 1997). This led to an increased velocity and riverbed erosion. Another consequence of these measures is the reduction of the floodplain area from 7,542 km² (HU: 4,637 km²) to 1,215 km² (HU: 914 km²).

2.2 Overview of selected studies on the spills in 2000 in the investigation area

- Bird et al. (2003): Szamos and Tisza (Romania, Hungary); sediment (< 63 µm) after 2000; BCR; As, Cd, Cu, Pb and Zn
- Hum & Matschullat (2002a, 2002b): middle and lower Hungarian Tisza; sediments in 1999/2000; heavy metals
- Macklin et al. (2003): Romanian section of Szamos and Tisza and tributaries; water and sediment (< 2 mm) in 2000; Cd, Cu, Pb and Zn
- Mages et al. (2004): Hungarian section of Tisza; biofilms in 2000 and 2002; major and trace elements
- Osán et al. (2002): Hungarian section of Tisza; sediment in 2000; major and trace elements; mineralogy
- Óvári et al. (2004): Hungarian section of Tisza; sediment (< 1 mm) in 2000 to 2003; BCR; As, Cu, Ni, Pb, Zn
- Soldán et al. (2001): Szamos (+tributaries) and Tisza (Romania, Hungary); sediment (< 2 mm) and water; As, Cd, Cr, Cu, Hg, Ni, Pb and Zn

⁴ rkm = river kilometer; distance from confluence with the Danube; all tributaries were projected on the Tisza for reasons of presentability

- Woelfl et al. (2004): Hungarian section of Tisza; sediment, water and benthos in 2003; major and trace elements (K, Ca, Mn, Fe, Ni, Cu, Zn, As, Sr, Pb)

2.3 Szamos

The Szamos River has its source in Northern Transylvania (Romania) and flows after 435 km in the Tisza River in north-east Hungary. It flows through an area with a long historic record of mining starting in pre-roman times (BGR, 1977). The permanent load of the Szamos with heavy metals is higher than that of the Tisza.

The mining spill of January 2000 occurred at a tributary of the Szamos flowing through the Baia Mare district. This area is characterized by mineralization with non-ferrous metals (Schönenberg & Neugebauer, 1997), e.g. Au, Cu, Sbm and Zn (Bailly et al., 1998). These mineralizations are mostly sulfides. Remains of this mining record are crushed ore (Pochsande), tailings and slag, which cover large areas.

Baia Borsa, where the second spill was released, is characterized by Pb and Zn mining.

2.4 Körös and Maros

During the sampling campaign in 2005, these two tributaries of the Tisza have been visited as well. Both rivers are fed by tributaries coming from the Bihor Massif, a region of intensive mining and metal processing with tailing ponds (UNECE Committee, 2001). This river was also polluted in the course of mining-related spills at its tributaries. One of the potential heavy metal sources is the Baia de Aries mine, which lies at the Aries River that subsequently flows into the Maros. The Aries River gets portions of its metal load from metal processing plants (Industria Sârmei in Câmpia Turzii, discharge of effluents), tailing ponds of Au mines (Brad, Abrud and Zlatna), U mines (Brad) and Cr (Tirnaveni; Greenpeace, 2000).

3. Methods

3.1 Sampling

3.1.1 Sampling locations and conditions

Several locations were chosen for sediment sampling on the Hungarian part of the rivers Szamos and Tisza (Fig. 3-1). They stretch from the Hungarian-Romanian border in the north-east to the Hungarian-Serbian border in the south. The sampled locations are listed in

Table 3-1. In 2005, two further tributaries of the Tisza were sampled for the assessment of additional heavy metal sources.

The sampling at the locations was laid out to retrieve sediments with a relatively high content of the fine grain sizes. Sediments were sampled along the river bank.

The median discharge during the sampling periods is displayed in Fig. 3-2. Comparing the discharge, it can be seen that during the years 2002 and 2005 the sampling took place during high water periods, while in July 2003 the discharge was at its minimum.

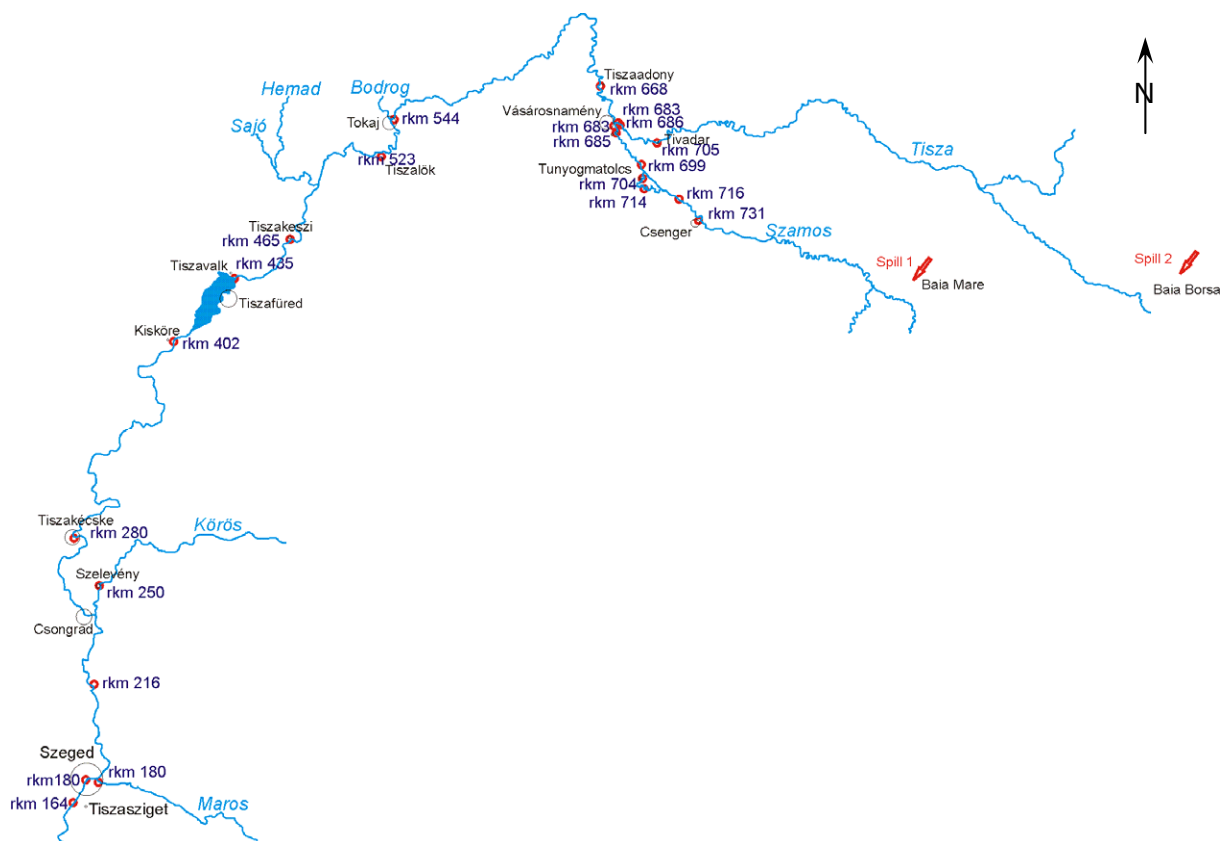


Fig. 3-1: Map of the Tisza River and the sampling locations

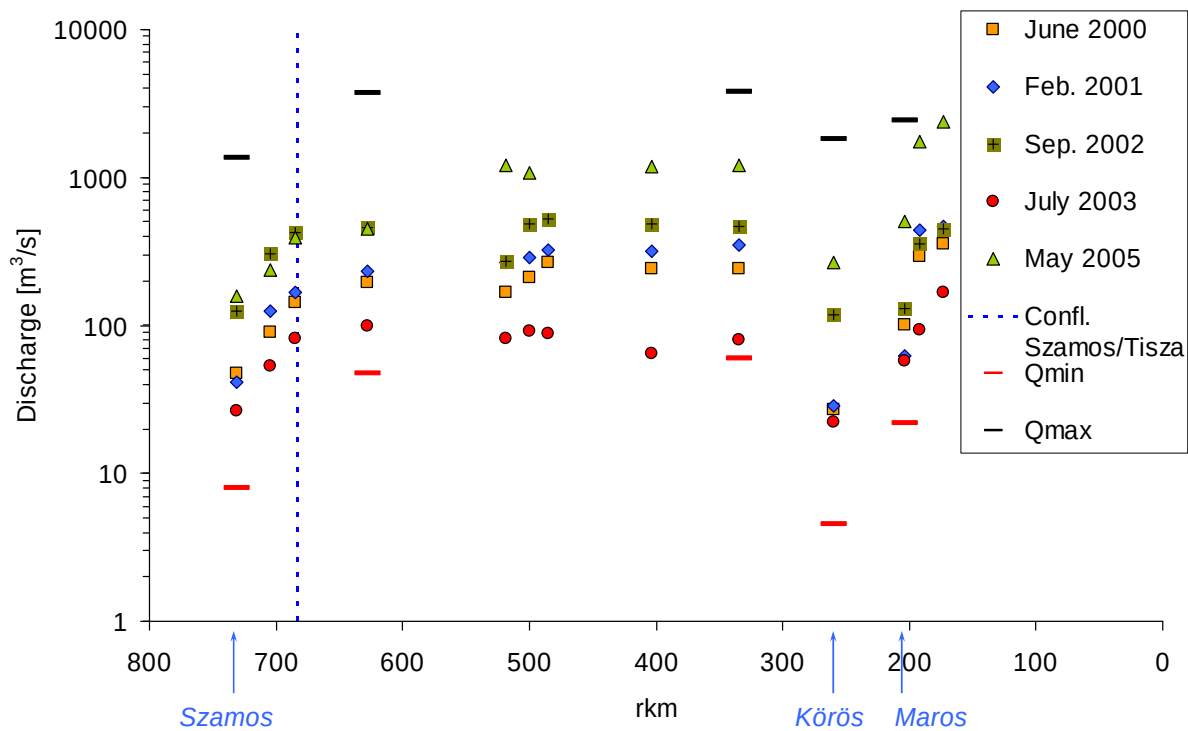


Fig. 3-2: Median discharge during sampling campaigns (Óvári, 2005) and characteristic discharge values (Q_{min} , Q_{max} ; Nagy & Tóth, 2005) in the investigation area

3.1.2 Sampling techniques (methods and depth)

The surface sediments comprise a thickness of up to 5 cm. They were collected by scooping carefully with a shovel.

The sediment profiles were retrieved with a gravitation corer (Mondsee corer, Uwitec, Mondsee, Austria) or in some cases by manually pressing the plastic inliner into the sediment. The cores were divided into depth-oriented sections according to visual characteristics. The sample conservation and preparation is described in chapter 3.2.

Table 3-1 summarizes the sampled locations and the type of samples.

Table 3-1: Sample locations, river distances and available samples (S = surface sediment; SC = sediment core; x = < 20 µm and < 1 mm; y = < 20 µm; z = < 1 mm)

River	Locality	rkm individual distance ⁵	rkm distance to Danube	2000		2001		2002		2003		2005	
				S	SC	S	SC	S	SC	S	SC	S	SC
Szamos	Csenger	48	731	x	x	y						y	
Szamos	Szamossályi (ferry)	33	716			y		z		z		y	
Old Szamos	Géberjén	31	714					z					
Old Szamos	Györtelek- Tunyogmatolcs	21	704			y	y						
Szamos	Nábrád	16	699			y							
Szamos	Olcsva(apati) (ferry)	2	685	x	x	y	y					y	y
Szamos	Vásárosnamény	0	683					z		z			
Tisza	Tivadar (lido)	705	705	x	x	y	y					y	
Tisza	Gergelyiugornya (above confluence with Szamos)	686	686			y							
Tisza	Vásárosnamény	683	683							z			
Tisza	Tiszaadony (ferry)	668	668	x	x	y						y	y
Tisza	Tokaj (above confluence with Bodrog)	544	544	x	x	y						y	y
Tisza	Tiszalök (hydroelectric power station)	523	523	x		y							
Tisza	Tiszakeszi	465	465	x		y							
Tisza	Tiszavalk (reservoir, northern shore)	435	435	x	x	y	y	z		z			
Tisza	Kisköre (reservoir, 500 m below outflow)	402	402	x	x	y		z		z			
Tisza	Tiszaécske	280	280	x	x	y						y	
Körös	Szelevény	10	250									y	
Tisza	Mindszent	216	216	x	x							y	
Maros	Szeged	0	180									y	
Tisza	Szeged-Tápé (ferry)	180	180	x	x							y	
Tisza	Tiszasziget	164	164	x	x							y	

3.2 Sample preparation and grain size fractionation

The wet samples were kept frozen (-40 °C; Kraft, 2002: ≤ 4 °C) in polyethylene bags until further preparation. The frozen samples were freeze-dried at -5 °C for 48 hours (Christ, Alpha 1, Osterode, Germany). Plant parts and stones were removed with tweezers. The dried samples were subsequently homogenized in an agate mortar and sieved through a 1 mm plastic sieve (Fritsch, Idar-Oberstein, Germany).

The elemental composition was determined for the grain size fractions < 20 µm and < 1 mm. For the separation of the < 20 µm fraction two different techniques were applied: (1) wet sieving with

⁵ distance till confluence with the Tisza or in case of the Tisza itself the distance to the confluence with the Danube

ultrasonic treatment and (2) a combination of sieving with ultrasonic treatment and sedimentation. The different separation techniques caused differences in the mass fraction of the < 20 µm fraction, but no significant changes of the element concentration (Kraft, 2002).

Table 3-3 shows the analyzed grain size fractions and the applied separation technique for each sampling campaign.

Table 3-2: Description of applied grain size separation techniques

Separation technique	Description
Wet sieving with ultrasonic treatment	freeze-drying of sample careful crushing in porcelain mortar dry sieving (nylon sieves): > 1 mm, 200–1000 µm, < 200 µm wet sieving (nylon sieves): 63–200 µm, 20–63 µm, < 20 µm; sieving until runoff stays clear
Combination of sieving with ultrasonic treatment and sedimentation in Atterberg cylinders	method described in detail by Bachmann et al. (2001)

Table 3-3: Overview of methods used for grain size fractionation

Year	Grain size fraction	Method	Institute
2000	< 20 µm	wet sieving with ultrasonic treatment	UFZ
2000	< 1 mm	dry sieving	UFZ
2001	< 20 µm	combination of sieving with ultrasonic treatment and sedimentation in Atterberg cylinders	TUBS
2002	< 1 mm	dry sieving	UFZ
2003	< 1 mm	dry sieving	UFZ
2005	< 20 µm	wet sieving with ultrasonic treatment	UFZ

3.3 Chemical analysis

The element concentrations are based on the dry weight of the samples if not stated otherwise.

3.3.1 Carbon analysis

The samples of the years 2000 and 2001 were analyzed for their content of total carbon (TC) and total organic carbon (TOC). TOC is determined after removing carbonates with HCl. The determination is based on the DIN ISO 10694. Total inorganic carbon (TIC) results from the difference between TC and TOC (Formula 3-1).

$$\text{TIC} = \text{TC} - \text{TOC}$$

Formula 3-1: Calculation of total inorganic carbon (TIC)

3.3.2 Aqua regia soluble element contents

All samples were digested in aqua regia. The samples of the years 2000 and 2002 to 2005 were treated in a microwave-assisted pressure- and temperature-controlled procedure (Mars 5, CEM). 250 mg of the < 20 µm/< 1 mm fraction were put in a PTFE microwave vessel with 6 mL 37 % HCl (Suprapure grade, Merck, Germany) and 2 mL 65 % HNO₃ (Suprapure grade, Merck, Germany). The digestion took place at the following settings: step 1) 1200 W, ramp 7 min, T_{max} 140 °C, P_{max} 24.16 bar; step 2)

hold 10 min, $T_{\max}$ 140 °C, $P_{\max}$ 24.16 bar; step 3) 1200 W, ramp 5 min, $T_{\max}$ 180 °C, $P_{\max}$ 24.16 bar; step 4) hold 10 min, $T_{\max}$ 180 °C, $P_{\max}$ 24.16 bar. After digestion the solution was transferred into a 25 mL volumetric flask and filled to the mark.

Major elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Optima 3000, Perkin-Elmer)

The determination of the trace elements was carried out after 1:10 dilution by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500c, Agilent Technologies, Waldbronn, Germany).

The samples of the sampling campaign in 2001 were digested in open PTFE vessels. 200 mg of the < 20 µm fraction were treated with 15 mL 37 % HCl and 5 mL 65 % HNO₃. The reaction was allowed to proceed for 1 h at ambient temperature before the vessels were heated on a hot plate (≤ 80 °C) until near dryness. The digests were taken up with 20 mL 1 M HNO₃.

The analysis of these samples was undertaken at the Geochemical Laboratory at the Technical University of Braunschweig. Major elements and some of the trace elements were determined by ICP-OES (Typ 3520, Bausch & Lomb, ARL; Maxim Fisons Instruments). The following trace elements were analyzed by ICP-MS (Micromass Platform): As, Cd, Mo, Pb, Sb, Se, U.

3.3.3 Sequential extraction

The sequential extraction gives the possibility to get information on the relative mobility of elements under certain conditions. Despite some drawbacks of this method (operationally defined bonding form fractions, intercomparability between different methods, reproducibility of results), this type of analysis gives a good first insight into potentially and environmentally effective element contents.

Depending on the applied scheme the total element content is divided into a certain number of fractions. In general the first fraction is the most mobile while the reactivity decreases with every following step. The extracted bonding form fractions of the different applied extraction protocols were matched in Table 5-1.

An overview of the applied extraction methods and samples is given in Table 3-4. The extracted fractions and the applied reagents are summarized in Table 3-5. All reagents used were of analytical grade or better.

The sequential extractions following the BCR protocols were accompanied by the determination of blanks and certified reference material (BCR 701, freshwater sediment). The obtained extracts were analyzed after 100-fold dilution by ICP-OES (major elements and Zn) and 25-fold dilution by ICP-MS (trace elements).

The element data are given either as concentrations based on the dry weight of the samples or as the relative content based on the sum of the extracted fractions. In case of the year 2003, the relative content is based on the aqua regia soluble element content of the sample (Ch. 3.3.2).

Table 3-4: Overview of applied sequential extraction methods and investigated grain size fractions (a: residual fraction calculated (= aqua regia soluble – sum of sequentially extracted fractions); b: residual fraction extracted)

Year	Grain size fraction	Method	Extracted fractions	Reference
2000	< 20 µm	modified Tessier	6	Jakob et al. (1990)
2001	< 20 µm	modified Tessier	6	Jakob et al. (1990)
2002	< 1 mm	BCR ^a	3	Quevauviller et al. (1997)
2003	< 1 mm	BCR ^b	4	Quevauviller et al. (1997)
2005	< 20 µm	optimized BCR	4	Pueyo et al. (2001)

Table 3-5: Applied sequential extraction protocols

Method	Step	Description	Reagent	Reference
modified Tessier	1	adsorbed	ammonium acetate (1 mol L ⁻¹ ; pH 7)	Jakob et al. (1990)
	2	carbonate	sodium acetate (1 mol L ⁻¹ ; pH 5)	
	3	easily reducible	hydroxylammonium chloride (0.1 mol L ⁻¹ ; pH 2)	
	4	moderately reducible	ammonium oxalate/oxalic acid (0.2 mol L ⁻¹ ; pH 3)	
	5	oxidizable	hydrogen peroxide (300 mg g ⁻¹); ammonium acetate (1.0 mol L ⁻¹ ; pH 7)	
	6	residual	aqua regia or HF/HNO ₃ /HClO ₄	
BCR	1	acid-soluble	acetic acid (0.11 mol L ⁻¹)	Quevauviller et al. (1997)
	2	reducible	hydroxylammonium chloride (0.1 mol L ⁻¹)	
	3	oxidizable	hydrogen peroxide (300 mg g ⁻¹); ammonium acetate (1.0 mol L ⁻¹)	
	4	residual	aqua regia	
optimized BCR	1	acid-soluble	acetic acid (0.11 mol L ⁻¹)	Pueyo et al. (2001)
	2	reducible	hydroxylammonium chloride (0.5 mol L ⁻¹)	
	3	oxidizable	hydrogen peroxide (300 mg g ⁻¹); ammonium acetate (1.0 mol L ⁻¹ ; pH 2.0±0.1)	
	4	residual	aqua regia	

3.4 Data evaluation

Statistical data analysis was performed with SPSS 13.0 for Windows (Release 13.0.1). The following parameters and tests were computed:

- Descriptive statistics (average; median; standard deviation)
- T-test: independent samples test (Levene's test for equality of variances, t-test for equality of means)
- Correlation analysis (Spearman's rank-order correlation coefficient)
- Hierarchical agglomerative cluster analysis (Ward algorithm, squared Euclidian distance)

4. Results

4.1 Sediment composition

Above the confluence of the Tisza with the Szamos the sediments are oxic with a neutral reaction. The grain size fraction contains 2.1–2.4 % total organic carbon (TOC) and no detectable inorganic carbon (TIC).

In the subsequent course of the Tisza, the fine fraction (< 20 µm) contains about the same amount of TOC (2.2 %) and low TIC (0.4 %). The sediments are slightly oxidized. The Szamos has reduced sediments with neutral reaction. The TOC of the fine fraction is slightly higher than in the Tisza

(3.0 % TOC; 0.3 % TIC). The sediments from the Old Szamos (old arm) are reduced and slightly acid with a higher TOC content (7.4 %).

Based on data from the sampling campaign 2001 (Kraft, 2002), it can be stated that the sampled sediments show a heterogeneous grain size composition. The main components are silt and sand. The sediments can be described as loamy sand to silt (loamy sand – sandy loam – silt loam – silt).

Kraft (2000, 2002) also analyzed the mineralogy of the Hungarian sediments. The clay ($< 2 \mu\text{m}$) and the silt ($2\text{--}63 \mu\text{m}$) fraction contain a high proportion of quartz and a small proportion of feldspars (Kraft, 2000). The clay minerals are composed of illite, kaolinite and mixed-layer minerals.

In 2001, the clay fraction shows only minor differences in kaolinite and illite between the individual samples. The upper course of the Tisza and the old arm of the Szamos contain mixed-layer minerals, which are composed of illite with layers of montmorillonite. The lower course of the Tisza contains mixed-layer minerals only in traces. The silt fraction is composed of less mixed-layer minerals than the clay size fraction. In contrast to the Tisza sediments, the samples from the Szamos contain no swellable clay minerals.

Overall it can be derived that the adsorption capacity for heavy metals is low at the Tisza and higher at the Szamos. Due to a higher fraction of swellable clay minerals and a higher TOC content the adsorption capacity will be the highest at the old arm.

4.2 Aqua regia soluble element content

4.2.1 Comparison of aqua regia soluble element contents of the grain size fractions $< 20 \mu\text{m}$ and $< 1 \text{ mm}$

Two grain size fractions were analyzed from the samples of the sampling campaign in 2000: $< 20 \mu\text{m}$ and $< 1 \text{ mm}$. As expected (Ackermann et al., 1983), the element concentrations in the $< 1 \text{ mm}$ fraction are lower than in the fine fraction (Fig. 4-1). In some cases (e.g. rkm 435), the element content of both fractions has almost the same level. This can be explained by a high percentage of the fine fraction in the $< 1 \text{ mm}$ grain size fraction.

The enrichment of selected elements in the $< 20 \mu\text{m}$ fraction compared to the $< 1 \text{ mm}$ fraction is displayed in Fig. 4-2. The major elements (Al, Ca, Fe) are enriched to a similar degree along the river course. The enrichment factors vary between 2 and 5. Al shows the highest factor.

The trace elements follow the pattern of the major elements, although the maximum factors are higher (< 12). Cu shows the strongest enrichment, Co the weakest.

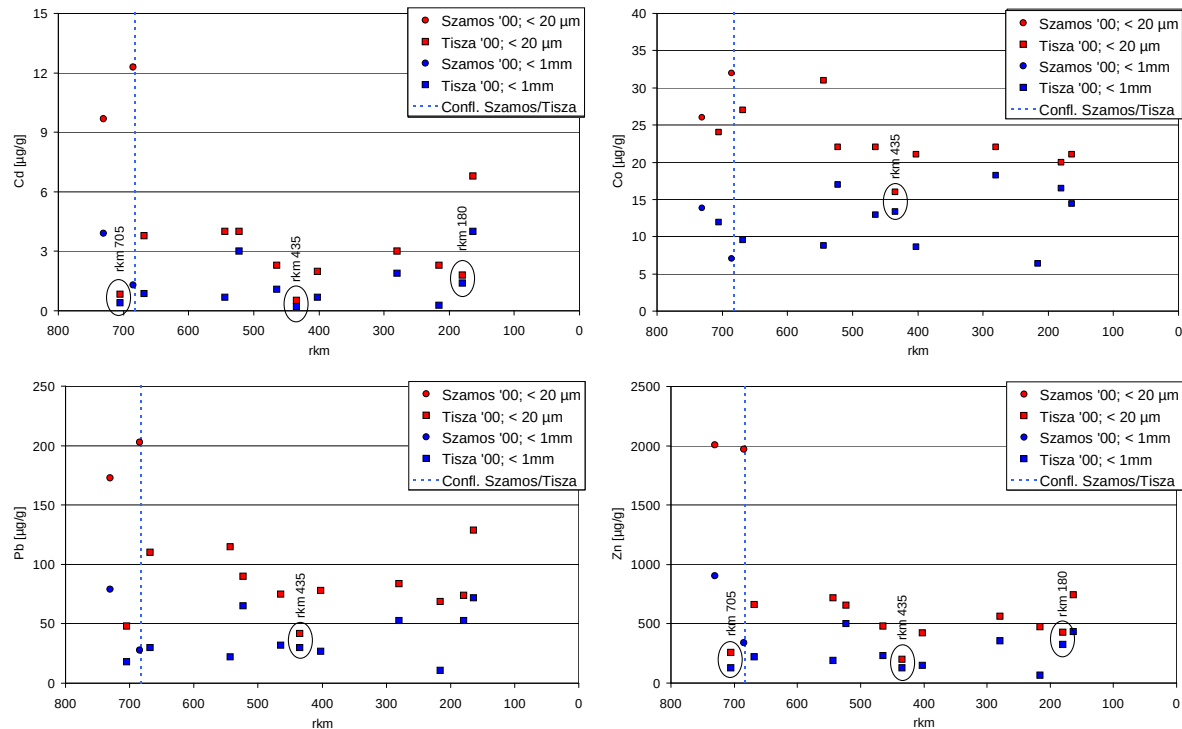


Fig. 4-1: Comparison of element concentrations of Cd, Co, Pb and Zn in the grain size fractions < 20 µm and < 1 mm of sediments (sampling campaign 2000)

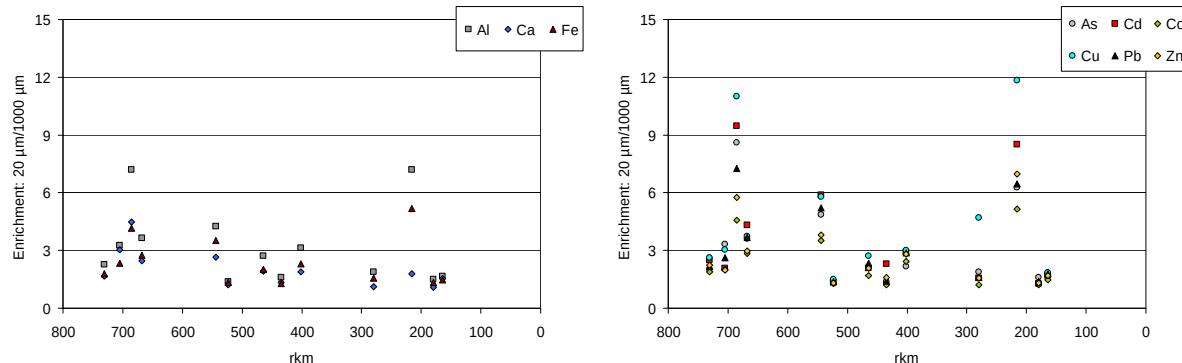


Fig. 4-2: Enrichment factors of element concentrations in the grain size fraction < 20 µm vs. < 1 mm

4.2.2 Geogenic vs. anthropogenic proportions of the heavy metal load

To assess the heavy metal load of the river sediments, reference values should be used. One of these reference materials is the average shale, which was introduced by Turekian & Wedepohl (1961). Although it is globally applicable, it has the disadvantage that local influences, *e.g.* a strong mineralization of an area like the north-western Romania, are disregarded. As a consequence, anthropogenic factors derived on that basis will overemphasize the human impact on element enrichment.

The application of local reference sites can be a useful alternative. An old arm of the Szamos River (rkm 704; Fig. 4-3) and a sampling point at the reservoir at the Tisza River (rkm 435) were taken into consideration. Both localities have in common that they are not affected by each flooding of the rivers. Therefore, the input of contaminants will be generally lower than that to the main channel.

The old arm of the Szamos is characterized by low concentrations compared to other sediments of the research area, but higher concentrations than the average shale. This shows that the anthropogenic

influence is relatively low and that some of the trace elements are already geogenically enriched due to mineralization. The sediment profiles (2001, 2003) show a relatively steady concentration development over the analyzed depth (Fig. 4-3). This is another indication for a low anthropogenic impact.

The reservoir (rkm 435) is also characterized by lower concentrations of the mining elements (Cd, Cu, Pb and Zn) compared to other localities. The increase of Cd and Zn in the profile of 2001 towards the top is a hint for anthropogenic influence.

The geogenic background concentrations were calculated based on the aqua regia soluble concentrations and are stated in Table 4-1 to Table 4-8.

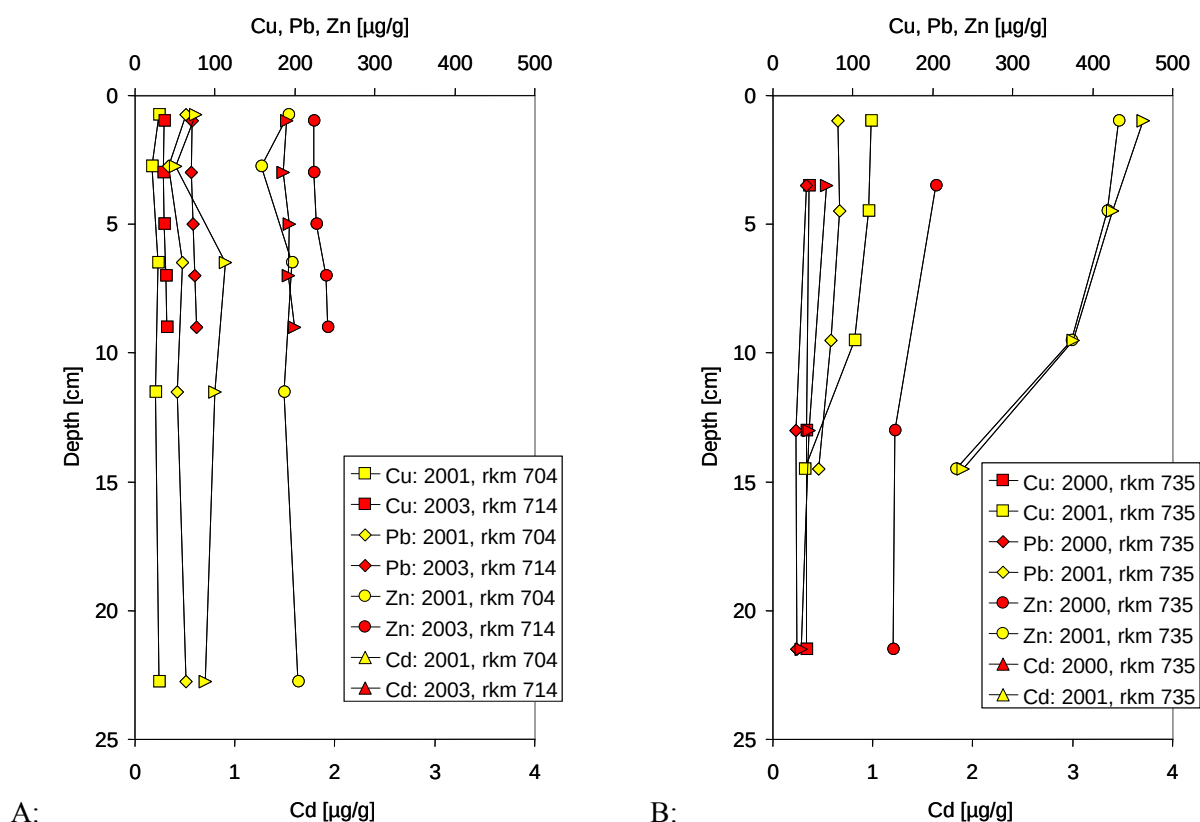


Fig. 4-3: Concentrations of Cd, Cu, Pb and Zn in sediments of the Old Szamos (A; rkm 704, rkm 714) and the reservoir at Tiszavalk (B; rkm 735)

4.2.3 Temporal changes of the concentration of selected elements

Arsenic

Table 4-1: Arsenic concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	8.8	80	31	25
Tisza above confluence (n = 1; rkm 705)				40
Szamos (n = 3)	39	80	54	44
Tisza below confluence (n = 7)	18	40	25	23
<i>local background</i>	<i>Tisza rkm 435, rkm 705 (2000, 2001)</i>			20
	<i>Szamos rkm 704 (2001)</i>			24
<i>Bird et al. (2003) Tisza</i>			18	
<i>(< 63 µm; AR) Szamos</i>			37	
<i>Average shale (T & W)</i>			13	
<i>NL list</i>	<i>target:</i>	<i>intervention:</i>		
	29	55		
<i>Henschel et al. (2003)</i>	<i>precaution:</i>	<i>test:</i>	<i>intervention:</i>	
	8	70	150	

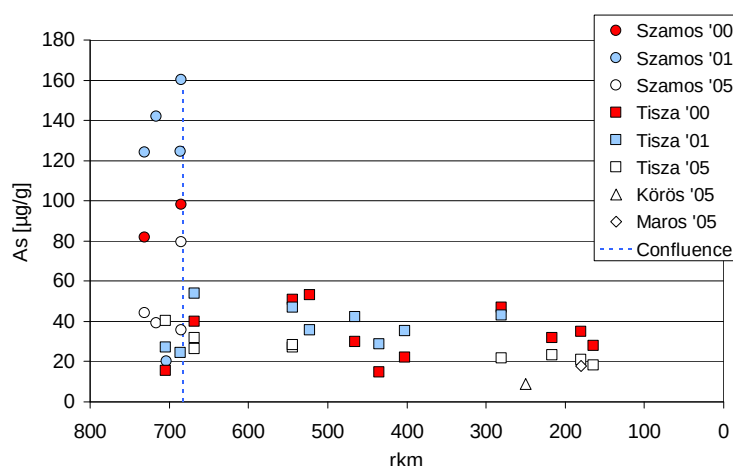


Fig. 4-4: Aqua regia soluble As content (grain size fraction < 20 µm)

Surface sediments

As is enriched in the grain size fraction < 20 µm of the sediments of Tisza and Szamos. In 2005, As is accumulated by a factor of 1.9 (median) compared to the average shale. The Szamos sediments contain the highest concentration (2001: 160 µg/g). In contrast to the generally high values of the Szamos, the samples from the old arm are characterized by low As contents (2001: 20 µg/g). The lowest As value was found in the Körös (2005: 9 µg/g).

For the observed years a general ranking of the As concentration can be recognized: 2001 > 2000 > 2005, which is especially distinct in the Szamos. This pattern could have been caused by transport in 2001 of higher contaminated material from the mining accident in 2000 further downriver. The decline afterwards is probably caused by a dilution effect by deposition and mixing of the surface sediment with relatively uncontaminated material or by erosion of the highly contaminated surface layer. Five years after the accident, As in the Szamos sediment has declined to “only” twice the background value of the Szamos.

The As concentration shows a steady decline below the confluence of Tisza and Szamos until rkm 435.

Two distinct areas can be distinguished based on the As content. The sample from the Szamos, except for the old arm sample, are characterized by high As concentrations that lie for the years 2000-2001 (and 2005) well above the intervention limits of soil protection regulations (NL list, Table 4-1; HU list, e.g. HU-C3: 60 µg/g, Table 4-9). The Tisza samples generally show lower As contents, most of them lying below the intervention limits (< 60 µg/g). Only in very sensitive areas intervention measures might be required (HU-C1: 20 µg/g).

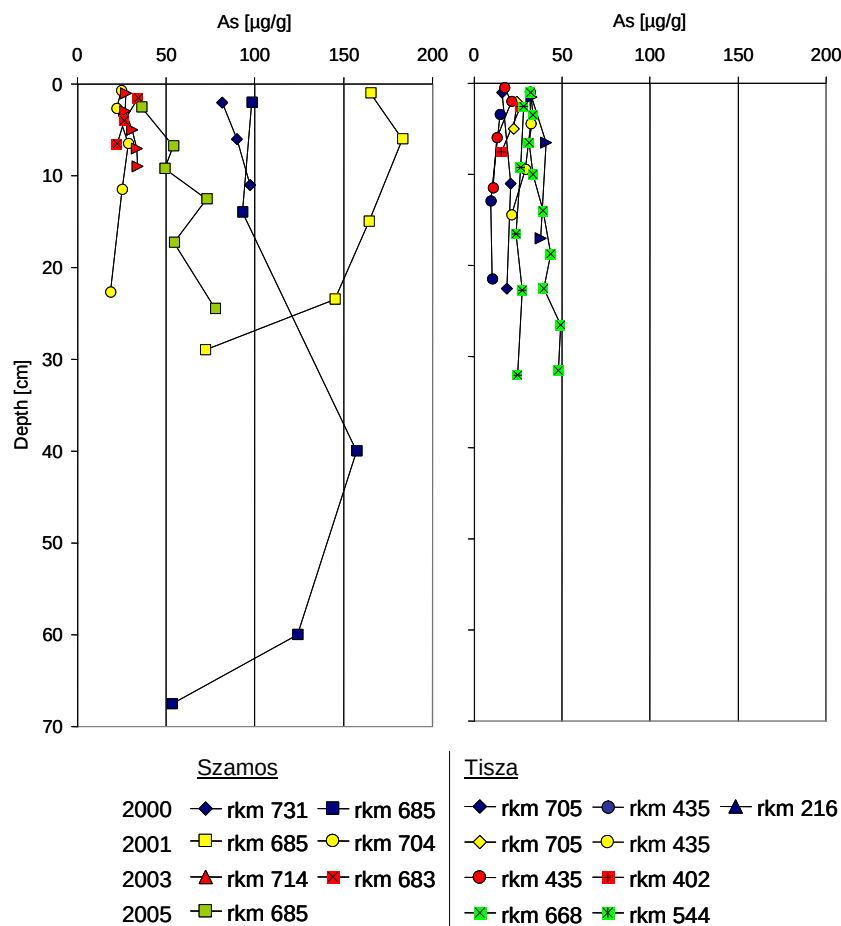


Fig. 4-5: As concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

Sediment profiles

The sediment profiles of the Szamos main channel are characterized by As concentrations above 50 µg/g, while the Szamos old arm and the Tisza river sediments have As contents below 50 µg/g (Fig. 4-5). The concentrations in the latter areas are relatively stable over the sampled sedimentation period. The Szamos samples from the main channel show stronger variations (e.g. rkm 685 in 2000: 53–157 µg/g).

The sampling point rkm 685 differs quite strongly between the years 2000 and 2001. In 2001, the As concentration at the surface is clearly higher (0–27 cm: 145–183 µg/g; max. at 8 cm) than in 2000 (0–20 cm: ca. 100 µg/g; max. at 40 cm). The strong deviation between the sampling campaigns is probably caused by local inhomogeneities. Other reasons might be the erosion of the top layers.

Cadmium

Table 4-2: Cadmium concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	0.4	7.6	3.3	2.9
Tisza above confluence (n = 1; rkm 705)				5.8
Szamos (n = 3)	4.0	7.6	5.7	5.4
Tisza below confluence (n = 7)	1.3	5.8	2.9	2.8
<i>local background</i>				1.5
<i>Tisza</i>				0.7
<i>Szamos</i>				
<i>Kraft et al., 2003 (< 20 µm, total; 2001)</i>				
<i>loc. backgr.</i>			2.1	
<i>Tisza</i>			7.7	
<i>Szamos</i>			22	
<i>Bird et al. (2003) Tisza</i>			1.3	
<i>(< 63 µm; AR) Szamos</i>			9	
<i>Average shale (T & W)</i>			0.3	
<i>NL list</i>	<i>target:</i> 0.8	<i>intervention:</i> 12		
<i>Henschel et al. (2003)</i>	<i>precaution:</i> 1.2	<i>test:</i> 10	<i>intervention:</i> 50	

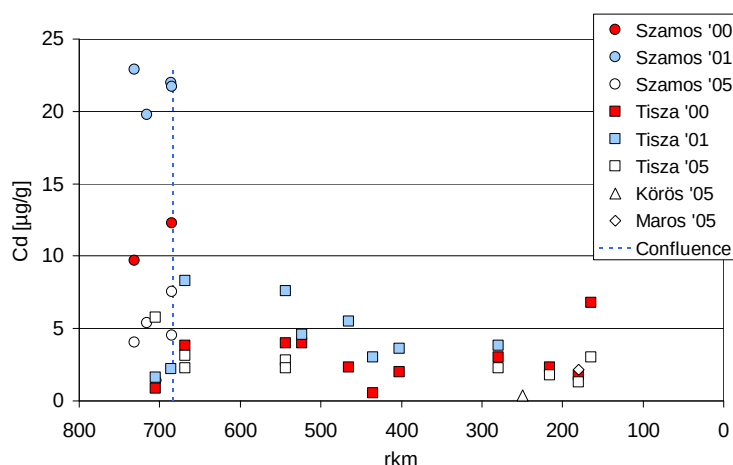


Fig. 4-6: Aqua regia soluble Cd content (grain size fraction < 20 µm)

Surface sediments

The concentration pattern of Cd is similar to that of As. In general the Cd concentrations are highest in 2001 with a decline towards 2005 (2001 > 2000 > 2005). Contrary to that trend, Cd has the highest concentration in the Tisza at rkm 705 in 2005 (6 µg/g) and lower concentrations in 2000 and 2001 (1–2 µg/g). The highest contents are found in the Szamos (< 23 µg/g), the lowest in the Körös (< 0.4 µg/g). There is a steady decrease below the confluence of Tisza and Szamos until approximately rkm 435.

Cd is strongly accumulated in the sediments compared to the average shale (median, 2005: 11). Most samples exceed the target and precaution values for Cd but not the intervention limits (Table 4-2, Table 4-9).

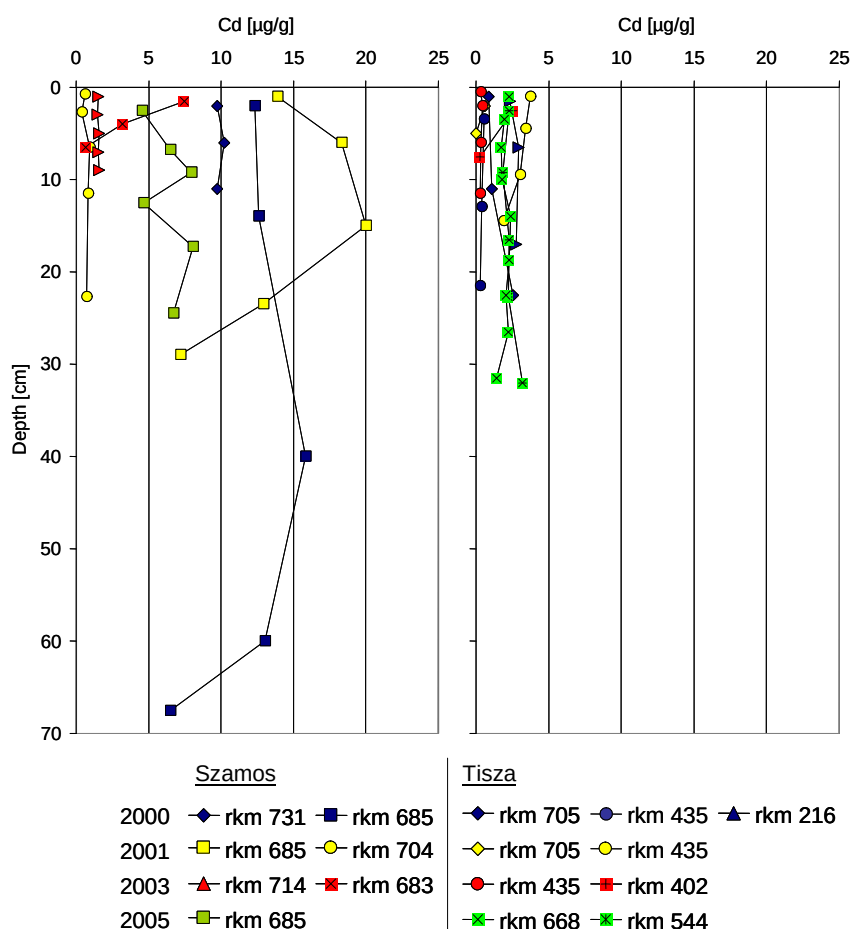


Fig. 4-7: Cd concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

Sediment profiles

The sediment profiles show a relatively stable Cd concentration in the Tisza. All Tisza profiles have concentrations below 4 µg/g. The samples from the Old Szamos (old arm, rkm 704) are also characterized by stable and very low contents (≤ 1 µg/g), while the rest of the Szamos profiles contain significantly higher concentrations with stronger variations (5–20 µg/g). As an indication for the long historic record of Cd input into the Szamos, the Cd concentration at the sampling point rkm 685 lies at a high level of 13 µg/g from 0 to 60 cm depth.

Cobalt

Table 4-3: Cobalt concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	15	24	19	19
Tisza above confluence (n = 1; rkm 705)				24
Szamos (n = 3)	18	23	20	19
Tisza below confluence (n = 7)	16	24	19	17
local background				17
				11
Average shale (T & W)			19	
NL list	target: 20	intervention: 240		

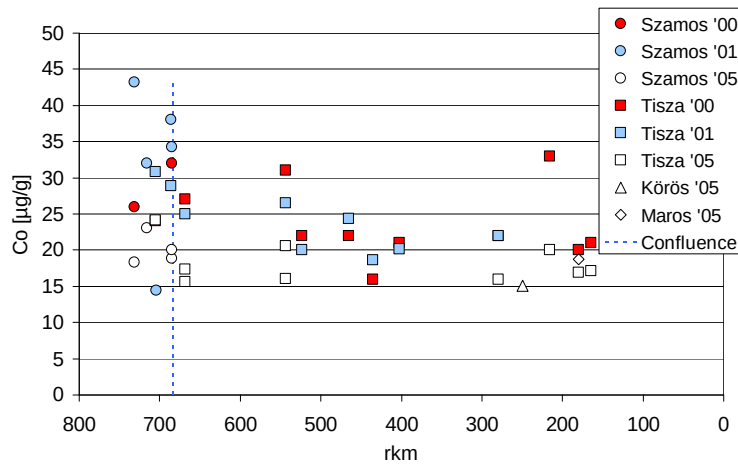


Fig. 4-8: Aqua regia soluble Co content (grain size fraction < 20 µm)

Surface sediments

Co is not enriched in the sediments compared to the average shale (median, 2005: 0.97). The median concentration slightly exceeds the background concentration of the Hungarian list (Table 4-9: 15 µg/g). The concentration level of 2005 is generally lower than that of the years 2000 and 2001.

In 2000 and 2001, the Szamos sediments contained about twice as much Co as the Tisza sediments. During this period, the Co content of the Szamos sediments exceeds the B value of the Hungarian list (Table 4-9: 30 µg/g), which indicates a polluted state.

The Co concentration declines with increasing distance from the Szamos and stabilizes after rkm 435. This gradient almost disappeared in 2005.

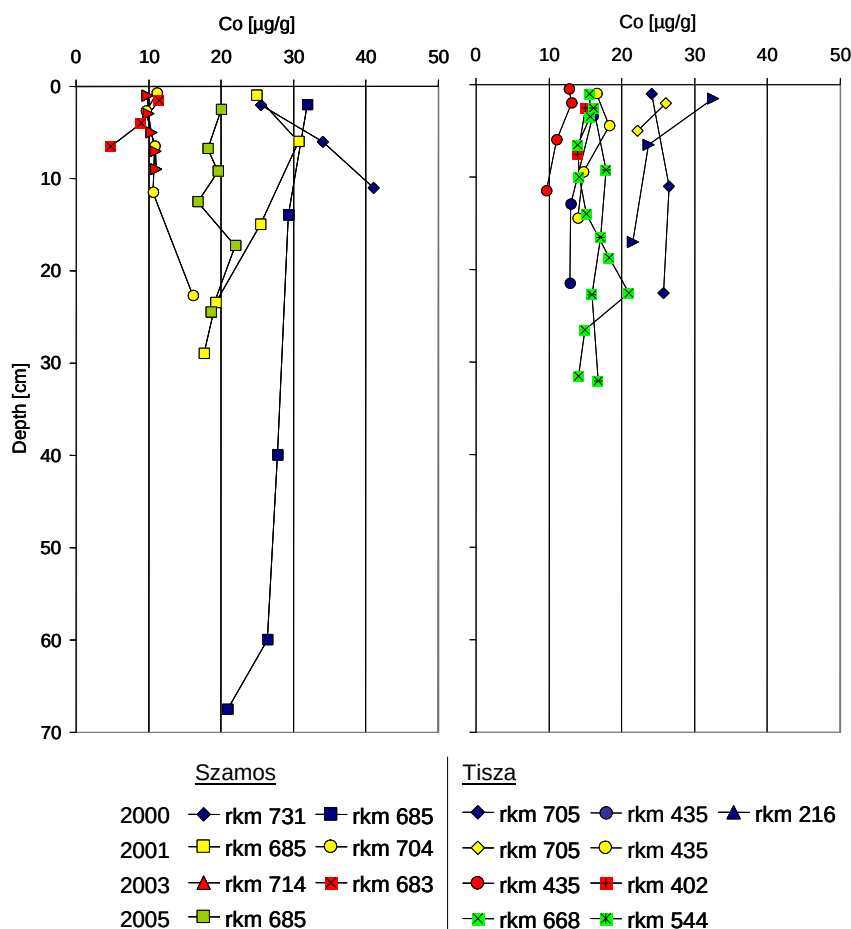


Fig. 4-9: Co concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

Sediment profiles

The sediment profiles show mostly weak variations in the Co content. At the Szamos, the Co concentration steadily increases towards the top. The 70 cm deep profile at rkm 685 (2000) changes from 20 µg/g at 70 cm depth to 30 µg/g at the top. The lowest Co content was found in the old arm sediments (rkm 704: 10 µg/g). The Tisza samples display a similar variation width (10–32 µg/g).

Copper

Surface sediments

The median Cu content of 2005 (94 µg/g) corresponds to twice the average shale (median: 2.1). The legal limits for sensitive (C2) and not very sensitive (C3) areas are exceeded during the years 2000 and 2001 at the Szamos. The sediments at the Tisza lie in most cases below the value for very sensitive areas (C1; Table 4-9) but above the B value (2000, 2001) indicating a pollution. The target value of 30 µg/g (A) corresponds to the geogenic background calculated for the Szamos (Table 4-4).

Table 4-4: Copper concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	30	325	105	94
Tisza above confluence (n = 1; rkm 705)				107
Szamos (n = 3)	96	325	173	99
Tisza below confluence (n = 7)	60	118	88	85
<i>local background</i>				
<i>Tisza</i>				77
<i>Szamos</i>				29
<i>Kraft et al., 2003 (< 20 µm, total; 2001)</i>				
<i>loc. backgr.</i>			30	
<i>Tisza</i>			170	
<i>Szamos</i>			560	
<i>Bird et al. (2003) Tisza</i>			54	
<i>(< 63 µm; AR) Szamos</i>			220	
<i>Average shale (T & W)</i>			45	
<i>NL list</i>	<i>target:</i>	<i>intervention:</i>		
	36	190		
<i>Henschel et al. (2003)</i>	<i>precaution:</i>	<i>test:</i>	<i>intervention:</i>	
	30	300	600	

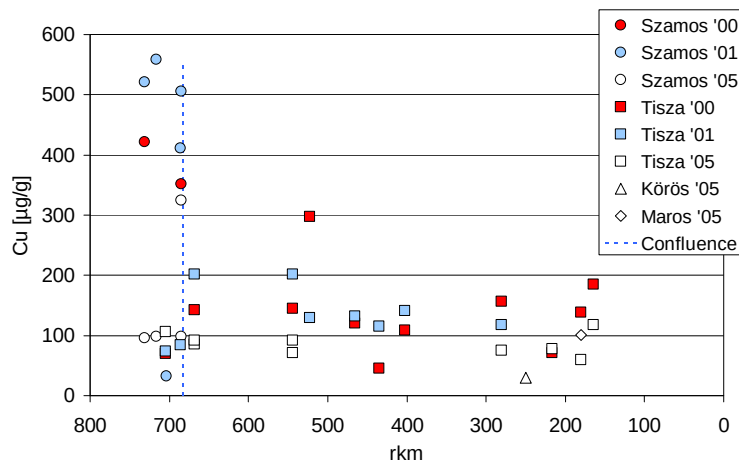


Fig. 4-10: Aqua regia soluble Cu content (grain size fraction < 20 µm)

Sediment profiles

The sediment profiles of the Tisza show relatively stable Cu concentration within the sampled depth of 35 cm. Only slight local variations can be detected. The situation at the Szamos is different. The profiles at rkm 685 (2000, 2001) and rkm 731 have distinctly higher Cu concentrations accompanied by stronger historic changes. The maximum Cu content of 961 µg/g is reached at a depth of 40 cm (rkm 685, 2000). The other profiles behave similar to the Tisza samples: low and stable concentrations (≤ 200 mg/g).

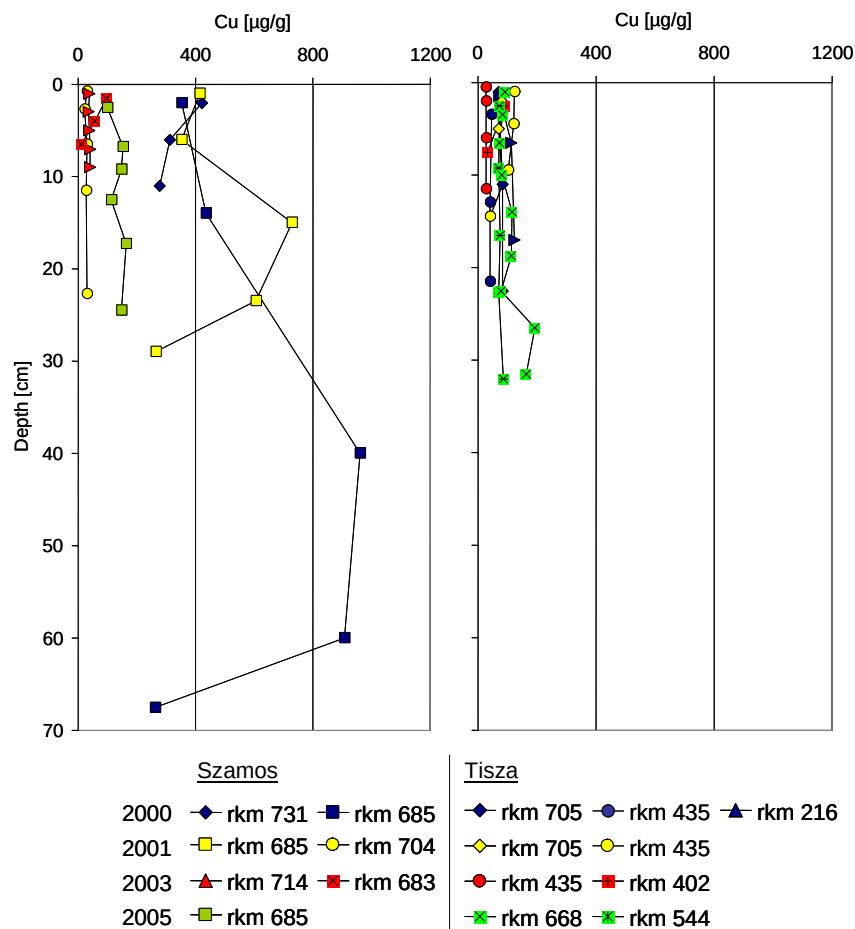


Fig. 4-11: Cu concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

Molybdenum

Table 4-5: Molybdenum concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	0.3	1.6	1.0	1.1
Tisza above confluence (n = 1; rkm 705)				1.6
Szamos (n = 3)	1.0	1.5	1.2	1.1
Tisza below confluence (n = 7)	0.7	1.6	1.1	1.0
local background				0.7
Tisza				
Szamos				1.3
Average shale (T & W)			2.6	
NL list	target: 10	intervention: 200		

Surface sediments

The median concentration of Mo (2005) corresponds to 0.40 of the average shale. The Mo content of the Szamos is almost at the same level as the Tisza samples. In both rivers, Mo varies between 0.5 and 2.0 µg/g with only a few exceptions ranging up to 3.0 µg/g (e. g. rkm 731, 2000).

Sediment profiles

The sediment profiles display mostly stable Mo contents. At rkm 685 (2000), Mo varies insignificantly over the depth of 0 to 65 cm. There is a strong peak (3 $\mu\text{g/g}$) in ca. 3 cm depth (rkm 731, 2000; rkm 704, 2001)

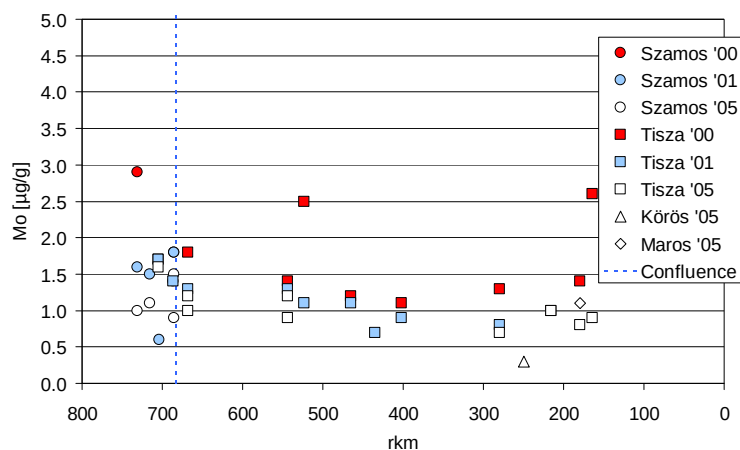


Fig. 4-12: Aqua regia soluble Mo content (grain size fraction < 20 μm)

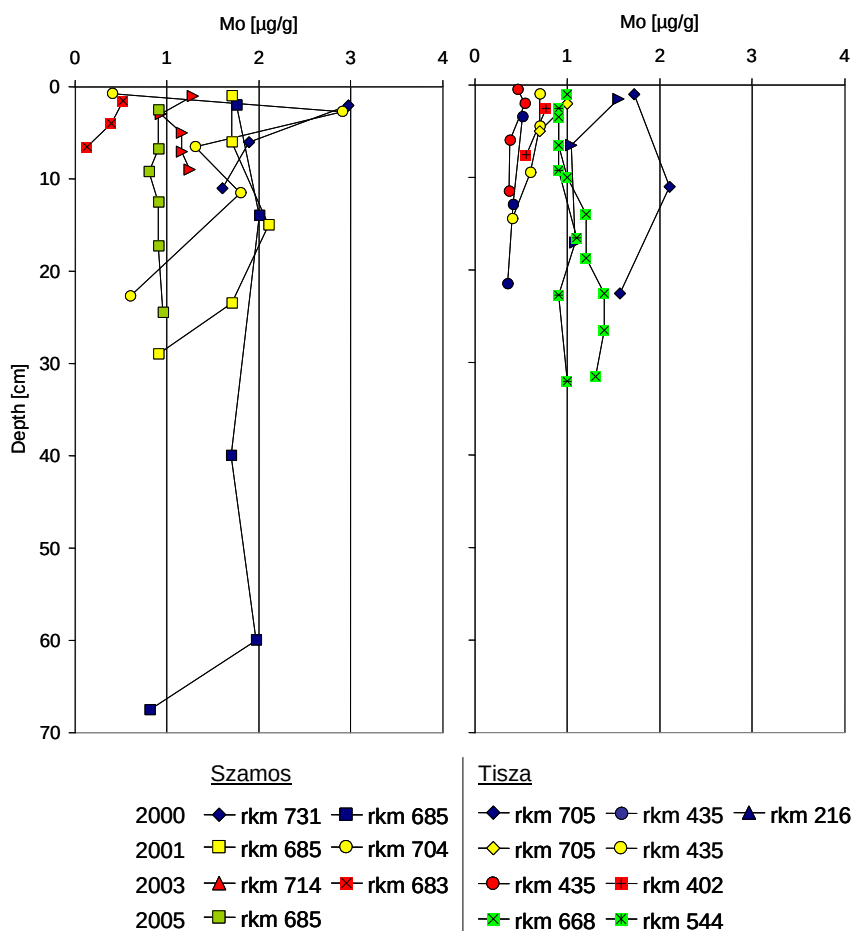


Fig. 4-13: Mo concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 μm ; 2003: < 1 mm)

Nickel

Table 4-6: Nickel concentration ($\mu\text{g/g}$) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	50	69	59	58
Tisza above confluence (n = 1; rkm 705)				69
Szamos (n = 3)	55	65	60	61
Tisza below confluence (n = 7)	52	69	61	60
<i>local background</i>	<i>Tisza</i>			56
	<i>Szamos</i>			45
<i>Kraft et al., 2003 (< 20 μm, total; 2001)</i>				
	<i>loc. backgr.</i>			54
	<i>Tisza</i>			69
	<i>Szamos</i>			80
<i>Average shale (T & W)</i>				68
<i>NL list</i>	<i>target:</i>	<i>intervention:</i>		
	35	210		
<i>Henschel et al. (2003)</i>	<i>precaution:</i>	<i>test:</i>	<i>intervention:</i>	
	20	50	600	

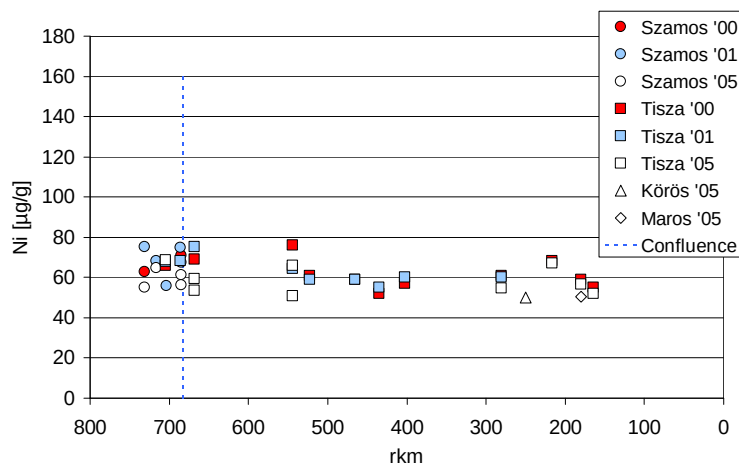


Fig. 4-14: Aqua regia soluble Ni content (grain size fraction < 20 μm)

Surface sediments

The Ni content of the surface sediments is lower than that of the average shale (median, 2005: 0.84). The variation along the river course is small. There is no significant difference between Szamos and Tisza.

Sediment profiles

The sediment profiles reflect the stable Ni concentrations of the surface sediments. The sediments of both rivers shift around 50 $\mu\text{g/g}$ and show stable trends down to 70 cm depth. The reference profile (rkm 704, old arm) at the Szamos is not different from the other profiles. Only one profile holds less than 40 $\mu\text{g/g}$ (rkm 683, 2003). Its low Ni content is most likely due to the analyzed coarser grain size fraction of < 1 mm instead of < 20 μm .

At the Tisza, there is only one layer with an explicitly higher Ni content (rkm 216, 2000, 0–3 cm: 89 $\mu\text{g/g}$), all other samples show almost no changes with time.

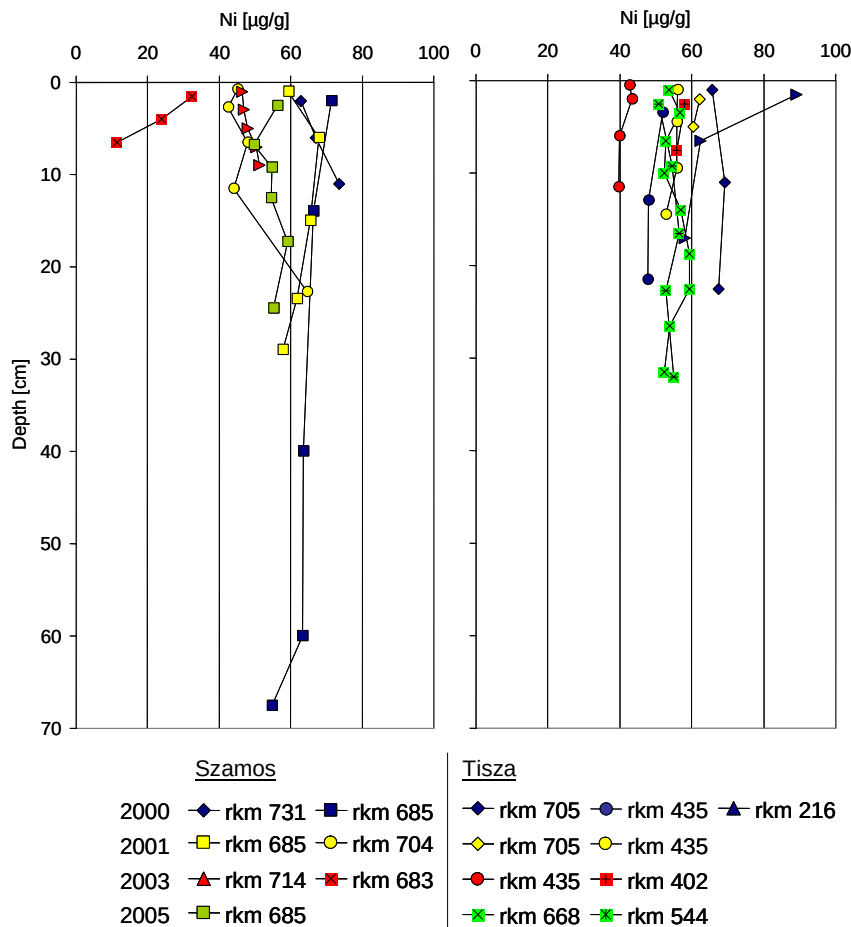


Fig. 4-15: Ni concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

Lead

Table 4-7: Lead concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	26	166	92	78
Tisza above confluence (n = 1; rkm 705)				147
Szamos (n = 3)	116	166	141	141
Tisza below confluence (n = 7)	55	147	83	76
local background Tisza				53
Szamos				60
Kraft et al., 2003 (< 20 µm, total; 2001)				
loc. backgr.			47	
Tisza			110	
Szamos			350	
Bird et al. (2003) Tisza			38	
(< 63 µm; AR) Szamos			97	
Average shale (T & W)			20	
NL list	target: 85	intervention: 530		
Henschel et al. (2003)	precaution: 50	test: 200	intervention: 1000	

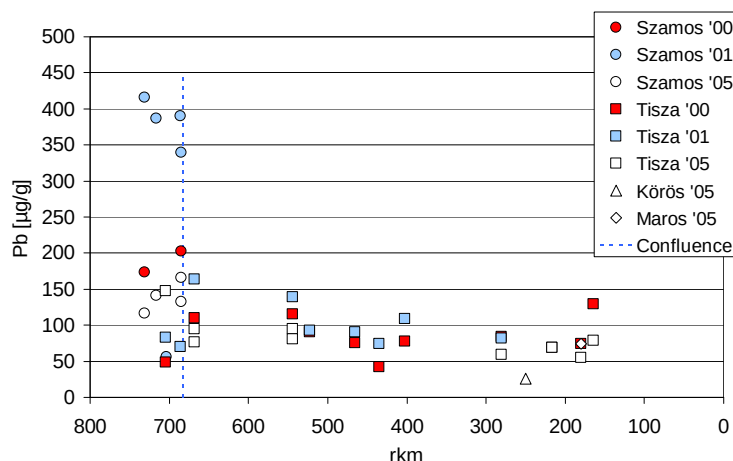


Fig. 4-16: Aqua regia soluble Pb content (grain size fraction < 20 µm)

Surface sediments

Pb is compared to the average shale strongly enriched in the grain size fraction < 20 µm of the sediments. The median of 2005 corresponds to 3.9 times the average shale. The local background concentration is by a factor of 2.5 to 3.0 distinctly higher than the average shale reflecting the strong mineralization of this area (20 µg/g; Table 4-7). In contrast to this strong enrichment, only the samples at the Szamos and the upper Tisza exceed the legal level for not very sensitive areas (C1). Most samples of the Tisza fall below the B level ("polluted").

The highest concentrations were detected in the sediments of the Szamos. Below the confluence of the Szamos with the Tisza, the Pb content shows a steady decrease, which is slowing down after ca. rkm 400. The lowest Pb content was measured in the sample of the Körös.

Like most other trace elements, the concentrations were the highest in 2001 and the lowest in 2005 (2001 > 2000 > 2005).

Sediment profiles

The sediment profiles split into three groups: (1) < 100 µg/g (old arm, rkm 683), (2) around 200 µg/g (rkm 685 (2000, 2005), rkm 731), (3) < 400 µg/g (rkm 685 (2001)). The profile at rkm 685 (2000) demonstrates the long history of Pb deposition in the river. The sediments at this location show a high and stable Pb content down to a depth of 60 cm.

At the Tisza, all sediment profiles contain less than 100 µg/g. Temporal variations are small with the exception of rkm 402 (2003, < 1 mm), which shows a strong gradient. This might be caused by an increasing proportion of finer grain sizes towards the top, which generally results in higher trace metal contents.

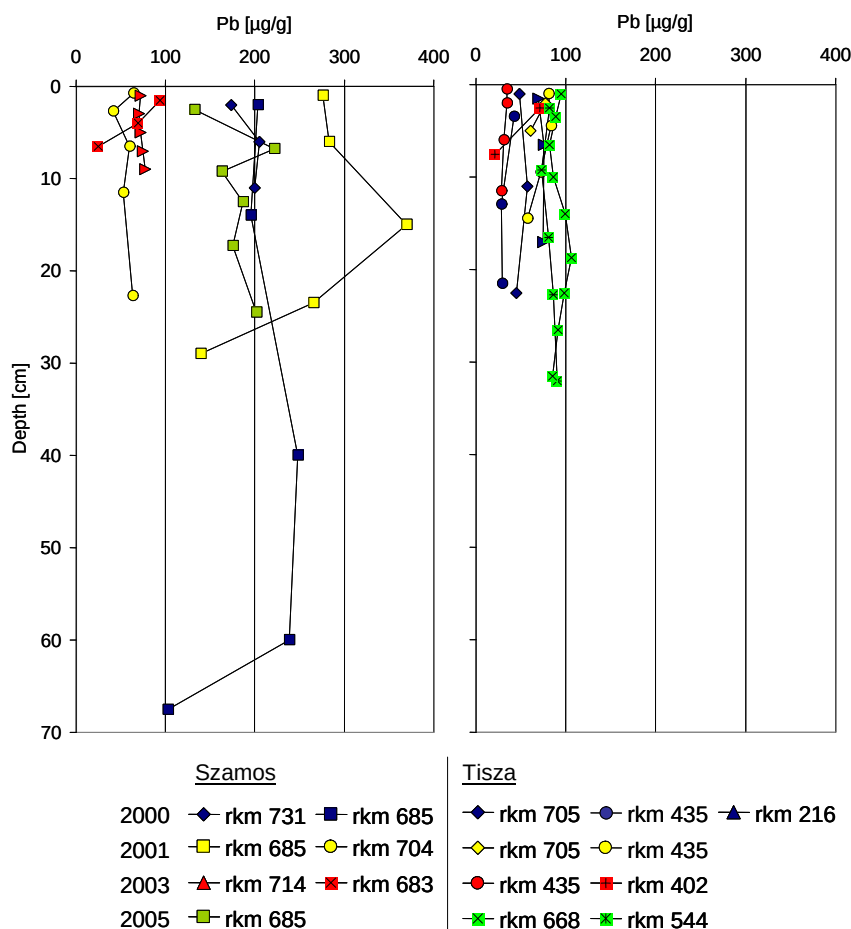


Fig. 4-17: Pb concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

Zinc

Surface sediments

Like Pb, Zn is highly enriched in the river sediments compared to the average shale. The median corresponds to 5.8 of the average shale. The high Zn content of this mineralized region is also displayed in the high background concentrations of Tisza and Szamos (Table 4-8).

The Zn concentration is well above the target value of the Hungarian list (Table 4-9) and also exceeds the B value ("polluted"). The lowest concentration was detected at the Körös and rkm 435 of the Tisza. Most samples step over the C1 level for very sensitive areas as well. The Szamos sediments break the C2 limit (1000 µg/g) for sensitive areas and in the years 2000 and 2001 even the limit for not very sensitive areas.

Table 4-8: Zinc concentration (µg/g) in sediments from Tisza and Szamos compared to reference values

2005	min	max	mean	median
all (n = 12)	130	1714	749	553
Tisza above confluence (n = 1; rkm 705)	1258			
Szamos (n = 3)	1113	1714	1369	1281
Tisza below confluence (n = 7)	401	1258	618	473
<i>local background</i>				
<i>Tisza</i>				266
<i>Szamos</i>				191
<i>Kraft et al., 2003 (< 20 µm, total; 2001)</i>				
<i>loc. backgr.</i>			214	
<i>Tisza</i>			820	
<i>Szamos</i>			2690	
<i>Bird et al. (2003) Tisza</i>			200	
<i>(< 63 µm; AR) Szamos</i>			1200	
<i>Average shale (T & W)</i>			95	
<i>NL list</i>	<i>target:</i>	<i>intervention:</i>		
	140	720		
<i>Henschel et al. (2003)</i>	<i>precaution:</i>	<i>test:</i>	<i>intervention:</i>	
	150	400	1500	

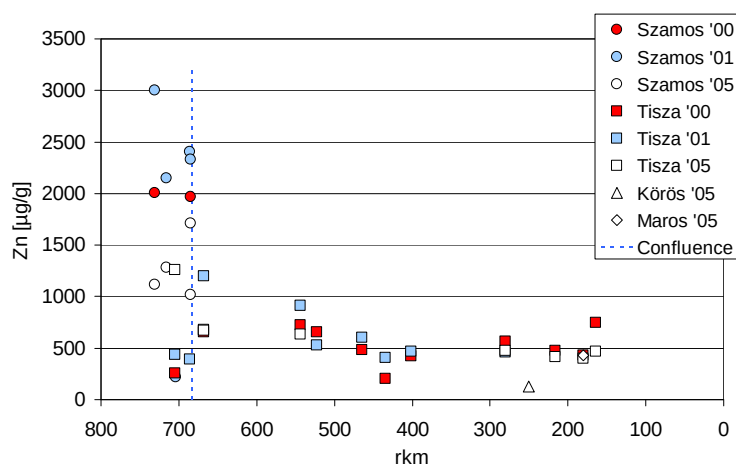


Fig. 4-18: Aqua regia soluble Zn content (grain size fraction < 20 µm)

Sediment profiles

The sediment profiles at the Szamos clearly show the use of the profile at rkm 704 as the reference profile for calculating the background concentration. This sampling point has a distinctly lower Zn content (≤ 250 µg/g) than the other profiles (> 1000 µg/g). Profile rkm 685 (2005) has the strongest variations over time, while in 2000 this sampling point was characterized by a stable Pb content up to a depth of 65 cm.

At the Tisza the Zn content does not exceed 1000 µg/g, most profiles lie below 500 µg/g.

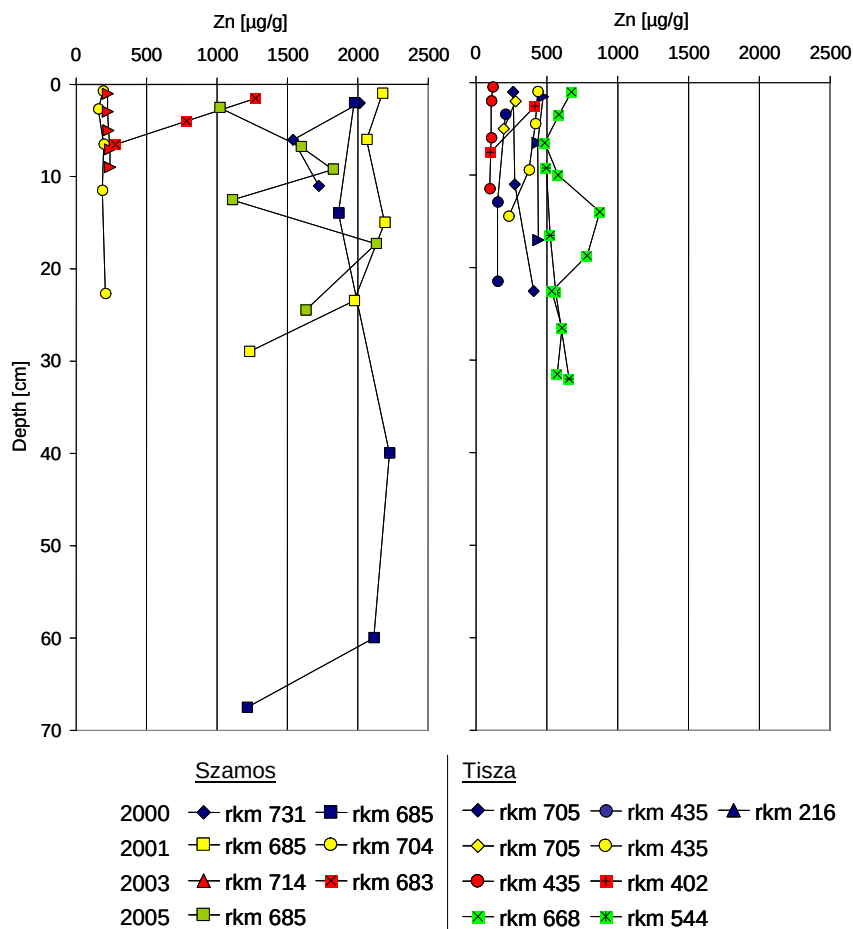


Fig. 4-19: Zn concentration in sediment profiles of the rivers Tisza and Szamos (grain size fractions: 2000, 2001, 2005: < 20 µm; 2003: < 1 mm)

4.2.4 Comparison with legal values and guidelines for sediments and soils

Table 4-9: Legal values and guidelines for the assessment of contamination of soils and sediments with selected elements: Hungarian authority standards, KVO (values in brackets valid if soil contains less than 5 % clay and/or the pH is between 5 and 6), NL list, Henschel et al. (2003) and T&W

Medium	Source	Level	As	Cd	Co	Cu	Mo	Ni	Pb	Zn
						[mg/kg]				
Soil	Hungarian standards	authority A	10	0.5	15	30	3	25	25	100
		B	15	1	30	75	7	40	100	200
		C	C1	20	2	100	200	20	150	500
			C2	40	5	200	300	50	200	500
			C3	60	10	300	400	100	250	600
Soil	KVO	Soil	1.5 (1)			60		50	100	200
		Sewage sludge	10 (5)			800		200	900	2500 (2000)
Soil	NL list	Target	29	0.8	20	36	10	35	85	140
		Intervention	55	12	240	190	200	210	530	720
Sediment	Henschel et al. (2003)	Precaution	8	1.2		30		20	50	150
		Test	70	10		300		50	200	400
		Intervention	150	50		600		600	1000	1500
Sediment	T&W	Average clay	13	0.3	19	45	2.6	68	20	95

In a first approach, the most recent heavy metal concentrations were compared with the KVO, which regulates the deploying of sewage sludge on farm land. It is forbidden to deploy sewage sludge on a soil, if one of the elements, listed for the KVO in Table 4-9, exceeds the concentrations in the soil or in the sewage sludge. If the samples of the sampling campaign 2005 were treated as soil, no further input of heavy metals would be allowed. The median concentrations exceed the legal limits. It has to be noted, that Pb only lay above the limit at the Szamos River.

If the samples are regarded as sewage sludge, it would be allowed to “fertilize” soil with it. None of the values exceeded the legal limits for sewage sludge.

4.3 Bonding form distributions of selected elements

4.3.1 General remarks

Bonding form analyses were performed for all sampling campaigns. Two sequential extractions procedures were applied during this study (Table 3-4). The available data for the sequential extraction of the sediments should be compared with caution due to the fact that the extraction schemes extract a different numbers of bonding form fractions two different extraction schemes. Table 5-1 proposes the attribution of the extracted fractions to bonding form groups. In 2002 and 2003 the grain size fraction < 1 mm was used instead of < 20 µm. Despite potential pitfalls, it should be possible to derive trends for changes in the partitioning especially for those localities that have been sampled more than once. Major elements like Al, Ca and Fe will be described, since they represent important bonding form partners for heavy metals in sediments, e.g. oxides/hydroxides, clay minerals and carbonates. As trace elements As, Cd, Cu, Pb and Zn were selected. These are enriched in the analyzed river sediments and therefore possess an environmental relevance.

The percentages given in the following paragraphs refer to the proportion of a bonding form fraction:

$$\text{Element}_{\text{fract}_x} \text{ in \%} = \frac{[\text{Element}_{\text{fract}_x}] \cdot 100}{\sum_{i=1}^n [\text{Element}_{\text{fract}_i}]}$$

BCR protocol : $n = 4$

Tessier protocol : $n = 6$

Table 4-10: Comparison of sequential extraction results of the reference material BCR-701 with certified values (expressed as mg/kg)

Element	Step 1		Step 2		Step 3	
	certified	measured	certified	measured	certified	measured
Cd	7.34 ± 0.35	6.56 ± 0.80	3.77 ± 0.28	3.69 ± 0.13	0.27 ± 0.06	0.16 ± 0.01
Cr	2.26 ± 0.16	2.28 ± 0.38	45.7 ± 2	62.7 ± 2.2	143 ± 7	112 ± 10
Cu	49.3 ± 1.7	44.5 ± 6.4	124 ± 3	144 ± 1	55.2 ± 4.0	38.7 ± 2.7
Ni	15.4 ± 0.9	14.1 ± 2.3	26.6 ± 1.3	33.1 ± 0.8	15.3 ± 0.9	13.4 ± 0.4
Pb	3.18 ± 0.21	2.57 ± 0.30	126 ± 3	132 ± 6	9.3 ± 2.0	7.0 ± 0.5
Zn	205 ± 6	216 ± 16	114 ± 5	124 ± 7	45.7 ± 4.0	43.1 ± 1.0

4.3.2 Major elements

Aluminum exhibits a relatively uniform bonding form distribution in all rivers (2005: fract.1:fract.2:fract.3:fract.4 = 0:5:2:93). The situation in the previous years is similar, although reducible Al is slightly higher (2001: 9 %). Most of Al is fixed in the residual phase, which is extracted from silicates (clay minerals, feldspars etc.) and stable oxides (e.g. corundum, Al_2O_3). The clay minerals play an important role in the binding of trace elements in sediments. Fe oxides are another source for Al in the residual fraction because Al can substitute Fe in oxides like goethite ($\alpha\text{-FeOOH}$) and hematite (Fe_2O_3).

As expected, **calcium** is extracted to a high degree in the acid-soluble form. This comprises adsorbed Ca, Ca carbonate (e.g. calcite, CaCO_3) and Ca sulfate (e.g. gypsum, CaSO_4). In 2005, Tisza, Szamos and Körös show a similar distribution of Ca: 74–79 % acid-soluble, 15–20 % reducible, while the Maros has a lower proportion of Ca bound in the acid-soluble fraction (62 %), which is reflected by a shift towards the reducible fraction (29 %).

Iron is one of the most important bonding partners for heavy metals in sediments due the high adsorption capacity of its oxides and hydroxides. The bonding form distribution of Fe for 2005 shows only minor variations within the analyzed samples along the rivers (fract.1:fract.2:fract.3:fract.4 = 2:21:5:72; Fig. 4-20).

In the very mobile acid-soluble fraction, Fe is present in only a few samples and only to a low proportion (≤ 5 %). This fraction can contain adsorbed and exchangeable Fe as well as carbonates (e.g. siderite, FeCO_3 ; ankerite, $\text{CaFe}(\text{CO}_3)_2$). In comparison with the previous analyses, no significant changes occurred. In case of the six-step sequential extraction protocol (2000, 2001), the first two fractions have to be summed up (Table 5-1).

The reducible fraction of the BCR scheme contains between 20 and 35 % in 2005. It is comprised of low crystalline Fe oxides/hydroxides (e.g. ferrihydrite, $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$). This fraction increased compared to 2002 and 2003, which is most likely caused by the coarser grain size (< 1 mm) used in 2002 and 2003.

The Tessier protocol discriminates between easily and moderately reducible Fe oxides/hydroxides., the latter containing Fe oxides/hydroxides with a higher crystallinity. From 2000 to 2001, the proportions of the reducible fractions increased, while the proportion of the easily reducible Fe oxides/hydroxides decreased by half.

The highest proportion of residually bound Fe, was detected in 2005 (Maros, rkm 180: 79 %; median: 72 %). While the maximum values are similar for the applied methods, the minimum proportions are lowest for the six-step procedure. This can be ascribed to a carry over of crystalline Fe oxides/hydroxides from the reducible to the residual fraction (Dodd et al., 2000). The Tessier scheme with its two reducing extraction steps probably extracts also Fe oxides/hydroxides with a higher stability compared to abilities of the BCR scheme.

In the analyzed river sediments, the oxidizable fraction has a very low proportion in the bonding form distribution of all sampling campaigns (≤ 6 %). Only one sample (Szamos, rkm 714, 2003) contained oxidizable Fe in significant proportions (ca. 30 %). An underestimation of sulfidic Fe is very likely. Pyrite is very abundant in particles of the sediments from the Tisza River basin according to X-ray analyses by Osán et al. (2002).

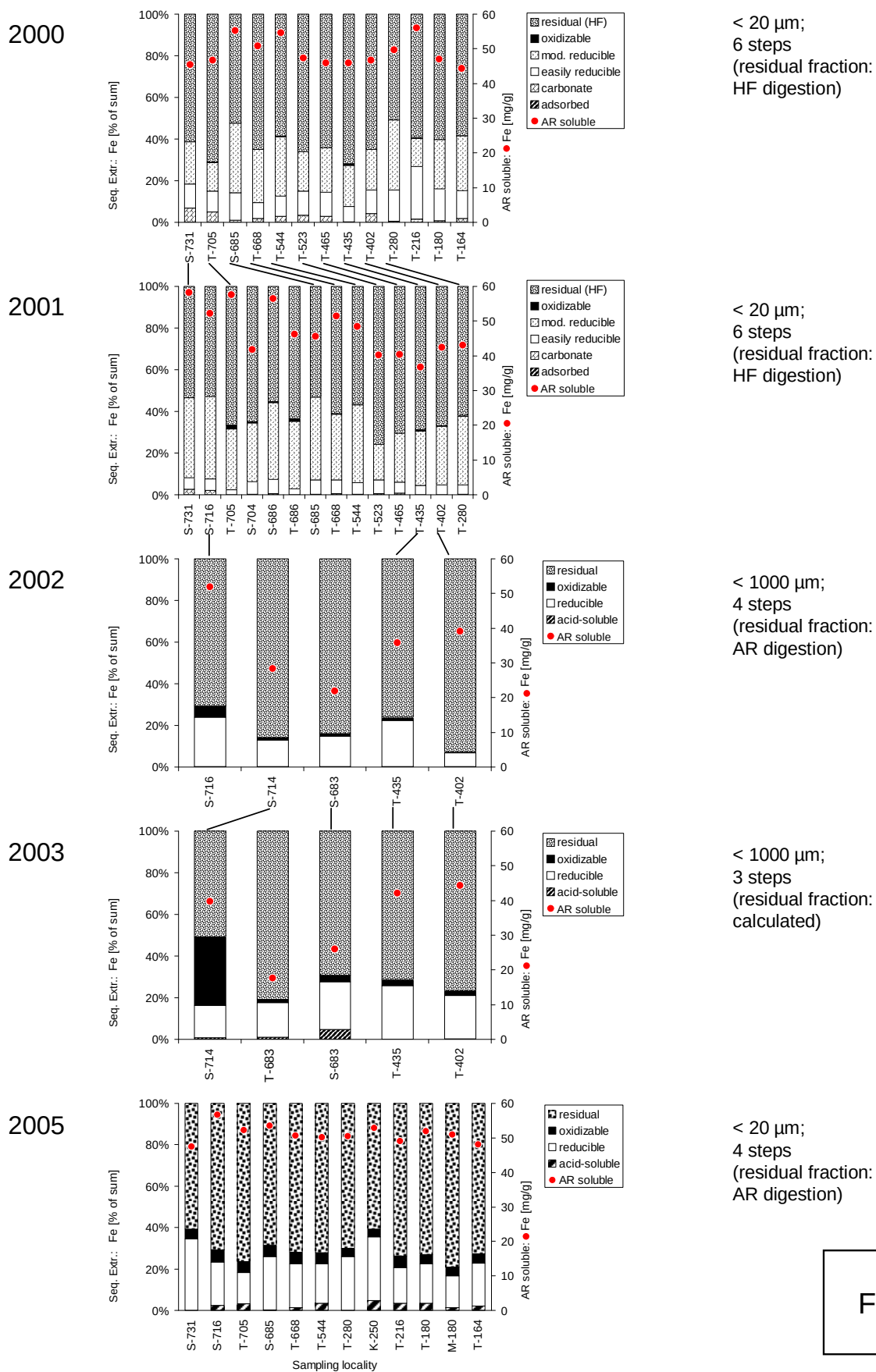


Fig. 4-20: Fe bonding form distribution (2000–2003, 2005)

4.3.3 Trace elements

The data on **arsenic** for the Tisza are in good agreement with Bird et al. (2003). The differences between the four rivers are unincisive. Tisza, Szamos and Maros show a similar behavior, while the Körös deviates more clearly. The residual phase clearly dominates in all sediments (58–81 % of As_{sum}). Therefore the mobility of As is relatively low in the sediments of the Tisza River basin. This is confirmed by the fact that acid-soluble As was only detected in the sediments from the Maros River (4 % of As_{sum}). The content of As in the oxidizable fraction is also relatively low. Only 4 to 6 % of As_{sum} were detected in this form. The reducible phase has a range of 11 to 36 % of As_{sum} . The highest value was found in the Körös River, which coincides with lowest percentage for the residual phase (58 % of As_{sum}).

Table 4-11: Bonding form distribution of selected elements in 2005 (% of sum; median; $\bar{x}$ = average values of < 63 μm grain size fraction from Bird et al., 2003)

River	n	rkm	SeqExtr	As		Cd		Co	Cr	Cu		Mn	Ni	Pb		Sb	Sr	Zn	
					<i>x</i>		<i>x</i>				<i>x</i>				<i>x</i>				
Tisza	7	164–705	acid-soluble	0	<i>1</i>	59	<i>74</i>	22	0	14	<i>20</i>	65	8	4	<i>6</i>	2	35	31	<i>36</i>
Tisza	7	164–705	reducible	16	<i>17</i>	34	<i>16</i>	25	7	47	<i>29</i>	21	16	77	<i>65</i>	3	14	37	<i>38</i>
Tisza	7	164–705	oxidizable	4	<i>3</i>	5	<i>6</i>	10	10	9	<i>11</i>	3	14	4	<i>5</i>	0	2	8	<i>5</i>
Tisza	7	164–705	residual	73	<i>79</i>	0	<i>4</i>	43	83	28	<i>40</i>	12	62	12	<i>24</i>	92	49	20	<i>21</i>
Szamos	3	685–731	acid-soluble	0	<i>1</i>	71	<i>81</i>	24	1	19	<i>21</i>	60	11	3	<i>3</i>	2	46	45	<i>58</i>
Szamos	3	685–731	reducible	18	<i>36</i>	27	<i>16</i>	29	8	53	<i>31</i>	25	18	78	<i>80</i>	6	16	42	<i>31</i>
Szamos	3	685–731	oxidizable	5	<i>6</i>	3	<i>2</i>	9	11	9	<i>22</i>	2	13	4	<i>2</i>	2	2	6	<i>5</i>
Szamos	3	685–731	residual	73	<i>57</i>	0	<i>2</i>	38	80	23	<i>27</i>	9	57	11	<i>16</i>	88	36	8	<i>6</i>
Maros	1	180	acid-soluble	4		65		25	1	14		61	8	5		2	50	29	
Maros	1	180	reducible	11		27		26	10	50		19	15	75		3	13	37	
Maros	1	180	oxidizable	4		7		9	12	8		3	12	4		1	2	9	
Maros	1	180	residual	81		1		41	78	29		17	65	15		94	35	26	
Körös	1	250	acid-soluble	0		55		15	0	12		57	9	1		0	28	0	
Körös	1	250	reducible	36		39		31	7	50		30	20	74		2	16	29	
Körös	1	250	oxidizable	6		6		11	7	8		3	14	5		0	2	11	
Körös	1	250	residual	58		0		43	86	31		11	57	20		98	54	60	

Cadmium is characterized by a high fraction of mobile bonding forms. Between 54 and 71 % were extracted in the acid-soluble phase in 2005. The sediments from the Szamos exhibit the highest potential mobility (Szamos > Tisza > Maros > Körös). The reducible fraction is the second largest bonding form group of Cd (2005: 27–39 %). In this fraction Cd is most likely bound to Fe oxides/hydroxides and can be remobilized under reducing conditions. The oxidizable fraction varies between 3 to 7 % (Maros highest). The high potential mobility of Cd is also reflected in the very low proportion of the residual phase (≤ 1 %).

Shortly after the accident in 2000, the sediments were dominated by the highly mobile fractions with a predominance of the carbonate-bound Cd (adsorbed and carbonate; 40–80 %). These fractions increased along the river course. In 2001, the portions of these bonding forms were significantly lower in the Tisza samples (≤ 50 %), which can be ascribed to a decrease of the carbonate forms. In 2002, the samples from the Szamos are still marked by a high percentage of the acid-soluble forms, while the Tisza samples show distinctly lower values.

In contrast to all other sampling campaigns, the samples from 2001 display a relatively high proportion of oxidizable Cd (≤ 30 %). The high percentage might be due to differences in sample preparation or in the extraction protocol.

The data from 2002 and 2003 are based in the same coarser grain size fraction (< 1 mm) and therefore can be compared without restrictions. In general the differences between the years are relatively large, e.g. the acid soluble fraction of S-714 strongly decreased from 2002 to 2003 (75 % $\rightarrow$ 18 %). Sample

T-435 is marked by a strong percentage decrease of the residual fraction (30 % → 7 %), on the other hand the concentrations increased. The aqua regia soluble content of Cd remained relatively stable over this time (0.33 → 0.35 µg/g). On the other hand, sample S-683 did not change much on these years, although the aqua regia content increased (4.2 → 7.4 µg/g).

The bonding form distribution of **copper** shows only minor variations among the sampling localities in 2005. The samples from the Szamos show a stronger deviation from the general distribution, but still the basic pattern remains. Most of Cu is bound in reducible and residual forms (50 %, 27 %, resp.). Cu with a relatively high potential mobility was extracted in the acid-soluble fraction and varies between 12 and 20 %. Oxidizable Cu (9 %) is probably present as sulfides or can also be organically bound.

Lead (2005: fract.1:fract.2:fract.3:fract.4 = 4:78:4:13; Fig. 4-24) is predominantly bound in reducible forms. This fraction can be represented by Pb adsorbed on or bound to Fe/Mn oxides/hydroxides or by separate Pb oxides. PbO was detected in riverbank sediments from the Tisza River basin (Osán et al., 2002). Only a small fraction is bound in the very mobile acid-soluble fraction (4 %). Oxidizable Pb is also contained in a relatively low proportion (4 %), which is notable regarding the fact that the mineralization of the region yielded mostly sulfides and sediment particles contained PbS (Osán et al., 2002). The residual fraction certainly contains Pb from sulfides due to a carry over effect (oxidation of sulfide, formation of Pb sulfate, low solubility, residue). The bonding form distribution of Pb (2005) is in good agreement with Bird et al. (2003) for both rivers (Tisza and Szamos).

The data from Bird et al. (2003) for **zinc** also match with the results for the Tisza sediments (2005). At the Szamos a shift can be noted between the first two steps of the extraction scheme. Bird et al. (2003) extracted a greater acid-soluble proportion than this study. The last two steps (oxidizable and residual) are almost identical in both studies. The bonding form distribution of zinc (2005: fract.1:fract.2:fract.3:fract.4 = 34:37:8:20; Fig. 4-25) is characterized by the emphasis on the relatively mobile fractions: acid-soluble and reducible. The results of the BCR scheme for the grain size fraction < 20 µm are in good agreement with the results from the Tessier scheme. Although the oxidizable fraction of the latter is even lower (≤ 2 %). Osán et al. (2002) detected ZnS in sediment particles from the Tisza River basin. Temporal changes cannot be stated. Variations of the years 2002 and 2003 can be ascribed to the analyses of a coarser grain size spectrum (< 1 mm).

Sediments with a low aqua regia soluble Zn content are characterized by a low proportion of the acid-soluble fraction and are dominated by the residual fraction (e.g. rkm 435, rkm 250). This could correspond to a low anthropogenic influence. Anthropogenic input of heavy metals is generally marked by a higher potential mobility (Singh et al., 1998).

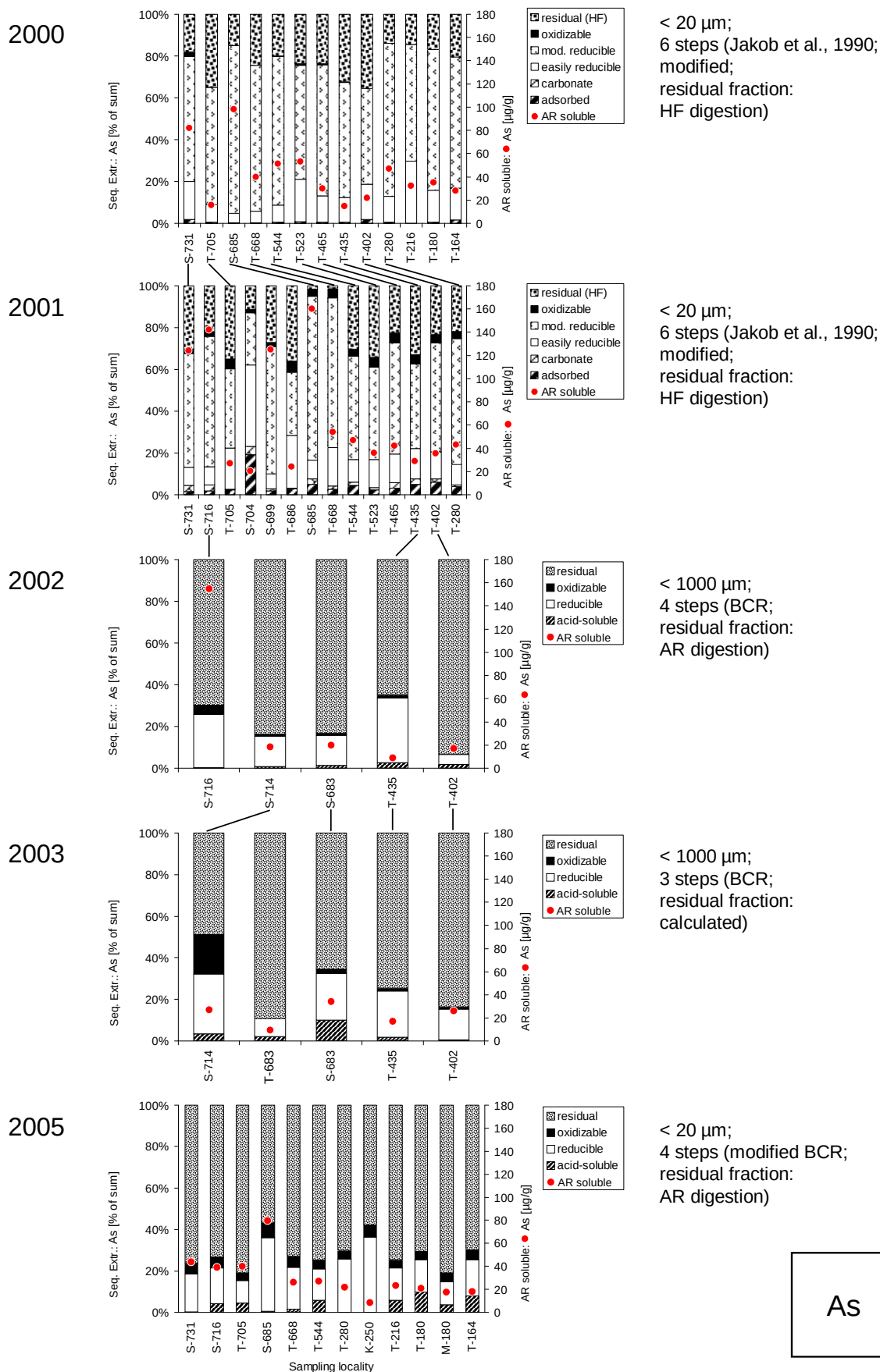
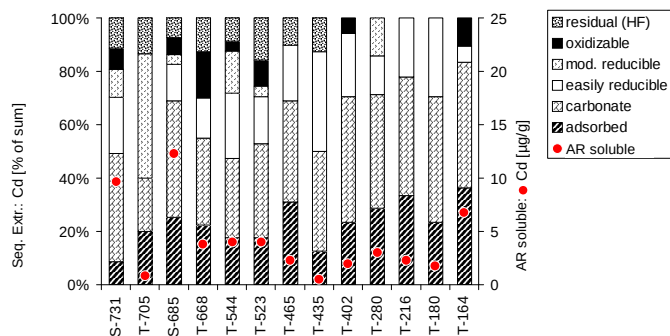


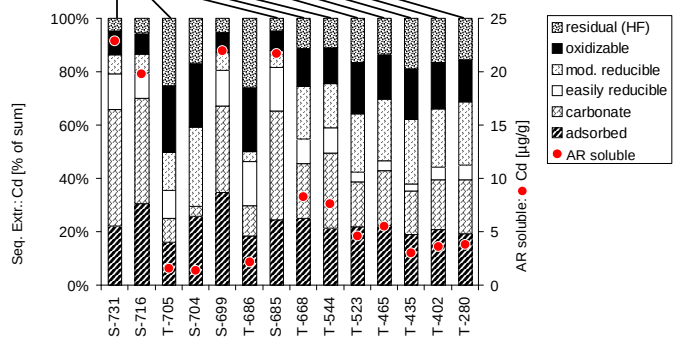
Fig. 4-21: As bonding form distribution (2000–2003, 2005)

2000



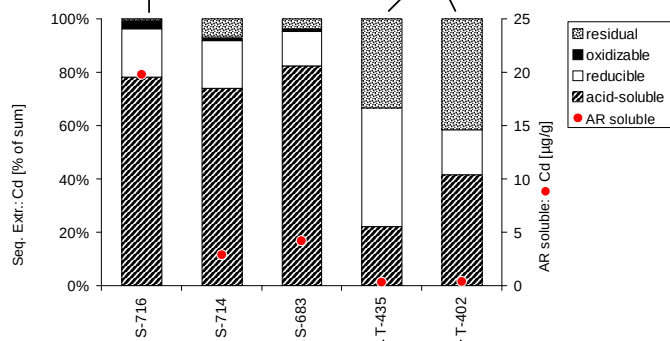
< 20 µm;
6 steps
(residual fraction:
HF digestion)

2001



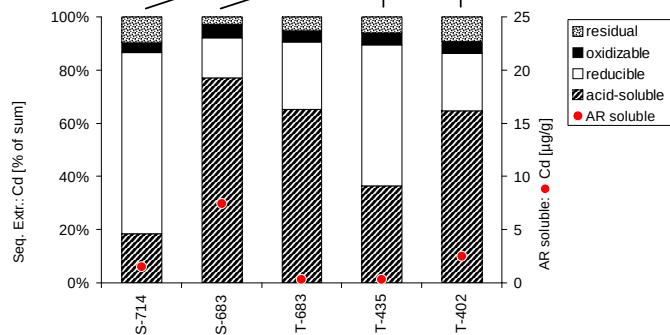
< 20 µm;
6 steps
(residual fraction:
HF digestion);
data: Ovari, Endbericht
residual fraction correcter
(conc. divided by 10)

2002



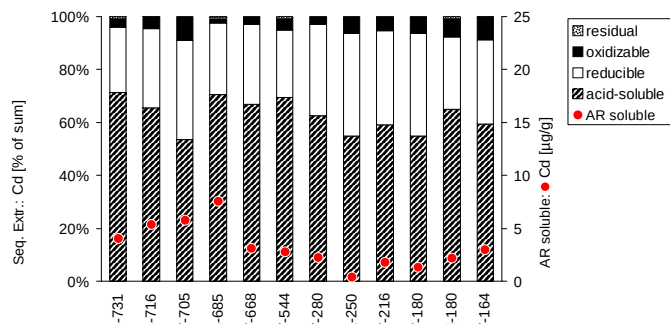
< 1000 µm;
4 steps

2003



< 1000 µm;
3 steps
(residual fraction:
calculated)

2005



< 20 µm;
4 steps

Szamos bayou: S-714, S-704

Cd

Fig. 4-22: Cd bonding form distribution (2000–2003, 2005)

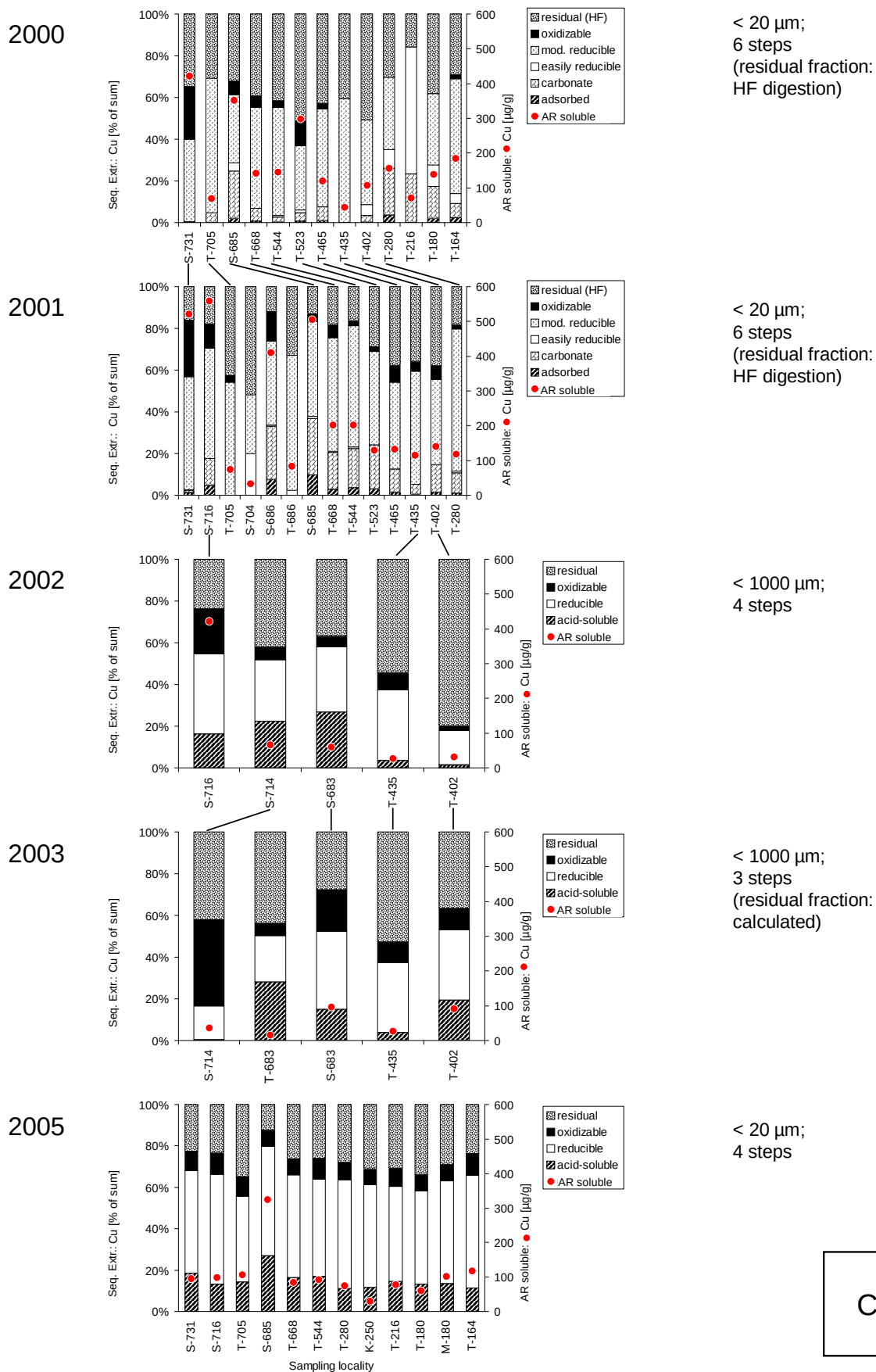


Fig. 4-23: Cu bonding form distribution (2000–2003, 2005)

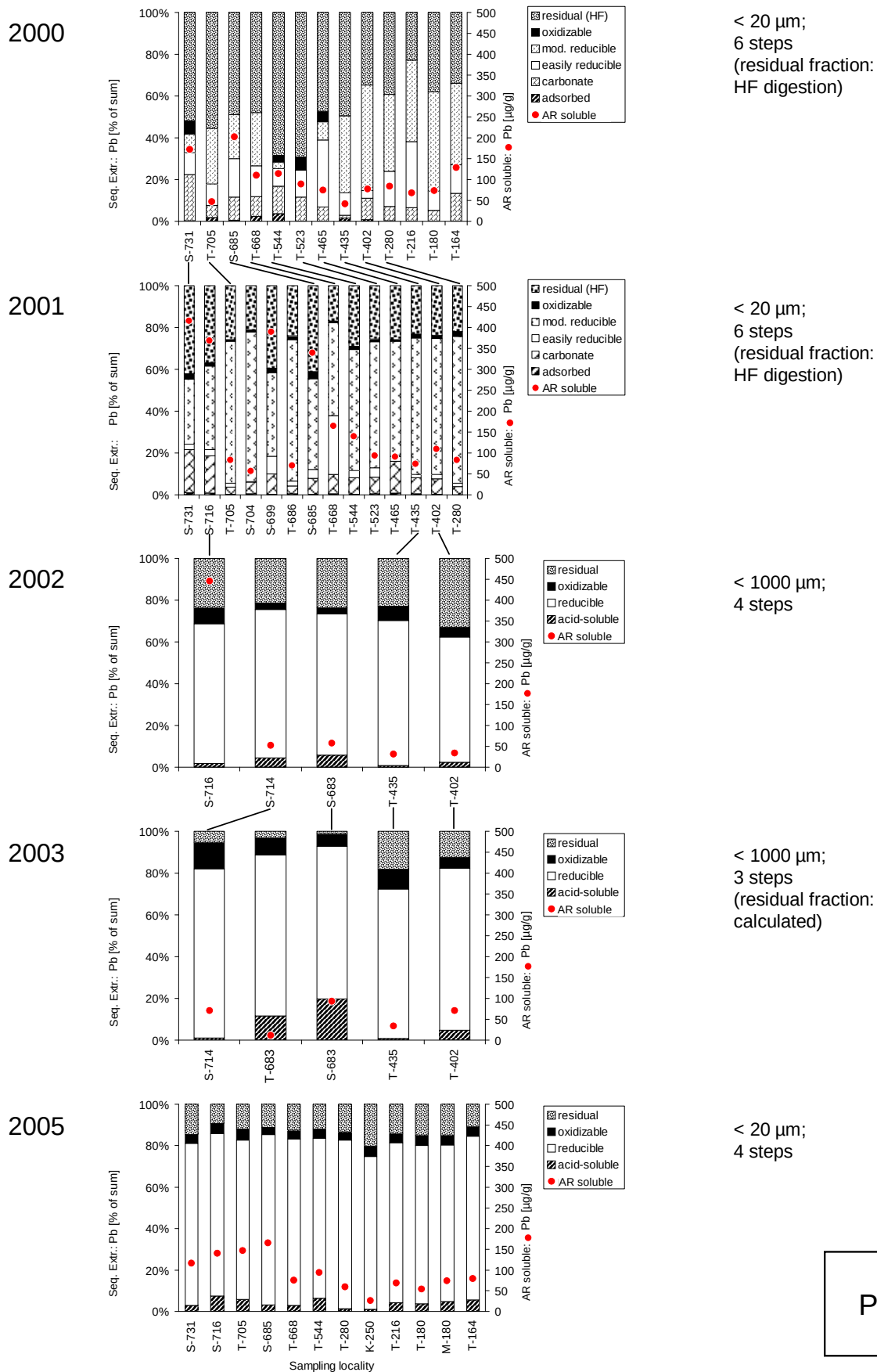


Fig. 4-24: Pb bonding form distribution (2000–2003, 2005)

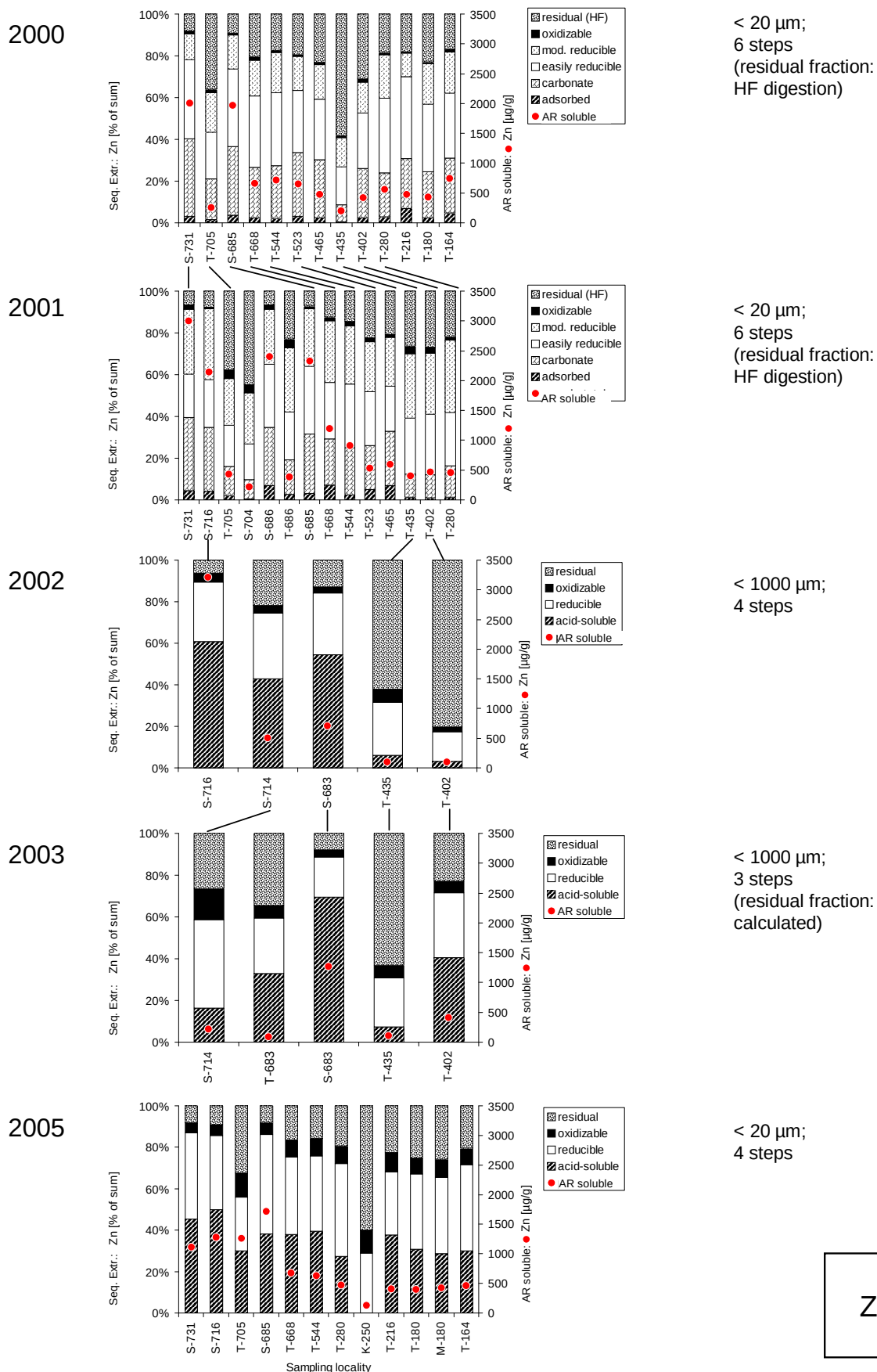


Fig. 4-25: Zn bonding form distribution (2000–2003, 2005)

5. Discussion

5.1 t-Test

Surface sediments – 2005 – Tisza/Szamos

The element content in the grain size fraction < 20 µm allows a distinction of the two rivers Tisza and Szamos only for four trace elements: Cd, Pb, Sb and Zn. All other analyzed elements show no significant difference between both rivers (As, Au, Ba, Co, Cr, Cu, Mo, Ni, Rb, Sn, Sr, U, Al, Ca, Fe, K, Mg, Mn).

5.2 Correlation analysis

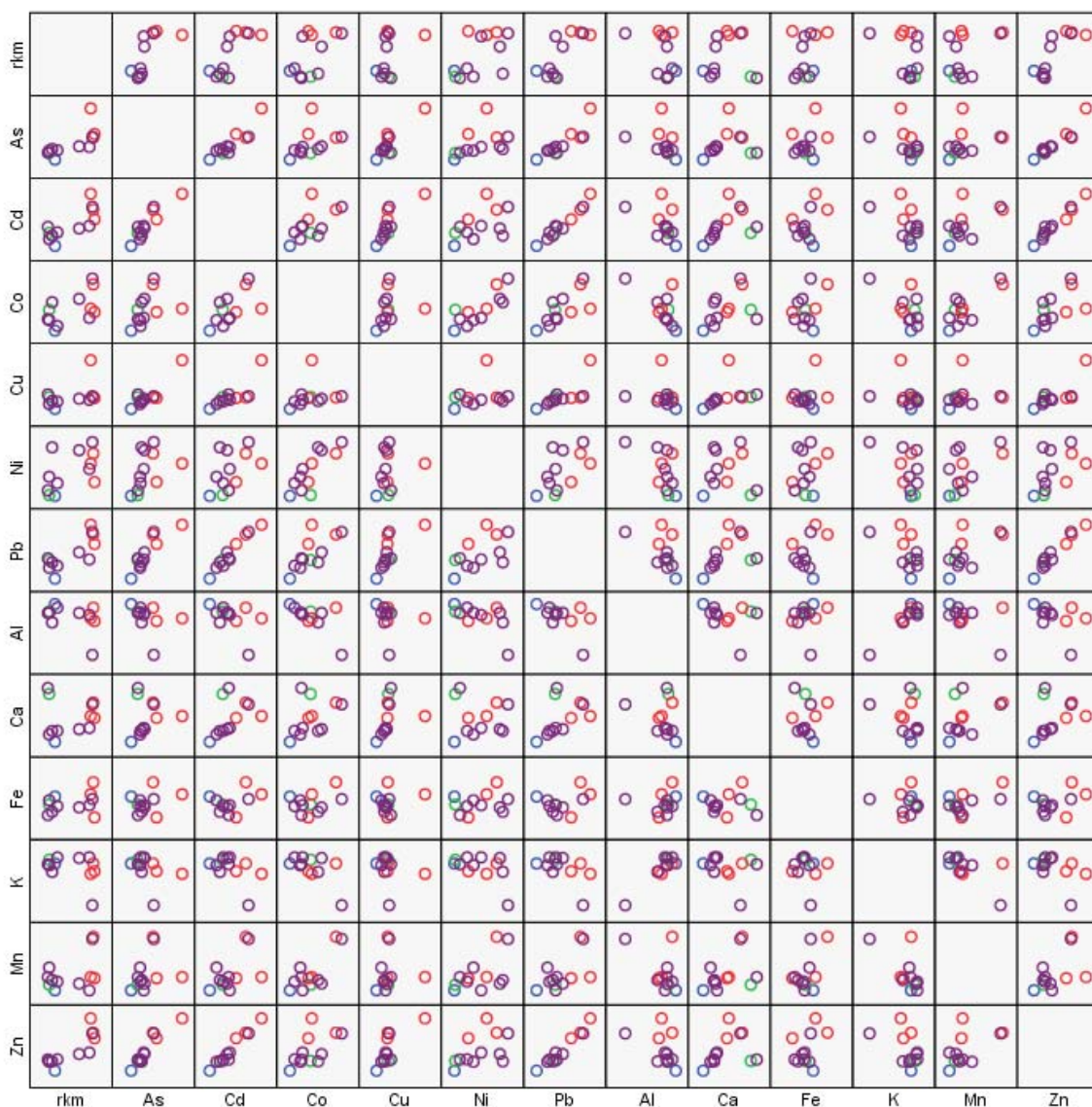


Fig. 5-1: Correlation matrix for the sampling campaign 2005 (rkm, As, Cd, Co, Cu, Ni, Pb, Al, Ca, Fe, K, Mn, Zn; blue: Tisza; red: Szamos; green: Maros; purple: Körös)

As the correlation matrix in Fig. 5-1 shows only Ca correlates with some of the trace elements; Cd, Co, Cu, Pb and Zn. This relationship is probably based on the type of mineralization and the geology of the investigation area, as Miocene calc-alkaline volcanic rocks host the ores of the Baia Mare district. In the Metaliferi Mountains⁶ (e.g. Baia de Aries), the metal deposits (Au-Ag, Pb-Zn) are bound to quartz and Ca/Mn carbonate veins in the Miocene andesitic⁷ and the surrounding sedimentary rocks. The mineralization is bound to epithermal veins and small skarn-like bodies (Bailly et al., 2002).

The correlation matrix of the major elements (Fig. 5-2) shows only a correlation of Fe with Mg, which is valid for all rivers. The otherwise typical correlations of Al and K, reflecting the geochemical relationship in silicates (e.g. clay minerals and feldspars), is not visible. The major elements are not influenced by the sampling locality, which is indicated by a missing correlation between the major elements and rkm.

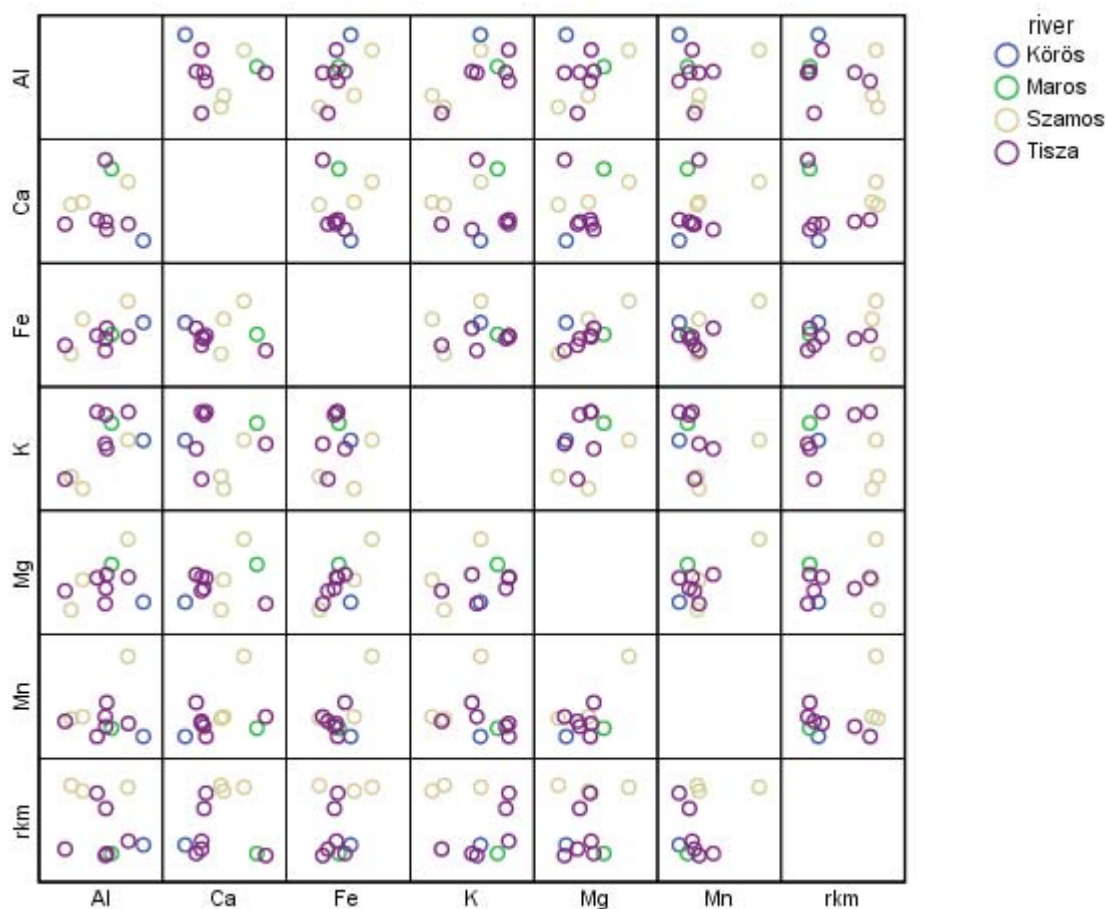


Fig. 5-2: Correlation matrix for the sampling campaign 2005: Major elements and rkm

⁶ Szamos and Maros flow through this area.

⁷ calc-alkaline volcanic rock

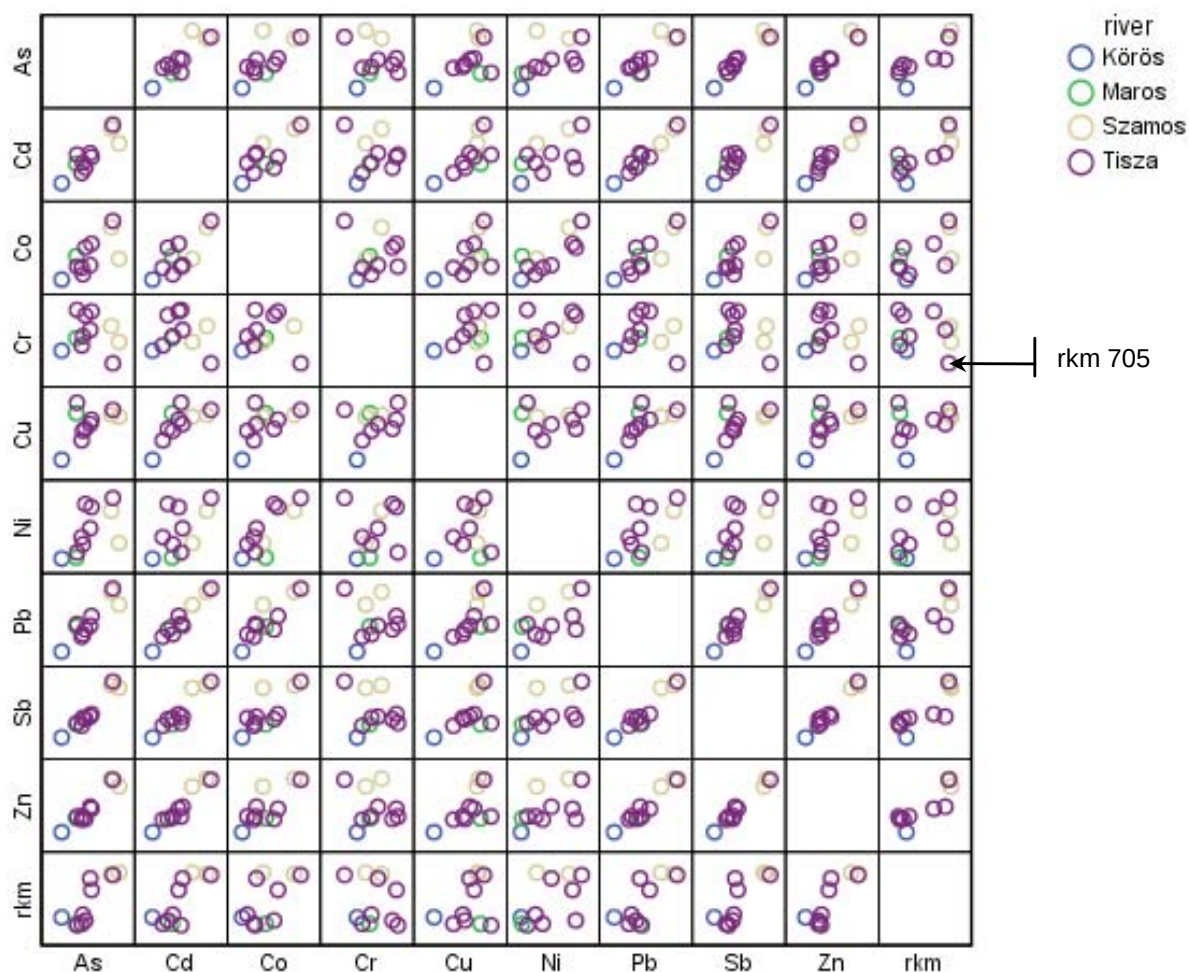


Fig. 5-3: Correlation matrix for the sampling campaign 2005: Trace elements and rkm

In contrast to the major elements, the trace elements display distinct correlations between each other (Fig. 5-3). The strongest correlations exist between As, Cd, Pb, Sb and Zn. These relationships are most likely based on the mineralization of the Maramureş region and the constant input of these elements into the river system. The correlation of Cu with the aforementioned group of trace elements is less pronounced. One of the reasons might be an independent mineralization.

Fig. 5-4 displays the correlation matrixes for the Tisza and the Szamos. In both rivers the relationships between the mining elements persist over the investigation period (2000–2005). The difference in grain-size seems to have no influence on the correlation.

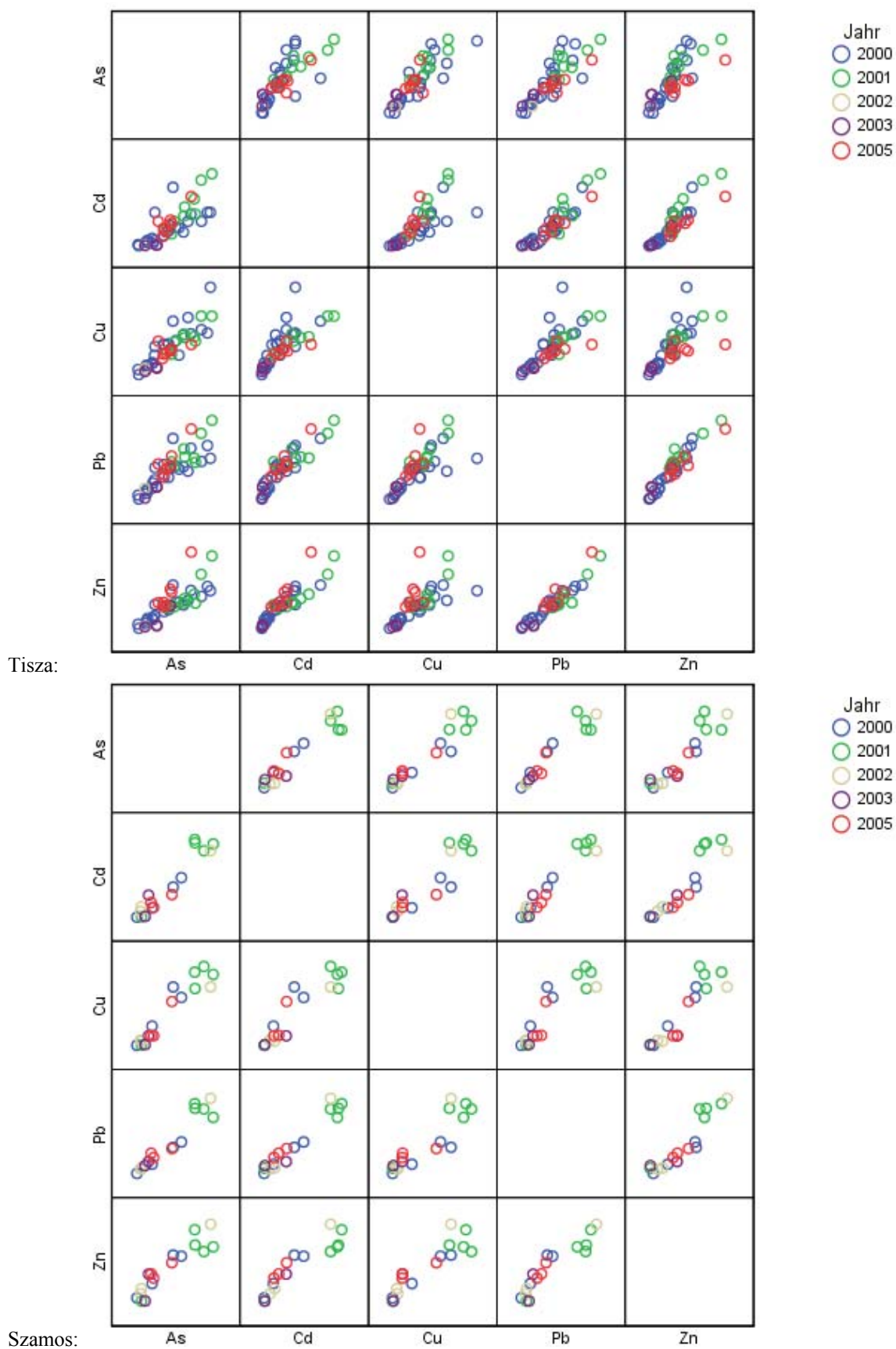


Fig. 5-4: Correlation matrix for the trace elements As, Cd, Cu, Pb and Zn

5.3 Cluster analysis

The presented dendrograms are based on hierarchical cluster analyses calculated with the Ward algorithm. Similar results were obtained by using other algorithms, *e.g.* average linkage.

5.3.1 Grouping of sampling locations based on As and selected heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn) for each sampling campaign (< 20 µm; Z-score)

For the years in question (2000, 2001, 2005), the hierarchical cluster analysis yields well-defined clusters (Fig. 5-5). Two clusters are formed for the three analysis: Tisza and Szamos. The clustering in the Tisza cluster shows some similarities during the years, but is not identical, which might have been caused by elemental composition as well as the changing sample locations. The rivers Körös and Maros are integrated into the Tisza cluster (2005).

In 2001 the sample locations are grouped according to their position in the river system: A) Tisza: rkm 523–280; B) Tisza: rkm 705–544; C) Szamos. This is based most likely on the level of contamination with heavy metals. Group A is characterized by relatively low element concentrations, group B shows higher concentrations and group C, the river Szamos, has the highest contamination grade.

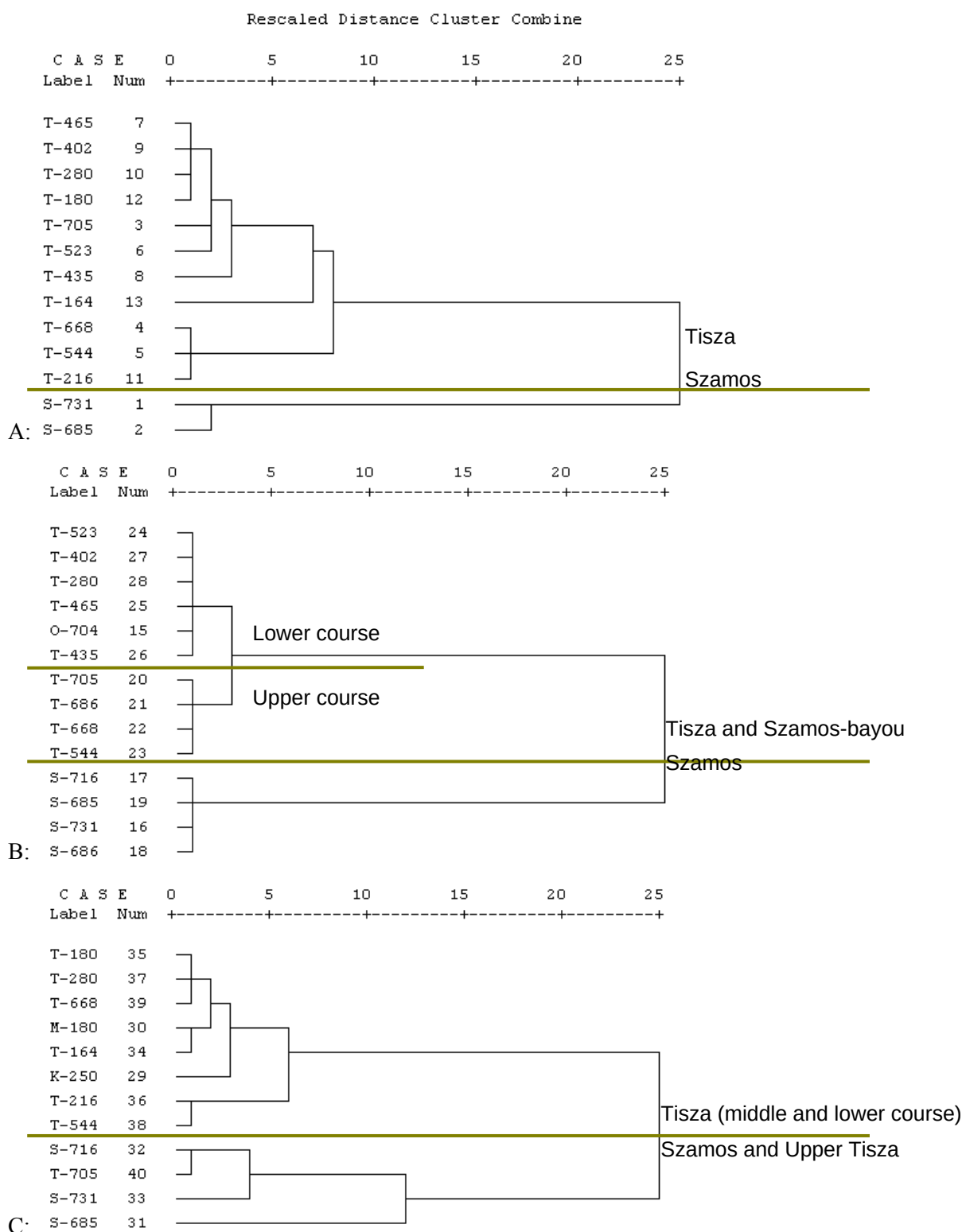


Fig. 5-5: Dendrograms of hierarchical cluster analysis (Ward algorithm; A: 2000, B: 2001, C: 2005)

5.3.2 Grouping of heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn) and As for each year (< 20 µm; Z-score)

The clustering of the investigated elements remains similar over the years (Fig. 5-6). Only the coefficients on which the clusters are formed change.

- Cd, Pb, Zn – As, Cu — Cr — Co, Ni
 - o Cd, Pb, Zn mineralization in NW Romania
 - o As, Cu Cu also from mineralization in NW Romania; As probably from sulfides (sulfide mineralization predominant type in NW Romania)
 - o Cr only small changes over the river course
 - o Co, Ni concentrations do not change significantly over the river course, no anthropogenic influence visible; similar geochemical characteristics

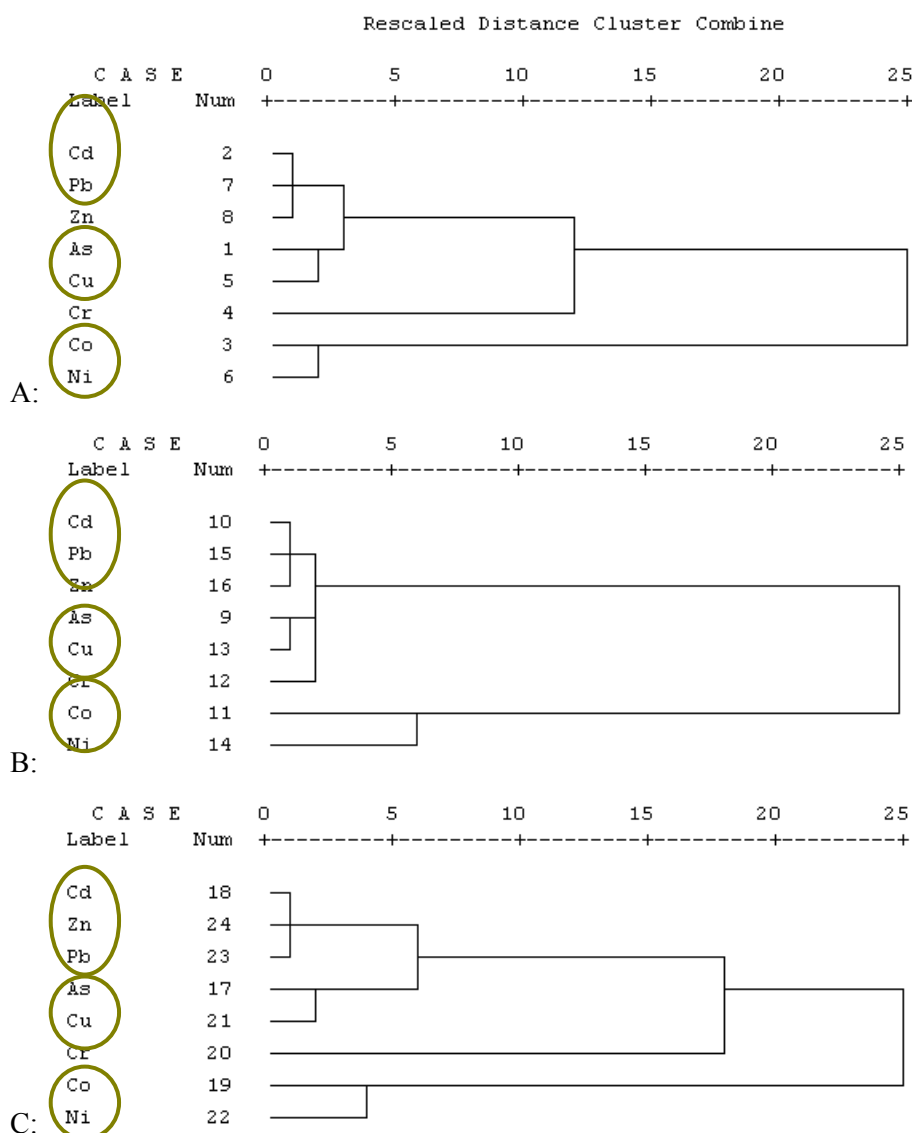


Fig. 5-6: Dendrograms of hierarchical cluster analysis (trace elements; Ward algorithm; A: 2000, B: 2001, C: 2005)

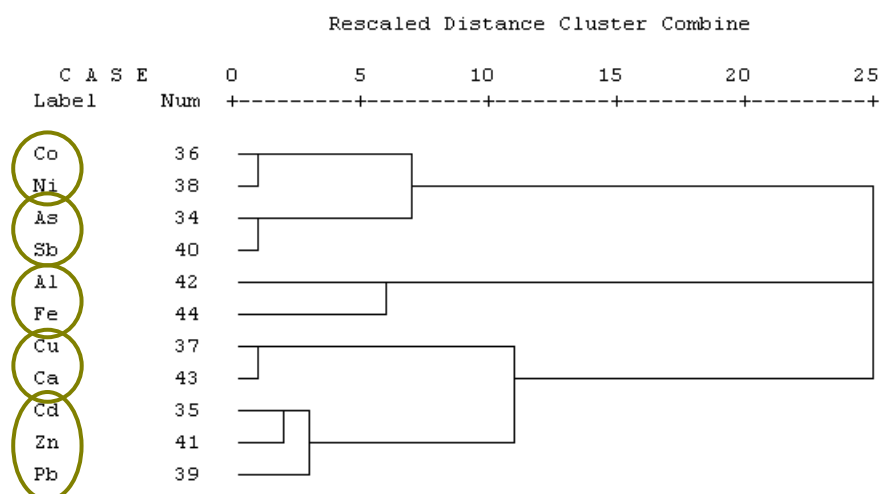


Fig. 5-7: Dendrograms of hierarchical cluster analysis (Ward algorithm; 2005)

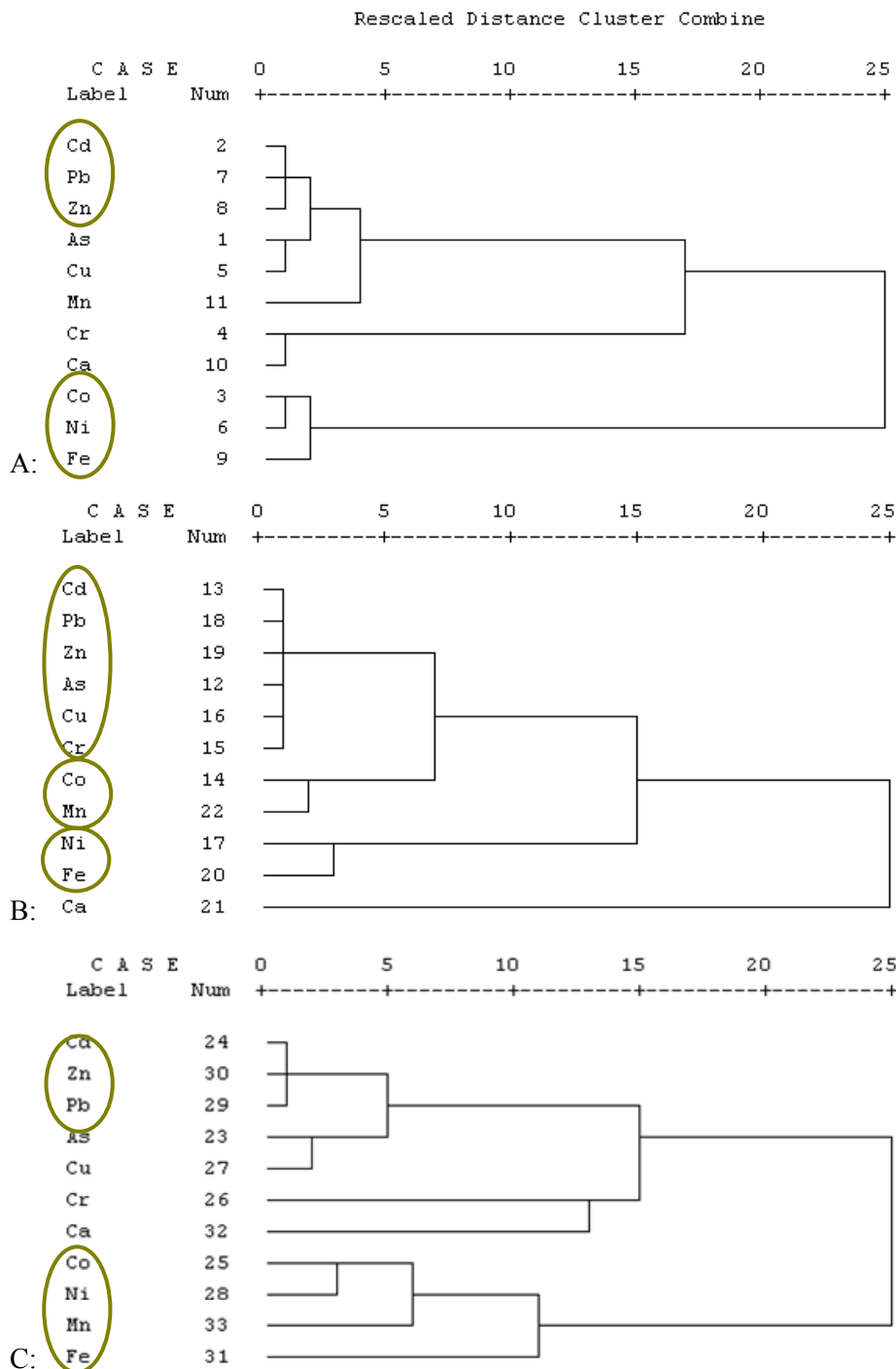


Fig. 5-8: Dendrograms of hierarchical cluster analysis (trace elements + Ca, Fe and Mn; Ward algorithm; A: 2000, B: 2001, C: 2005)

5.4 Changes in heavy metal concentration

The trace element concentrations of the years 2002 and 2003 have a tendency to be lower than those of the other investigated years due to the larger grain size fraction ($< 1 \text{ mm}/< 20 \text{ }\mu\text{m}$), because trace elements are usually enriched in the finer sediment fractions (Ackermann et al., 1983). This is caused by a higher percentage of clay minerals or generally speaking adsorption surface.

A concentration decline along the river course is visible for almost all elements (*e.g.* As). This behavior can be ascribed to a diluting effect by the input of “cleaner” material from the tributaries to the Tisza after its confluence with the Szamos (Lewin & Macklin, 1987). Other reasons for the concentration decline might be the loss of contaminated material to floodplain sediments or the exchange with the latter, the hydraulic sorting according to differential particle density and chemical dispersal through solution or biological uptake (Lewin & Macklin, 1987).

According to Bradley (1995) the causes of concentration decline are compound. Lewin & Macklin (1987) identified several possible mechanisms:

- hydraulic sorting according to differential particle density
- chemical dispersal through solution or biological uptake
- mixing with “extra” clean sediment, especially contribution from a tributary channel that is not mineralized
- loss to /exchange with stored floodplain sediments

Hydraulic sorting is plausible due to the high density of the heavy metal sulfides (*e.g.* pyrite: 5.5 g/cm³) released with the spill. But this might have a greater influence close to the accident site. The transported heavy metal containing particles in the river result from the flotation process and have a small grain size permitting long-range transport (0.7–1.5 µm, > 200 km, Osán et al., 2002).

5.5 Changes in heavy metal bonding forms

The comparison of the collected data is problematic due to changes in the method and the analyzed grain size fraction (Table 3-4). The sequential extraction according to Jakob et al. (1990) leads to a more differentiated picture with its six resulting fractions than the BCR methods with just four fractions. The individual fractions can only be compared with care, keeping in mind that the fractions are operationally defined. Some of the bonding form fractions should be comparable in between methods (Table 5-1).

Table 5-1: Comparison of bonding form fractions

Category	Sequential extraction method		Bonding form description, possible mineralization
	BCR	Jakob et al. (1990)	
highly mobile	acid-soluble (1)	adsorbed (1) + carbonate (2)	adsorbed elements; carbonates
easily reducible	reducible (2)	easily reducible (3)	easily reducible oxides (mostly amorphous or poorly crystalline)
oxidizable	oxidizable (3)	oxidizable (5)	organically bound elements; sulfides
relatively immobile	residual (4)	moderately reducible (4) + residual (6)	crystalline oxides (<i>e.g.</i> goethite); silicates (<i>e.g.</i> clay minerals, feldspars)

6. Conclusions

Overall it can be concluded that the contamination level of the sediments in Tisza and Szamos has decreased. The concentrations of heavy metals and As declined significantly since the mining spills in early 2000. The decrease is especially pronounced at the extremely contaminated locations at the Szamos. But still most of the investigated elements exceed target values recommended for sediments and soils.

Since heavy metals are not biodegradable other mechanisms must have caused the decrease. These could be the redistribution of contaminated sediment during subsequent floods, which is connected to an increase in the contaminant concentration in adjacent floodplains and sediments downriver. This can be seen in the concentration increase from 2000 to 2001 in the Szamos and to a lesser degree in the Tisza, which is most likely caused by the transport of sediment with a relatively higher element concentration from further upstream (= closer to the source).

Mixing with non-contaminated sediment could also be responsible for some of the concentration decline since the spill. This material can be derived from tributaries of the Tisza from non-mineralized regions. Dissolution can also play a role in the contaminant decrease, although the data from the performed bonding form analysis do not give a consistent picture.

The sediment profiles lack in most cases significant concentration peaks, an exception is the profile at rkm 685 of the Szamos in 2001 (Fig. 4-17). At some locations a continuous increase in the trace element content can be stated, while at others the changes over time remain small. This can have multiple causes. One reason might be the continuous input of heavy metals based on the high element concentrations in the mineralized regions, which is enhanced by anthropogenic activities (mining, metal processing, other industrial processes). Another cause could be that the sediments are intensively reworked due to repeated flooding and a high erosional force, which would eventually weaken any distinct signal from mining spills.

The bonding form analysis showed that the environmentally relevant elements are present in relatively mobile forms (*e.g.* Cd). This means that a mobilization of toxic elements from the sediments into the water is relatively probable and poses a further threat to aquatic organisms and finally to humans via enrichment over the food web.

Based on the results of the sediment analyses, an estimation of the potential input of contaminants bound on sediments into floodplains and adjacent areas of the Tisza and Szamos was made. This first rough assessment showed that the soil element content increased strongly during repeated flooding; in a few cases the increase was extremely high. This first assessment of the risk potential of heavy metal contamination for soils in floodplains demonstrates their high contamination threat and the need for further research.

7. Need for further research: Contamination potential in soils along Tisza and Szamos

7.1 Contamination of soils in adjacent floodplains

The sediment analyses showed that the contamination level of the sediments with heavy metals decreased over the six years after the accidental spills. As heavy metals are not biodegradable and the sediment profiles did not show significant historic changes of the element contents, the heavy metals must have been redistributed along the river course. The relatively frequent flooding in the investigation area lets assume that contaminated sediment might have been transported out off the riverbed into the floodplains and adjacent regions.

In order to assess the potential input of contaminated material from the river into adjacent areas, a few assumptions were made for a first rough estimation. The calculations are based on the sedimentation of suspended particulate matter (SPM) on the adjacent areas. A sedimentation rate of 10 mm/a was assumed to be reasonable based on data from other rivers (e.g. Elbe: Schwartz et al., 2004). Due to the high sediment load of the Tisza (10/11 M t/a; Gastecu, 1990) a relatively high sedimentation rate is justified. The SPM input was mixed with soil up to a depth of 10 cm according to legal regulations (e.g. KVO: grassland) and the resulting heavy metal concentration was calculated. The heavy metal content of soil at a specific location was set to the geogenic background level, which was determined in this study (Ch. 4.2.2).

The trace element content of the SPM was determined indirectly by the difference between the total trace element concentration of water samples and their dissolved concentration. The SPM element content was based on water samples of the year 2000. The calculation of the influence of SPM sedimentation on soil was repeated for five times, which is relatively likely to happen regarding the frequency and the level of flooding in Hungary along the Tisza (EUR/02/5036813).

The start value for the soil was set at the geogenic background level, which is below the B value of the Hungarian soil authority standards (Table 4-9) for the selected elements except for As. In case of As, the analyzed geogenic concentration is already higher than the A and B values of the HU list.

$$\text{element}_{\text{flooded_soil}} = \frac{\text{element}_{\text{SPM}} \cdot \text{layer} + \text{element}_{\text{soil}} \cdot (\text{depth} - \text{layer})}{\text{depth}}$$

element _{flooded_soil} :	element content in soil after flooding
element _{SPM} :	element content in SPM
element _{soil} :	element content in soil before flooding
layer :	thickness of deposited SPM layer (e.g. 10 mm)
depth :	mixing depth (e.g. 100 mm)

Formula 7-1: Calculation of element content in a soil after deposition of suspended particulate mater (SPM) under the assumption of the equality of the bulk density⁸ of SPM and soil

The development of the soil element content in Fig. 7-1 shows that the increase depends on the sampling location. In a few cases the increase is extremely high, while in others almost no changes occur.

⁸ Lagerungsdichte

It should be emphasized again that the presented data on heavy metal input in to soils and the development of soil element content are a first rough estimation. This assessment needs to be confirmed by real data regarding the actual soil element content and the actual input of SPM in flooded areas along the Tisza and Szamos.

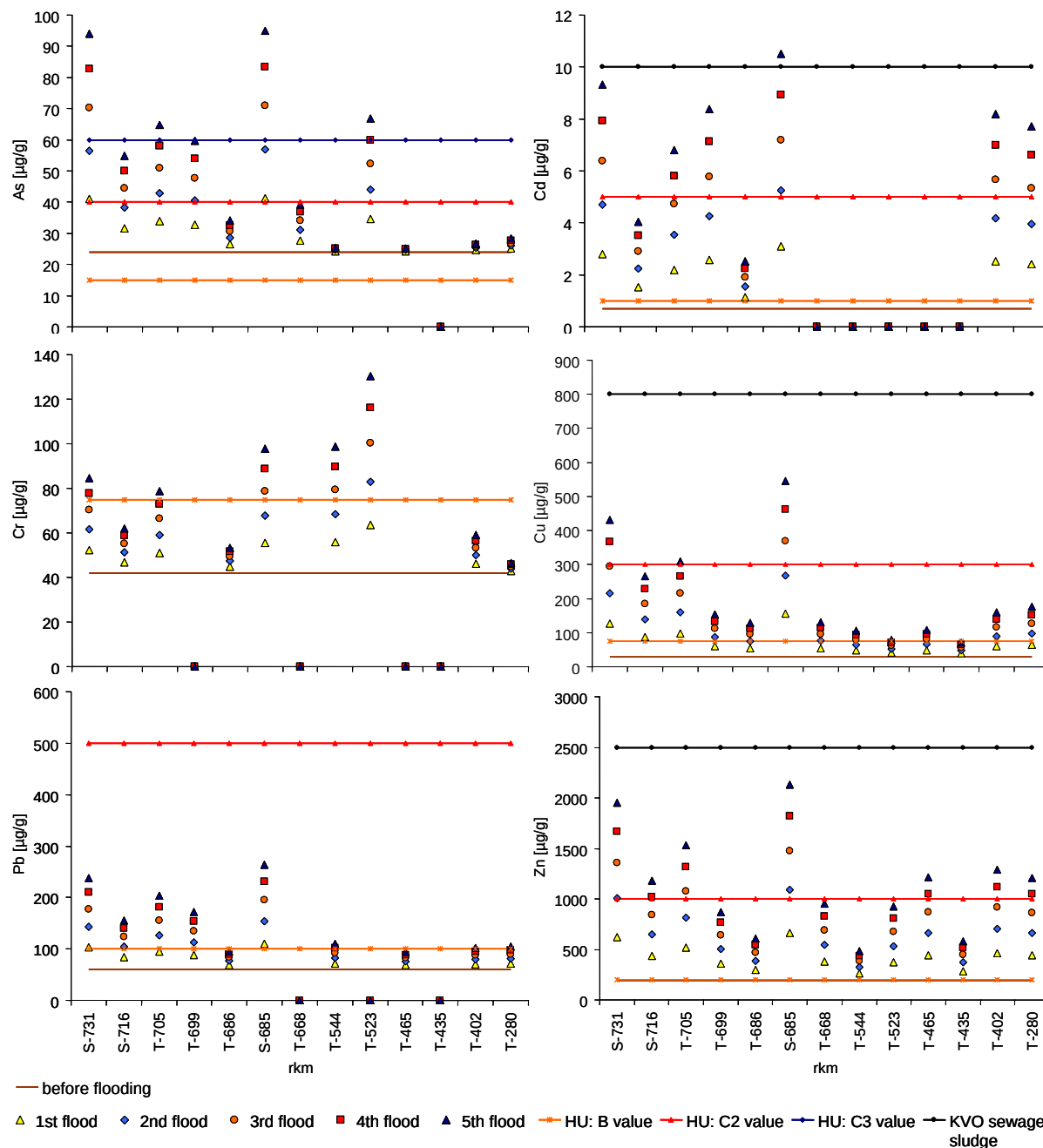


Fig. 7-1: Calculated input of heavy metals and As by SPM deposition into soil by repeated flooding (assumptions: 10 mm deposition of SPM, 10 cm mixing depth)

8. Abbreviations

<i>AR</i>	aqua regia
<i>HF</i>	total digestion (HF/HNO ₃ /HClO ₄)
<i>HU</i>	Hungary/Hungarian
<i>HU A value</i>	Hungarian authority standards for soil: natural background (Table 4-9)
<i>HU B value</i>	cf. above: polluted (some risks)
<i>HU C value</i>	cf. above: interaction needed: C1 = very sensitive area; C2 = sensitive area; C3 = not very sensitive area
<i>KVO</i>	Klärschlammverordnung (German sewage sludge ordinance; Table 4-9)
<i>Mt</i>	million tons
<i>NL list</i>	Dutch list for soil remediation (VROM, 2000; Table 4-9)
<i>rkm</i>	river kilometer
<i>Q</i>	discharge
<i>SPM</i>	suspended particulate matter
<i>S-xxx</i>	sampling location at the Szamos at rkm xxx
<i>T-xxx</i>	sampling location at the Tisza at rkm xxx
<i>T & W</i>	average shale according to Turekian and Wedepohl (1961)

9. Sampling localities

Table: Description of sampling localities of the years 2000 to 2005

River	Locality	River km individual distance ⁹	River km distance to Danube
Szamos	Csenger	48	731
Szamos	Szamossályi (ferry)	33	716
Old Szamos	Géberjén	31	714
Old Szamos	Györtelek-Tunyogmatolcs	21	704
Szamos	Nábrád	16	699
Szamos	Olcsva(apati) (ferry)	2	685
Szamos	Vásárosnamény	0	683

⁹ distance till confluence with the Tisza or in case of the Tisza itself the distance to the confluence with Danube

Tisza	Tivadar (Strandbad)	705	705
Tisza	Gergelyiugornya (above confluence)	686	686
Tisza	Vásárosnamény	683	683
Tisza	Tiszaadony (ferry)	668	668
Tisza	Tokaj (above confluence with Bodrog)	544	544
Tisza	Tiszalök (hydroelectric power station)	523	523
Tisza	Tiszakeszi	465	465
Tisza	Tiszavalk (reservoir, northern shore)	435	435
Tisza	Kisköre (500 m below outflow of reservoir)	402	402
Tisza	Tiszaékcske	280	280
Körös	Szelevény	10	250
Tisza	Mindszent	216	216
Maros	Szeged	0	180
Tisza	Szeged-Tápé (ferry)	180	180
Tisza	Tiszasziget	164	164

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