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The solid state partitioning of contaminant metals and As in river channel sediments of the mining affected Tisa drainage basin, northwestern Romania and eastern Hungary

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Abstract

The solid state partitioning of metals and As in river channel sediments has been investigated along an 828 km study reach comprising the rivers Lapuș, Someș and Tisa, using a 4-stage sequential extraction procedure (SEP) that identified 4 chemical phases: (1) exchangeable, (2) Fe and Mn oxides, (3) organic matter/sulphides and (4) residual. Peak total concentrations of As (240 mg kg⁻¹), Cd (95 mg kg⁻¹), Cu (24,500 mg kg⁻¹) and Pb (21,100 mg kg⁻¹) were found in the River Lapuș immediately downstream of Băiuț base-metal mine, with Zn concentrations (23,000 mg kg⁻¹) peaking 2 km further downstream. Contaminant metals and As within samples close to Băiuț mine were largely bound to sulphides (>92%). Ten km downstream from Băiuț mine, however, Cd and Zn were found to be environmentally significant due to their strong association with the exchangeable phase (73 and 47%, respectively). Lead was found to be predominantly associated with Fe and Mn oxides (71%), but concentrations in the residual phase were relatively high in the upper Tisa. Copper was more evenly distributed between the 4 phases than the other 4 elements analysed. Elevated metal and As concentrations were found in the rivers Lapuș and Someș downstream of polluted tributaries, but sites on the River Tisa had total metal concentrations below Dutch guideline values. The implications of the river sediment metal partitioning results on the environment are considered in light of Cd and Zn ‘exchangeable hotspots’ at sites on the Lapuș and Someș Rivers.

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1. Introduction

Metals present in the fluvial environment are derived from a variety of natural and anthropogenic sources (Dawson and Macklin, 1998), and are intimately associated with fine-grained sediments frequently transported as suspended load (Miller, 1997). In locations where human interaction within the fluvial environment is widespread, the presence of metals in high concentrations within river sediments and soils constitutes an

important environmental problem (Haag et al., 2001; Hudson-Edwards et al., 2001). River channel sediments are most directly affected by releases of metal wastes into the surface drainage network and play a key role in the redistribution of sediment-bound metals during flood events, both downstream and into overbank and floodplain sediment stores (Macklin, 1996; Klimek, 1999). Metal ions in channel-sediment stores may also be re-mobilised into solution dependant upon the strength of sediment-metal adsorption and geochemical conditions.

In the riverine environment, metals have been found to partition into different chemical forms associated

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with a variety of various organic and inorganic phases, dependent on chemical and geological conditions (Chao, 1984). It has been argued by Krishnamurti et al. (1995) that delineating various forms of elements and their speciation in sediments is essential for assessing their bioavailability and toxicity. It is now generally accepted that determining the total metal content is usually insufficient in order to fully assess the environmental impacts of contaminated sediments (Barona et al., 1999). The development of sequential extraction procedures (SEPs) by numerous workers (Tessier et al., 1979; Salomons and Förstner, 1980; Campanello et al., 1995; Keon et al., 2001) has allowed the solid-state partitioning of metals to be more fully studied. SEPs consist of subjecting a sediment sample to a series of increasingly strong, phase specific, reagents under specified conditions, giving metal concentrations in a number of 'operationally-defined' physico-chemical phases. Sediment fractions that have been identified as being of particular importance are Fe/Mn oxides, carbonates, sulphide minerals, organic matter and silicate minerals commonly referred to as the 'residual phase'. SEPs are not without limitations and have been criticised by Nirel et al. (1986), Nirel and Morel (1990) and Ho and Evans (2000). Of particular importance in this respect is the potential for reagents to be non-phase specific and for metal ions solubilised by a reagent to re-adsorb onto a different sediment phase. However, it is apparent that SEPs have the potential to be very useful techniques for highlighting differences in mobility and reactivity in a particular environmental context (Hursthouse, 2001).

While there are numerous examples of metal partitioning studies in the fluvial environment (e.g. Khalid, 1981; Gadh et al., 1993; Baruah et al., 1996; Calace et al., 1997), relatively few have investigated downstream patterns of metal partitioning in channel sediments in large drainage basins, but see Macklin and Dowsett, (1989) and Klavins et al., (2000). In this paper, the authors address this key issue through a study of chemical speciation of metals and As in river channel sediments in the Tisa basin, eastern Europe. This work was prompted by two major tailings dam failures that occurred in January and March 2000 in NW Romania, and which contaminated the Sasar-Lapuș-Someș and Novaț-Vaser-Viseu river systems, respectively. These rivers are tributaries of the River Tisa, and downstream transfer of CN and contaminant metals resulted in severe pollution of the Tisa and River Danube in Hungary, Serbia, Romania and Bulgaria. The primary aims of this study were to: (1) document the downstream patterns of metal partitioning and environmental significance of metals in channel sediments along an 828 km study reach comprising the rivers Lapuș, Someș and Tisa in northwestern Romania and eastern Hungary, and (2) evaluate the environmental significance of metals still present in the rivers and the long-term effects of mine tailings spills.

2. Study area

The Rivers Lapuș and Someș flow through Maramureș County, Romania (Fig. 1), a region that has a long history of precious and base metal mining (Bailly et al., 2002). Maramureș County is underlain by Neogene volcanic bedrock comprising andesites of different types (Lang, 1979). The volcanic rocks are penetrated by veins of complex sulphides and native elements (Au, Ag) of hydrothermal origin (Donisa et al., 2000). The bedrock is overlain by a post-meso-Cretaceous sedimentary cover comprising volcanic-sedimentary formations and sedimentary fractions such as sandstones and marls (Cook, 1997).

The Lapuș and Someș Rivers have been shown by Macklin et al. (2003) to be contaminated with heavy metals sourced from past and present metal mining activity (including the 30 January 2000 Aurul tailings dam failure), industrial and urban waste. The Lapuș has a high gradient headwater in the Tibleș Mountains but downstream of the Băiuț mine, the gradient decreases and the channel is laterally active with a well developed floodplain. The Someș downstream of the Lapuș confluence has a high sinuosity, low-gradient channel with extensive flood embankments, particularly where it flows through urban areas.

The Someș joins the Tisa in Hungary and for most of its length is a low-gradient, high-sinuosity river, though lateral movement has been restricted since the nineteenth century by bank protection structures and extensive flood defence embankments. The drift geology of the Great Hungarian Plain over which the River Tisa flows comprises Holocene wind blown sands and clay upstream of Tisafüred and Pleistocene loess in its southern reaches (Pécsi and Sárfalvi, 1964).

3. Field sampling procedure and analytical methods

The Rivers Lapuș, Someș and Tisa were sampled during low flow conditions. At each site a 200–300 g (wet weight) sediment sample from a river bar surface was collected using a stainless steel trowel from approximately 10 spot sites within a 5 m radius. In the laboratory samples were air-dried, disaggregated and sieved through a stainless steel mesh to isolate the <63 μm fraction.

Sample preparation techniques have been shown to be particularly important in speciation studies (Bordas and Bourg, 1998). For example, although sample drying is a favoured starting-point in the preparation of samples for the determination of metal content (Davidson et al., 1994), several workers have highlighted the potential for changes in sediment speciation characteristics during sample drying (Davidson et al., 1999a). However, both air and oven-drying have been widely used in studies

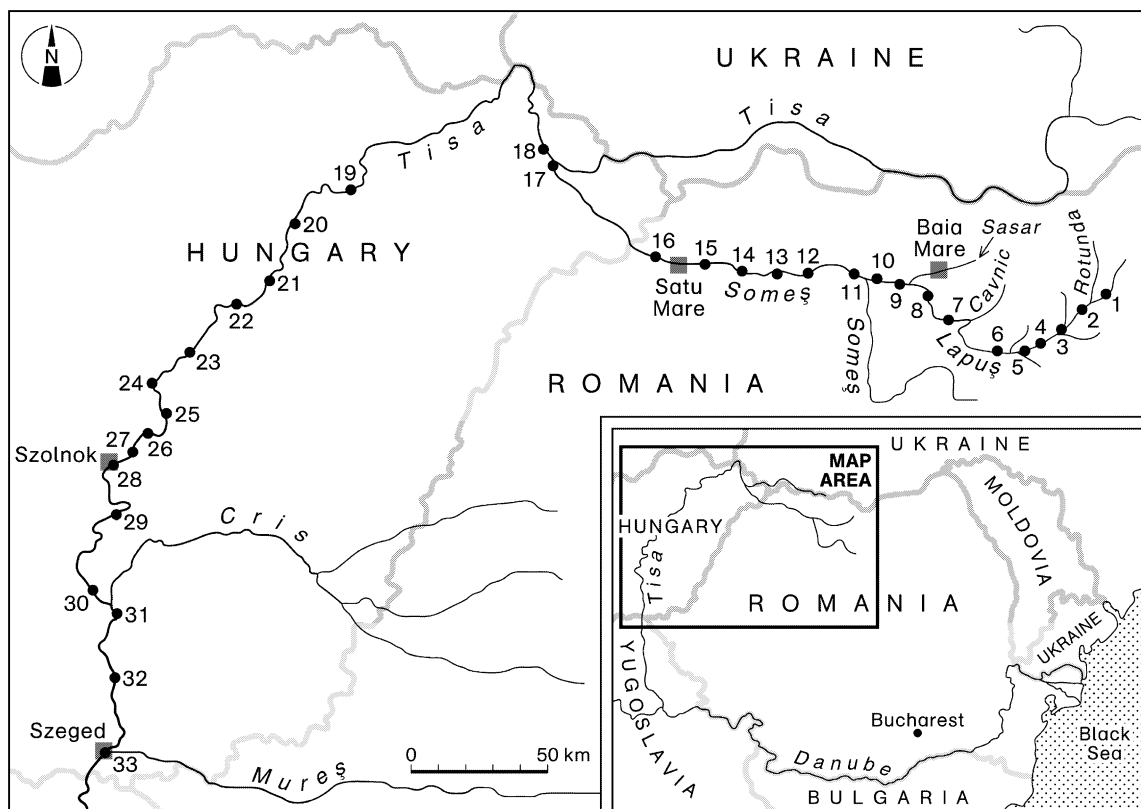


Fig. 1. Map of the upper Tisa basin showing sample site locations.

employing SEPs (Li et al., 1995; Baruah et al., 1996; Ho and Evans, 2000), with air-drying being the recommended preparation method for the Community Bureau of Reference (BCR) procedure (Quevauviller et al., 1993; Ure, 1993). Davidson et al. (1999a) indicate that summed metal recovery versus pseudo-total repeats using the BCR procedure on non-dried sediment was not within acceptable limits, unlike those for air-dried sediment. The advantages of using air-dried sediments have been identified by Davidson et al. (1994) with respect to the ease of handling, isolation of the chemically active $<63 \mu\text{m}$ fraction and ensuring similar analytical weights. In order to maintain procedural uniformity with respect to previous studies utilising the BCR procedure, and to reduce the potential for microbial and chemical reactions within the sediments between sampling and analysis (Davidson et al., 1999b), this study used air-dried sediments. Furthermore, given that metal partitioning has been assessed in oxidising surface sediments, which will dry following deposition at higher discharges, it is felt that air-drying of the sediments at ambient temperatures prior to analysis will not have altered speciation patterns beyond the extent of naturally occurring post-depositional processes.

In conjunction with the sediment sampling, measurements of river water pH, EC (Fig. 2) and Eh (samples 18–34 only using Pt electrode) were made at each site. Field measured values of Eh were calibrated using the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair measured in waters from an abandoned mine site at Cwmrheidol, mid-Wales following the method described by Ander (1998). Calibration gave a spatially stable Eh value for the River Tisa of 0.60 V. Eh-pH relationships are in accordance with those of surface water as defined by Garells and Christ (1965).

The SEP used was an adaptation of the BCR procedure (Quevauviller et al., 1993; Ure et al., 1993); the only difference being that samples were shaken horizontally as opposed to end-over-end. The 4 extractants used were (1) 0.11 M acetic acid, (2) 0.5 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, (3) 8.8 M H_2O_2 , and (4) concentrated *aqua regia*. This gave partitioning in 4 chemical phases analogous to: (1) 'exchangeable', (2) 'Fe/Mn oxides', (3) 'organic matter/sulphides', and (4) 'residual'. All supernatants were decanted into acid-washed plastic bottles and refrigerated prior to analysis. Between each phase of the SEP samples were washed using 10 ml of Milli-Q water. All reagents used were of Analar quality and reactions were performed in acid-washed 50-ml

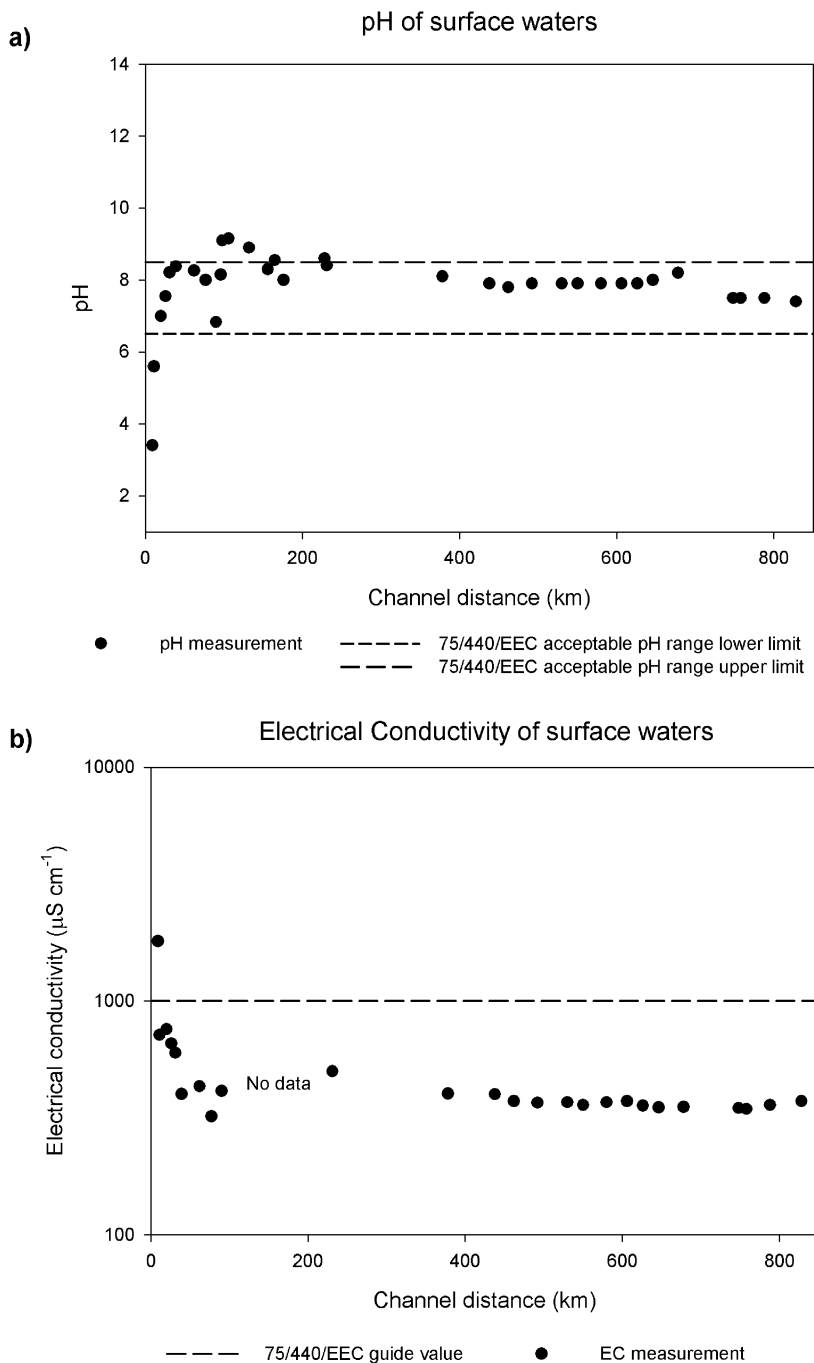


Fig. 2. (a) Surface water pH and (b) electrical conductivity at sample sites. Values are plotted with acceptable range and guide values quoted by EU directive 75/440/EEC. EC was not measured on the River Someş.

plastic centrifuge tubes. Supernatants were analysed for As, Cd, Cu, Pb and Zn using inductively coupled plasma–mass spectrometry (ICP–MS). Instrumental precision, monitored using blind duplicates was found to be within the range of $\pm 10\%$ normally adopted by analysts (Hamilton, 1980).

Given the potentially strong isobaric interferences for the determination of As in Cl^- bearing matrices (0.5 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and *aqua regia*), As concentrations were confirmed through mass abundance–ratio interference corrections for ArCl , Se and Ar_2H . Corrections were calibrated using the ratio between ^{66}Zn and ^{68}Zn .

Analytical precision, determined using blind duplicates, was found to be 11% for Cd and less than 10% for As, Cu, Pb and Zn. In order to monitor the accuracy of the procedure, summed metal concentrations in the 4 phases were compared with the values obtained for total (*aqua regia* soluble) concentrations (Li et al., 1995; Dawson and Macklin, 1998; Li and Thornton, 2001). Recovery rates for the 4 phases of the SEP ranged from 76–117% with a mean of 93%; these values compare favourably to results obtained in previous studies (e.g. Dawson and Macklin, 1998). The general tendency of underestimating metal concentrations is probably due to a slight dilution effect caused by the sediments never being fully returned to dryness before the addition of the next reagent.

4. Results and interpretation

4.1. Environmental quality guidelines

There is a need in environmental quality studies to assess metal concentrations with respect to threshold values, in order to evaluate the extent of pollution and its possible ecological impact. The use of environmental quality guidelines facilitates site-specific evaluation as well as the comparison with other metal-contaminated catchments (Macklin, 1992; Macklin and Klimek, 1992).

Unlike air and water, it is difficult to achieve a common approach to identifying contamination in soils and sediments (Visser, 1993). A number of countries have integrated soil/sediment protection and contamination prevention legislation with laws regarding environmental clean-up (Table 1). Romania and Hungary have seemingly developed no such legislation or guideline policy, and EU directives (86/278/EEC) apply only to the application of contaminated substances, such as sewage sludges, to non-contaminated sites (Table 1).

The Netherlands has a long history of soil/sediment protection policy dating back to 1962 (Visser, 1993), and guidelines were reformulated in the mid 1990s using eco-toxicological methods and considering potential human exposure routes (Table 1). These criteria have been adopted by many countries throughout Europe and have been used in numerous metal pollution studies as a means of evaluating contamination levels (Macklin and Klimek, 1992; Macklin et al., 2003). The Dutch guidelines have therefore been used in this study on the basis that they are a long established, tried and tested scheme, and that the stringent target and intervention values are based on extensive studies of both human and eco-toxicological effects of contaminants.

Downstream total metal and As concentrations at each site are plotted in Fig. 3 with Dutch Ministry of Housing, Spatial Planning and Environment guideline

values for metal concentrations in soils and sediments (Table 2). The results of the SEP for As, Cu, Cd, Pb and Zn are given in Fig. 4. Table 3 summarises mean metal concentrations in the 3 rivers and Table 4 presents mean percentage partitioning patterns for the Lapuș, Someș and Tisa rivers. In all cases distance downstream is measured from the source of the River Lapuș.

4.2. Total metal concentrations

Arsenic, Cd, Cu and Pb concentrations peak immediately below the Băiuș mine at site 1 with concentrations being 4, 8, 129 and 40 times greater, respectively, than their associated intervention thresholds. Zinc concentrations peak at site 2, 2 km downstream of site 1, where the concentration is 32 times the intervention threshold. The general reduction in metal concentrations downstream of Băiuș mine is most probably a result of dilution by inputs of cleaner sediment from river bank erosion and non-polluted tributaries such as the Rotunda, which conflues with the Lapuș between sites 1 and 2 (Fig. 1).

The marked decrease in metal concentrations downstream of site 1 also suggests that contaminated sediment from Băiuș mine has not been extensively dispersed down the River Lapuș. A secondary peak in metal concentrations is present in sediments sampled from downstream of the Sasar–Lapuș confluence (site 9 at 90 km). This peak is the result of polluted sediments being introduced from the River Sasar, a river that receives metal enriched wastes from mining, industrial activity and municipal sources in Baia Mare and Baia Sprie. At site 9, As (80 mg kg^{-1}), Cu (380 mg kg^{-1}) and Zn (1040 mg kg^{-1}) are present at concentrations higher than the intervention threshold (Fig. 3).

In the River Lapuș, Cu and Zn are consistently present in high concentrations relative to intervention thresholds. This pattern continues in the River Someș with Zn and Cu concentrations exceeding intervention thresholds at 5 of the 7 sample sites. In the River Someș concentrations of As, Cd (except site 12, 106 km) and Pb are all below their respective intervention thresholds.

Concentrations of metals in the River Tisa, downstream of its confluence with the River Someș, are below intervention thresholds at all of the 16 sample sites (Table 3 and Fig. 3). The highest metal concentrations in River Tisa sediments are found 3 km downstream of the River Someș confluence (site 18 at 231 km). This would suggest that metals are being introduced into the River Tisa adsorbed to sediment supplied from the River Someș.

Sites with metal concentrations exceeding intervention guidelines can be considered seriously contaminated and pose a threat to the functional properties of human and plant and animal life (VROM, 2000), these sites are in need of remediation.

Table 1

Soil/sediment quality criteria developed by various European countries (concentration in mg kg⁻¹ dry weight). Information adapted from Visser (1993; 1995) and Sedgwick (2000)

	The Netherlands		Germany		Switzerland	Finland	Denmark	United Kingdom		DEFRA ^g
	Target ^a	Intervention ^b	Multif. ^c	Agric. ^d	MAC ^e	MAC	MAC	Threshold trigger values ^f		
								Gardens	Parks	
As	29	55	20	40	–	50	20	10	40	20
Cd	0.8	12	0.6	1.5	0.8	20	–	3	15	1
Cr	100	380	–	–	75	800	100	600	1000	130
Cu	36	190	40	60	50	500	200	130	130	–
Pb	85	530	50	100	50	600	40	500	2000	450
Hg	0.3	10	0.3	1.0	0.8	10	–	1	20	8
Ni	35	210	–	50	50	500	–	70	70	50
Zn	140	720	120	200	200	3000	–	300	300	–

^a Dutch target value: if concentrations do not exceed this value, the site is considered clean with no eco-toxicological risk.

^b Dutch intervention value: if concentrations exceed this value they are considered as posing an environmental risk and clean-up is necessary.

^c Multifunctional land.

^d Agricultural land.

^e MAC: maximum accepted concentration.

^f UK threshold concentration stated by the Inter-departmental Committee for the Reclamation of Contaminated Land (ICRCL): concentrations below this value sites are considered uncontaminated. Higher 'action' trigger concentrations to identify unacceptable hazards have not been specified for these metals (Simms and Beckett, 1987).

^g Department for Food, Environment and Rural Affairs (DEFRA): March 2002 guidelines based upon 'bioavailable concentrations'.

4.3. As partitioning

At site 1, just downstream of Băiuț mine, 93% of As is associated with the H₂O₂ soluble phase suggesting adsorption to organic matter and(or) sulphides (Fig. 4). The close proximity of the sample site to the active extraction and processing of sulphide ore material suggests that As is bound to the sulphide fraction, this is supported by the fact that at site 3 (9 km downstream of the mine) only 2% of As reports to this phase. Along the rest of the River Lapuș, As is largely associated with the residual phase (66%) with the exception of site 10 (96 km) where partitioning is dominated by Fe/Mn oxides (80%). This site is situated just downstream of the confluence with the River Sasar and the Aurul tailings dam, suggesting that the geochemistry of channel sediments at this location may have been altered by the dam failure or by continual release of metal pollutants from the site. With the exception of site 11 (98 km) the percentage of As adsorption to Fe/Mn oxides is generally higher in the River Someș (mean = 36%) compared with the River Lapuș (mean = 17%) and River Tisa (mean = 17%). The percentage of As adsorbed to Fe/Mn oxides in the River Someș is at a maximum at sites 12 (106 km) and 15 (165 km) but thereafter progressively decreases downstream. In the River Tisa As partitioning is dominated by the residual phase (mean = 79%) with the Fe/Mn oxide fraction accounting for a majority of the remaining partitioning (mean = 17%). There is also a

gradual downstream increase in the proportion of As associated with the residual phase. This pattern, however, shows no statistically significant relationship with pH and Eh measured in surface waters.

4.4. Cd partitioning

In the Lapuș, Someș and Tisa Rivers, Cd is partitioned largely in the exchangeable phase (mean = 73%). Cadmium partitioning at the 'Baiu't mine is similar to As; being dominated by the sulphide fraction (97%) but reduces very rapidly to 5% at site 2 (11 km). The proportion of Cd present in the organic matter/sulphide phase remains very low along the entire study reach, particularly in the River Someș (2%). In the River Lapuș downstream of site 1, whilst a majority of Cd is partitioned in the exchangeable phase (65%), the Fe/Mn oxide fraction is relatively important (21%) compared with the Someș (15%) and Tisa (16%), with peak percentage partitioning in the Fe/Mn oxides (28%) occurring at site 10, downstream of the Sasar confluence. In the River Someș, Cd is also present in an exchangeable form (81%), with relatively little site-to-site variation. In the Tisa, although most Cd is bound to the exchangeable fraction (mean = 74%), there is site-to-site variation particularly of the exchangeable and Fe/Mn oxide phases. Cd partitioning in the residual phase is not significant anywhere along the study reach with values being less than 10% with a mean of 2.3%.

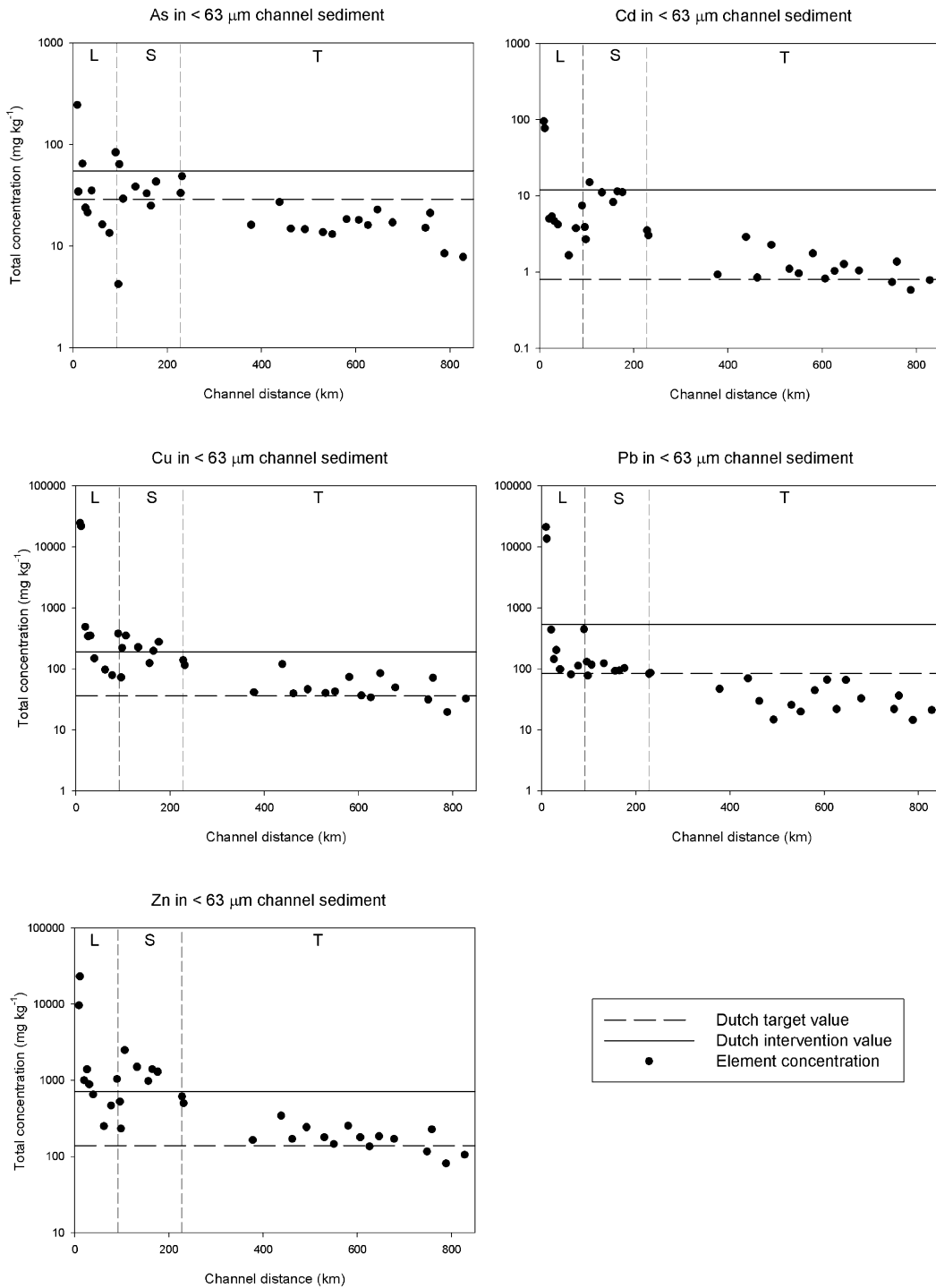


Fig. 3. Total metal and As concentrations in <63 μm river channel sediments along the study reach. Vertical lines show the limits of each river: L = Lapuș, S = Someș and T = Tisa.

Table 2
Dutch Ministry of Housing, Spatial Planning and Environment (VROM, 2000) values for metals in soils and sediments (New Dutch List)

Element	Concentration (mg kg ⁻¹)	
	Target	Intervention
As	29	55
Cd	0.8	12
Cu	36	190
Pb	85	530
Zn	140	720

4.5. Cu partitioning

With the exception of site 1, where 99% of Cu is associated with the sulphide phase, Cu exhibits a partitioning pattern that is more evenly distributed between the 4 phases than the other 4 metals (Table 3). On average, Cu in the River Lapuș is largely associated with the H₂O₂ soluble phase, particularly between site 3 (20 km) and site 5 (31 km). Downstream of site 5 the residual phase accounts for more of the metal partitioning until site 8 (77 km) where the importance of the H₂O₂ and hydroxylammonium chloride soluble phases increase and remain relatively high until site 15 (165 km). An exception to this pattern is site 11, immediately downstream of the Lapuș–Someș confluence at 98 km, where 81% of Cu is associated with the residual phase. This site also exhibits peaks in residual phase partitioning for As, Cd, Pb and Zn. Downstream of site 15, in the lower Someș and Tisa, the importance of the residual phase as a store of Cu increases and it is the dominant physico-chemical phase (40%). With the exception of site 2 (11 km), where 53% of Cu is associated with the exchangeable phase, the percentage of weakly-bound Cu in all 3 rivers is generally similar at around 20%. Copper also exhibits a stronger association with organic matter/sulphide fractions along the 828 km study reach than As, Cd, Pb or Zn.

4.6. Pb partitioning

With the exception of site 1 (96% bound to the sulphides) Pb is bound largely to Fe/Mn oxides in the Rivers Lapuș (69%), Someș (80%) and Tisa (65%) with the residual phase accounting for the majority of the remaining partitioning. In the River Lapuș the influence of the Băiuț mine is greatly reduced by site 2 (<1% associated with H₂O₂ soluble phase) and by site 10, downstream of the Aurul tailings pond, 97% of Pb is partitioned to the Fe/Mn oxide fraction. In the River Someș the association of Pb with oxides of Fe and Mn increases downstream of the Lapuș confluence to a peak

at site 15 (165 km), however, over the next 213 km the importance of the residual phase increases (up to 27%), particularly in the upper Tisa. Overall Pb partitioning displays a more variable downstream pattern than Cd, but changes in the relative importance of the Fe/Mn oxide and residual phases are not correlated to any measured changes in surface water geochemistry and may be a result of changes in adsorption–desorption processes unique to each site (Macklin and Dowsett, 1989). The importance of the Fe/Mn oxide phase in Pb partitioning, particularly as a coating to sediment particles, has been previously noted by Evans and Davies (1994) and Hudson-Edwards et al. (1996). The dominance and general stability of the Fe/Mn oxide phase, particularly in the River Tisa, is potentially facilitated by the thermodynamic stability of Fe and Mn at the ranges of pH and Eh measured in surface waters on the River Tisa. Eh/pH species stability diagrams presented by Garells and Christ (1965) and Faure (1995) suggest that under the geochemical conditions present in the Tisa, Fe and Mn are stable in solution as the oxides Fe₂O₃ (Hematite) and MnO₂ (Pyrolusite).

4.7. Zn partitioning

Zinc partitioning is dominated (97%) by the sulphide fraction at site 1 (9 km) but within 2 km has fallen to only 2%. The organic matter/sulphide phase for Zn is much higher than for either Cd or Pb. At sites downstream of site 1, Zn partitioning is dominated by the exchangeable and Fe/Mn oxide fractions, with mean values of 45 and 33%, respectively. In the River Lapuș the importance of the exchangeable phase reduces downstream between sites 2 (11 km) and 8 (77 km), accompanied by a general increase in Fe/Mn oxide partitioning. In the lower Lapuș, downstream of site 9 (90 km), the exchangeable phase increases and continues to rise in the upper-middle River Someș (106–176 km), where partitioning percentages are consistently high (63%). In this section of the River Someș increases in the exchangeable phase are accompanied by a decrease in partitioning in the organic matter/sulphide and residual phases, rather than the Fe/Mn oxides. In the lower Someș (228 km) the importance of the exchangeable phase reduces and continues to do so into the upper section of the River Tisa (up to 438 km). This is accompanied by a relative increase in partitioning in organic matter/sulphide and residual phases, with partitioning in the lower Tisa being dominated by the exchangeable (36%) and Fe/Mn oxide (38%) phases.

In the Rivers Lapuș and Someș (9–228 km) downstream of Băiuț mine, partitioning patterns of Cd and Zn are very similar (Spearman rank correlation coefficient of $r^2=0.97$). This is perhaps not surprising given that the chemistries of Cd and Zn are similar, particularly with respect to ionic structures, electro-

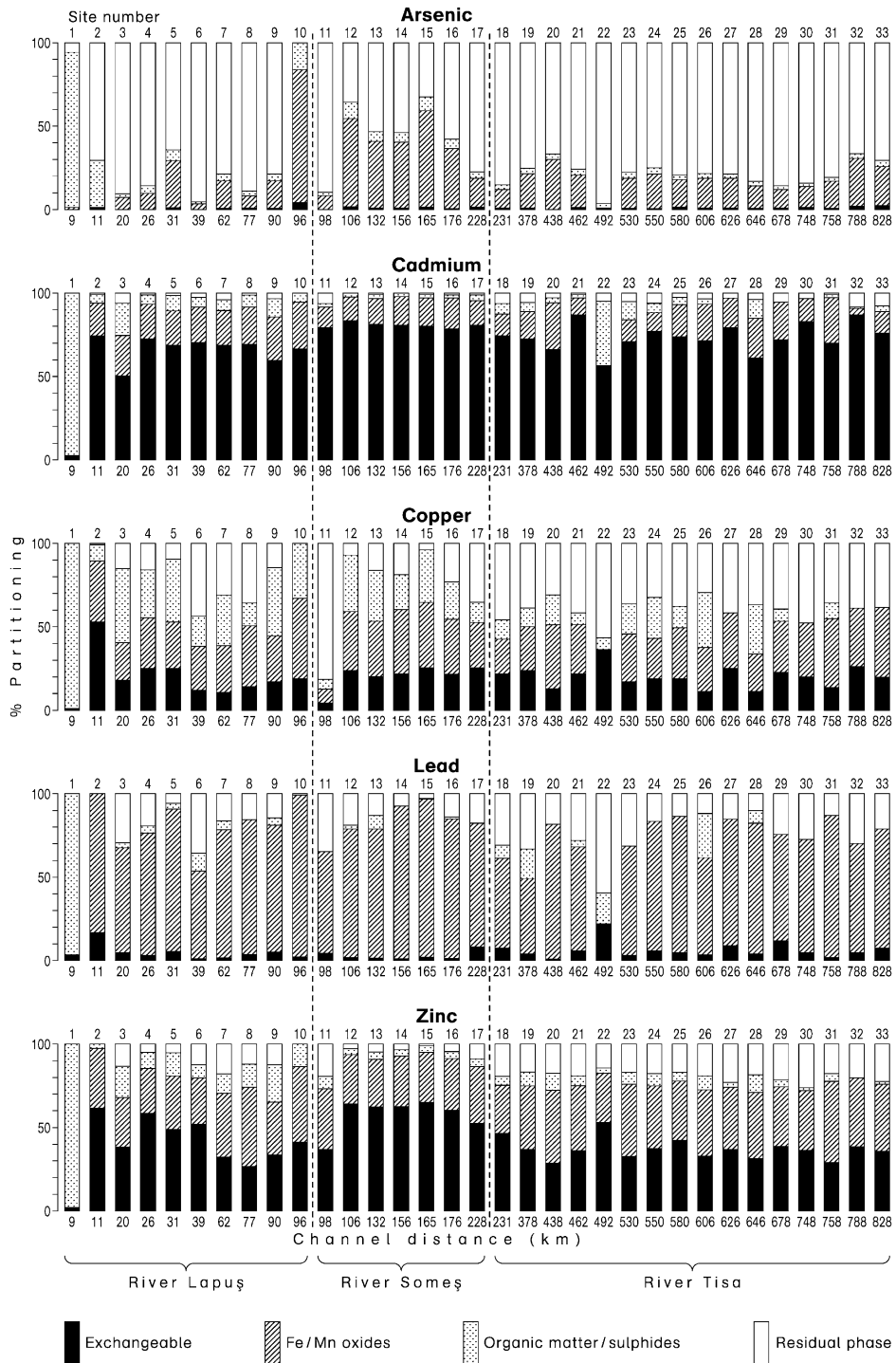


Fig. 4. Solid state partitioning of metals and As in < 63 μm channel sediments in the Rivers Lapuş, Someş and Tisa.

negativities and ionisation energies (Fuge et al., 1993). Cadmium and Zn have also been shown to be highly mobile elements in river and floodplain sediments (Salomons and Förstner, 1984; Macklin and Klimek,

1992) and their partitioning in the acetic acid soluble phase, particularly in the Rivers Lapuş and Someş, indicates that they are readily exchangeable.

Table 3

Mean total concentrations (mg kg⁻¹) of selected metals and As in the Rivers Lapuș, Someș and Tisa

River	As	Cd	Cu	Pb	Zn
Lapuș (0–96 km)	54	21	4850	3630	3890
Lapuș (20–96 km)	32	4	240	200	770
Someș (98–228 km)	37	9	220	97	1200
Tisa (231–828 km)	18	1.3	54	38	200

Table 4

Mean % values of metal partitioning in the Rivers Lapuș, Someș and Tisa

	Exchangeable	Fe/Mn oxides	OM/sulphides	Residual
<i>River Lapuș (0–96 km)</i>				
As	0.8	17.1	16.2	65.9
Cd	59.3	21.3	17.2	2.2
Cu	19.6	28.3	35.4	16.8
Pb	4.9	68.7	12.7	13.9
Zn	42	30.1	20.5	7.5
<i>River Someș (98–228 km)</i>				
As	1	36.2	5.8	57
Cd	80.7	15.6	2.2	1.5
Cu	20.6	30.6	22.2	26.6
Pb	2.9	79.9	1.6	15.5
Zn	57.9	31.3	4.5	6.3
<i>River Tisa (231–828 km)</i>				
As	0.9	17.4	2.6	79.1
Cd	73.9	16.1	5.6	4.4
Cu	20.1	28.7	10.9	40.3
Pb	6.3	65.4	4.8	23.5
Zn	36.4	37.7	5.1	20.8

4.8. Environmental significance of metal partitioning in Tisa basin river sediments

This study has highlighted the benefits of using sediment quality guidelines as a means of evaluating the level of contamination present in a mining affected river system, with total metal and As concentrations at 12 of the 17 sites in the Rivers Lapuș and Someș exceeding Dutch intervention limits. However, total concentrations on their own are not sufficient to make an assessment of whether elements are present in concentrations that may pose a significant environmental risk (Ma and Rao, 1997). Acetic acid has been used in several studies of metal availability and plant uptake (Little and Martin, 1972; Bjerre and Schierup, 1985a) with acetic acid-soluble concentrations providing an indicator of plant availability of metals (Bjerre and Schierup, 1985b).

To the authors' knowledge, there are no environmental quality guidelines regarding 'exchangeable'

metal and As concentrations that have been developed with upper and lower threshold values. To evaluate whether metal and As concentrations in river channel sediment pose a potential environmental risk, coded symbols have been plotted at each site showing where element concentrations in the exchangeable phase fall below or above target, or exceed intervention values (Fig. 5). Given that the Dutch guidelines are based on 'total' determinations, this will aid the identification of severely contaminated sites should metal or As levels from the milder acetic acid extractible phase exceed these limits.

In this study, As has been shown to partition strongly in the residual phase, even at sites where concentrations exceed Dutch intervention guideline values, suggesting that it is strongly bound to, or incorporated within the lattices of silicates and other resistant minerals. Given the partitioning of As in this relatively chemically inactive form, it may be considered at present to be environmentally insignificant with respect to ecotoxicity and chemical mobilisation within Tisa basin river sediments. Whilst the evidence of As contamination in the Rivers Lapuș and Someș should not be ignored, the data suggest that remediation strategies should principally focus on elements which partition predominantly to the exchangeable phase.

Zinc and Cd have been shown to partition strongly in the exchangeable phase and thus can be considered environmentally significant, particularly at the most polluted sites. Fig. 5b and e, indicate sites of particular environmental concern where Cd and Zn concentrations in the exchangeable phase exceed Dutch intervention thresholds. All these sites are in the Rivers Lapuș and Someș and can be considered 'exchangeable-metal hotspots'. The presence of exchangeable-metal hotspots on the upper Lapuș and the River Someș coincide with sites of elevated metal concentrations, which are in turn associated with mining and other industrial activity. Even at sites where Cd and Zn concentrations are below Dutch intervention values, (notably in the lower Lapuș and the River Tisa) metals are still strongly associated with the exchangeable phase. With respect to bioavailability and ecotoxicity, it is apparent that Cd and Zn pollution associated with metal mining activity is of particular concern in the upper Lapuș and River Someș, but not in the River Tisa.

Cadmium and Zn also offer the greatest potential for chemical remobilisation via resolution given their strong association with the acetic acid soluble phase. However, this is likely to be mitigated by the quasi-neutral surface water pH in most of the Tisa system and by the oxidising nature of the surface waters, which will promote adsorption rather than solution of metal ions. Possible exceptions to this are sites in the upper Lapuș where the pH of surface waters is below pH 6.

Copper and Pb are also present in an exchangeable form at high concentrations at the two sites downstream

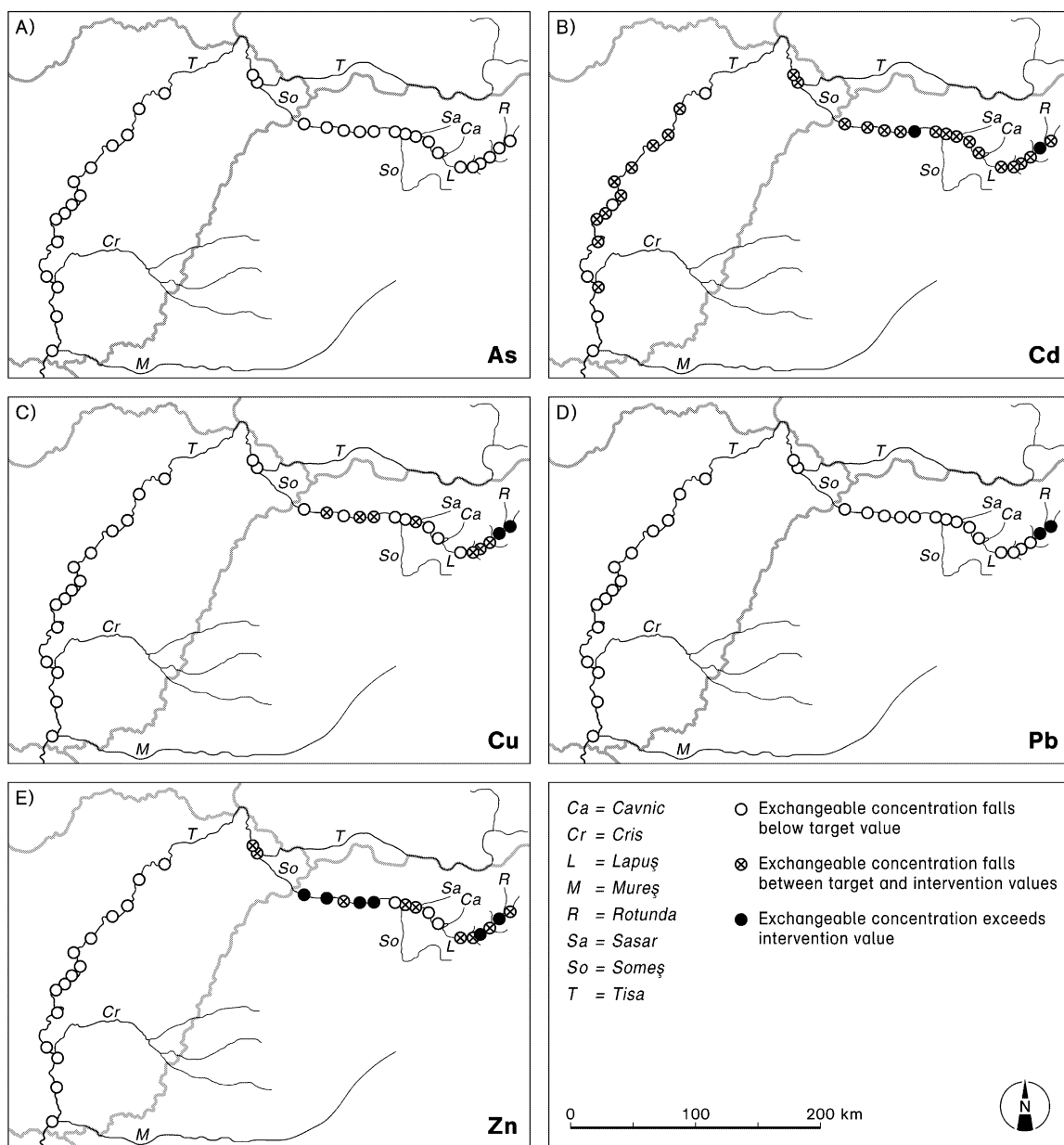


Fig. 5. Exchangeable concentrations of contaminant metals and As in the upper Tisa basin plotted relative to Dutch target and intervention values. Black circles indicate where exchangeable concentrations exceed Dutch intervention values, crossed circles fall between target and intervention values and open circles indicate concentrations comply with target values.

of Băiuț mine (Fig. 5c and d). But while Cu in an exchangeable form lies between target and intervention values at 7 sites in the Lapuș and Someș, along the remainder of the study reach exchangeable Cu concentrations fall below target values. For the remaining 31 of the 33 sites, exchangeable Pb concentrations fall below Dutch target values.

In March 2002, the United Kingdom's Department for Food, Environment and Rural Affairs published

soil/sediment quality guidelines for a number of elements including As, Cd and Pb based upon 'bioavailable' concentrations (Table 1; DEFRA, 2002). With the exception of Cd at site 31 (758 km), an identical pattern of As, Cd and Pb guideline failure occurs whether 'exchangeable phase', referenced to Dutch target (used in this paper), or 'DEFRA bioavailable' values are used. Given that the Dutch values represent a long-established and stringent set of figures that are already widely

used in studies of environmental contamination, the authors believe that using ‘exchangeable phase concentrations’ provides a valuable additional tool for identifying pollution hotspots assessing the environmental significance of metal partitioning.

5. Conclusions

This study has shown that river channel sediments in the upper Tisa basin downstream of Băiuț mine are severely contaminated with metals and As partitioned predominantly in the H₂O₂ soluble phase, suggesting the importance of sulphide minerals in metal precipitation. The geochemical influence of the mine as a source of pollution is substantially reduced less than 20 km downstream. There are, however, additional inputs of metals from tributaries such as the Rivers Cavnice and Sasar, which locally increase total metal concentrations above Dutch intervention values.

10 km downstream of Băiuț mine there is little change in the metal speciation patterns of As, Cd, Pb and Zn, with metals being largely adsorbed to single dominant phases. In terms of environmental significance, it has been shown by the partitioning of Cd and Zn with the weakly bound, acetic acid soluble phase that these metals could be highly mobile, as well as bioavailable. The potential for As remobilisation and bioavailability was found to be low, as most of this element was present in the chemically inert, residual phase.

Thus, although ‘total’ extractions indicated that metal and As in the upper Tisa basin were present in river sediments in potentially harmful concentrations, SEPs allow a more accurate assessment of the potential hazard sediment-associated metals may pose in the riverine environments.

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