Sediment Contaminants Baseline Report

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Executive Summary

This report addresses three objectives and provides the stipulated contract deliverables in terms of hard copy maps and electronic data files. First, a comprehensive river water and river sediment geochemical database has been developed (Objective 1) using RMGC (n = 272) and fluvio (n = 421) river water and river sediment sample data. Second, the geochemical footprint of Roşia Montana (Objective 2) was determined through a combination of i) catchment contamination maps, ii) composite sediment fingerprinting and sediment mixing models, and iii) Pb isotope analysis. By using these approaches it is estimated that the maximum downstream extent of the geochemical footprint associated with mining activity in the Roşia Montana catchment lies between 24 km and 30 km downstream of the Roşia/Abrud confluence; that is between Valea Lupsei and Braleşti. Finally, additional sites have been identified on the Abrud and Arieş which RMGC should integrate within their existing sampling network (Objective 3). Water and sediment samples should be taken routinely at all river sites within the RMGC network so that contaminant dispersal patterns can be fully monitored, evaluated and modelled.
1 Introduction

Roşia Montana, in the Metaliferi Mountains of western Romania, has a long history of base and precious metal mining dating back to pre-Roman times which has degraded local river quality particularly in the Valea Roşia, River Abrud and River Arieş. Given the plans to develop the Roşia Montana gold mine, a major multi-component environmental impact assessment (EIA) is presently being undertaken by teams of national (Romanian) and international consultants. fluvio were approached by the Roşia Montana Gold Corporation (RMGC) to contribute to the EIA; this report presents data and interpretations relating to three specific objectives:

- To collate all published and unpublished geochemical (water and sediment) data sets for the Abrud/Arieş catchment and integrate them within a GIS database.
- To identify the geochemical footprint associated with past and present mining activity in the Abrud/Arieş catchment.
- To identify areas within the Abrud/Arieş catchment which may require additional environmental monitoring and to collect suspended sediment samples.

Fluvio are UK experts on evaluating the impact of mining related metal pollution on river basins, particularly arising from tailings dam failures. They have worldwide experience including acting as scientific consultants in the recent mine tailings dam failures at Porco on the Rio Pilcomayo, Bolivia (Macklin et al., 1996; Hudson–Edwards et al., 2001), at Aznalcóllar, Rio Guadiamar, Spain (Macklin et al., 1999, Hudson-Edwards et al., 2003), and in Maramureş County, NW Romania (fluvio, 2000, Macklin et al., 2003, Bird et al., 2003). Furthermore, fluvio has extensive experience of working in Romania having been commissioned by Maramureş and Satu Mare County Councils to investigate the long-term impacts and environmental significance of metal mining activity on water and sediment quality in NW Romania (fluvio, 2002a; 2002b; 2003; 2004a; 2004b).
2 Objective 1: Information Review

The collation of all published and unpublished geochemical (water and sediment) data sets for the Abrud/Arieş catchment and integration within a GIS database.

All available published and unpublished geochemical data (river water and river sediment) for the Abrud/Arieş catchment have been collated and integrated within a GIS database. These data comprise:

1. bi-annual river water quality data collected by RMGC between November 2000 and November 2003 from 34 sites in the Abrud catchment and on the Arieş between Câmpeni and Lunca (272 samples). NB RMGC also routinely determine groundwater quality from 39 sites in the Abrud catchment; these are not included in the geochemical database because they were not provided to fluvio.

2. 102 river water and river sediment samples collected by fluvio from 53 sites in the Abrud/Arieş catchment in July 2002 (Table 8-1; Figure 9.1).

3. 106 river water and river sediment samples collected by fluvio from 53 sites in the Abrud/Arieş catchment in July 2003 (Table 8-1; Figure 9.2).

4. 164 river water and river sediment samples, and 49 catchment samples, collected by fluvio from 153 sites in the Abrud/Arieş catchment in March 2004 (Table 8-1; Figures 9.3 and 9.4).

Since July 2002, fluvio has collected and analysed 421 river water, river sediment and catchment samples in the Abrud/Arieş catchment (Table 8-1). This constitutes the largest, and most spatially extensive, geochemical database available for the Abrud/Arieş catchment. Furthermore, it is the only database that combines river water and river sediment quality, thus enabling potential chemical interactions between the two media (e.g. adsorption/desorption processes) to be assessed.

One other source of unpublished geochemical data on the Arieş was located, a PhD by Ferenc Forray from the University of Cluj (Forray, 2002). An application to borrow this thesis via the Inter-Library Loans Service was made in December 2003 but we were informed in March 2004 that the thesis would not be released. However, a partial summary of Forray’s thesis data is provided in a published abstract and in a journal article (Forray and Hallbauer, 2000); these data summaries are shown in Tables 8-2 and 8-3, respectively. NB these data have not been included in the geochemical database because precise sample locations, and sampling and analytical procedures, are unknown.

2.1 Field Sampling and Laboratory Metal Analysis

In July 2002 Fluvio conducted their first survey of water and sediment quality in the Abrud/Arieş catchment. The aim of this sampling programme was to ascertain the magnitude, spatial extent and environmental significance of heavy metal contamination in the catchment resulting from metal mining activity. Sample sites were selected according to two complementary criteria: first, immediately up- and downstream of known point pollution sources (e.g. mine sites, waste dumps, tailings ponds or mining affected tributaries), and second on a systematic and regularly spaced downstream basis (Figure 9.1). In July 2003 fluvio resampled all the 2002 sites in the Abrud catchment and on the Arieş River, but added 3 new samples sites on the Arieş (AR3a, AR15a and AR16a) and one on the Bucium (BU0) (Figure 9.2).
Although the samples collected by fluvio (July 2002 and July 2003) and by RMGC were collected independently, many were taken from identical locations (Table 8-4 and Figure 9.5). The degree of sample site commonality between the RMGC and fluvio datasets provides an opportunity to assess temporal water quality patterns in the Abrud/Arieş at a resolution previously not possible.

In March 2004 fluvio conducted a further water and sediment sampling programme to collect data necessary for the delivery of this report’s objectives 2 and 3 (see section 1). All sites on the Arieş were resampled (except AR1, AR2, and AR3; at, and downstream of, Turda), but 51 new sites were sampled on the Rivers Izbita, Corna, Cerbul, Abrudzel, Cernit, Roşia, Abrud, Stefanca, Musca, Sesei and Arieş (Figure 9.3). Furthermore, 49 catchment samples were collected for use in the sediment fingerprinting model (see below).

### 2.1.1 River Water Samples

All water and sediment samples were collected and analysed according to standard, and scientifically recognised, protocols. Samples of river water were filtered in the field through 0.45 µm cellulose nitrate membranes, acidified with three drops of HNO₃, and stored in acid-washed Nalgene bottles. At each water sampling site, measurements of temperature, pH, Eh (redox) and electrical conductivity (EC) were also taken using a YSI 556/MPS multiprobe, which had been calibrated with standard solutions.

All river water samples were analysed for their heavy metal and As content using a VG PlasmaQuad Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) at the University of Wales, Aberystwyth (UWA). In an ICP-MS each sample is nebulised into an Ar-plasma ‘flame’ where it rapidly undergoes desolvation, vaporization to the molecular level and dissociation into atoms, some of which are ionised. Argon is preferred as a plasma gas as it is: a) inert and will not easily chemically react with samples, b) has a high first ionisation energy therefore allowing the effective ionisation of almost all elements, and c) because it has a moderately low thermal conductivity meaning heat is retained within the plasma.

Once a stream of ions has been generated they are focused through a series of ion lenses into a mass analyser, which retards the ion beam and, based upon element mass, allows ions of each element to pass into the mass spectrometer in a set order. The mass spectrometer measures elemental concentration as raw ion counts; this can then be scaled against an internal calibration standard (Ru at a working concentration of 100 µg l⁻¹) and processed to give elemental concentration in solution.

For the analysis of river waters, accuracy and precision were assessed using standard solutions (1 µg l⁻¹; 10 µg l⁻¹ and 100 µg l⁻¹) and blind duplicates, respectively. Accuracy and precision, with the exception of Cd due to low concentrations (< 0.05 µg l⁻¹), were within ± 10%. The 10% limit has been routinely adopted by analysts as indicating acceptable data quality (Hamilton, 1980).

### 2.1.2 River Sediment Samples

Samples of river sediment were collected using a stainless steel trowel from exposed bar surfaces, with 10 spot samples taken within a 5 m radius which were then aggregated to form a sample of around 300–400g wet weight. Samples were stored in wet-strength bags geochemical soil bags prior to laboratory analysis. In March 2004, catchment samples (n = 49) were also collected from within the Abrud basin to facilitate the determination of the Roşia Montana geochemical footprint (Objective 2). These samples were collected in a similar fashion to the bar samples but were taken from slope regolith exposures (e.g. road cuttings, slope failure scars) and from sites associated with mining activity (e.g. open cast pits, tailings ponds, spoil tips).
Sediment samples were air-dried for at least 48 hours, manually disaggregated using a pestle and mortar and sieved through a stainless steel mesh to isolate the chemically active silt and clay fraction (< 63 µm). Heavy metal concentrations in sediment samples (< 63 µm) were determined using ICP-MS following digestion of the sediment with concentrated HNO₃ at 100°C for 1 hour. Precision of the analytical procedure was monitored by inserting an extra 10% of the total number of samples as ‘blind duplicates’. Analytical accuracy was assessed by analysing a certified reference material (GSD12) from the Community Bureau of Reference (BCR) and also an ‘in-house’ reference material (ABS1) that has been routinely characterised for its heavy metal content at UWA over a number of years.

Analytical precision and analytical accuracy, versus both GSD12 and ABS1, were found to be within 10%, the only exception being Cu and Zn versus GSD12, which returned slightly lower accuracies of 13.8 and 13.1% respectively. The 10 percent limit has been routinely adopted by analysts as indicating acceptable data quality (Hamilton, 1980).

2.2 Environmental Quality Guidelines

In environmental quality studies it is often necessary to assess metal concentrations with respect to threshold values, so that the extent of pollution and its possible environmental impacts can be assessed. The use of environmental quality guidelines not only facilitates site-specific evaluation but also enables comparisons with other metal-contaminated catchments to be made (Macklin, 1992; Macklin and Klimek, 1992).

2.2.1 River Water

In this report river water quality is assessed using three sets of guideline values. First, EU target and imperative values (directive 75/440/EEC) which are used for river water that is abstracted for use as drinking water (Table 8-5). Second, Romanian STAS values quoted in directive S4706/1988 (Table 8-6) which again apply to river water that is abstracted for use as drinking water, and third, limits proposed in the Romanian Ministerial Order (MO) 1146/2002 (Table 8-7).

In order to utilize the water quality guidelines set out in MO1146/2002, there is a requirement to use background concentrations as the threshold value for ‘Limit I’. Background dissolved metal concentrations in river water (mean values) have been determined from samples collected within the Arieş catchment from rivers that either contain no mining activity, or alternatively, from locations upstream of mine sites (Arieş, Upper Bucium, Cerbul and Cerniţa Rivers). Table 8-8 summarises calculated background values for each of the three fluvio sampling programmes and presents a weighted mean background figure for each element that is used as the ‘Limit I’ value in this report. In some instances, calculated background concentrations equal or exceed the values quoted in MO1146/2002 for ‘Limit II’. Where this has occurred, the background ‘Limit I’ value has been discarded in favour of the ‘Limit II’ value.

2.2.2 River Sediments

Unlike for water, a common approach to identifying contamination in soils and sediments (Visser, 1995) has not been established across Europe. A number of countries (e.g. United Kingdom) have integrated soil/sediment protection and contamination prevention legislation with laws regarding environmental clean-up, however, Romania has so far not developed such legislation, and EU directives (86/278/EEC) presently apply only to the application of contaminated substances (e.g. sewage sludges) to sites that are believed to be uncontaminated.
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. The Dutch guidelines have, therefore, been used in this study on the basis that they are a long established, tried and tested scheme, where stringent target and intervention values are based on extensive studies of both human and eco-toxicological effects of contaminants (Table 8-9). In addition, a second set of sediment quality guideline values, supplied by Roșia Montana Gold Corporation, have been used; these relate to the physical-chemical composition of sediments (Table 8-9).

2.3 The Geochemical Database

The geochemical database is stored on a CD accompanying this report and is provided in a number of different formats:

1. As an Excel spreadsheet, formatted according to a template provided by Agraro Consult SRL, Bucharest. This spreadsheet contains river water data collected by RMGC (November 2002 – November 2003) and river water and river sediment data collected by fluvio (July 2002, July 2003 and March 2004). In keeping with the template provided by Agraro, fluvio’s geochemical data are only shown for As, Cd, Cu, Ni, Pb, Zn, Cr, Hg and Mo.

   (CD: Rosia Montana\Geochemical database\RMGC and fluvio geochemical database.xls)

2. As an Excel spreadsheet containing fluvio’s water and sediment geochemical data (July 2002, July 2003 and March 2004) for all elements analysed on the ICP-MS (Table 8-10).

   (CD: Rosia Montana\Geochemical database\fluvio all element geochemical database.xls)

3. As a suite of ESRI ARC shapefiles (*.shp) that can be imported into MAPINFO (using the ‘Universal Translator’ utility in MAPINFO), or that can be imported into ARCVIEW. There are 9 shapefiles in total, each containing fluvio geochemical data (Agraro format) for one sample type in one sample year (Table 8-11). NB All shapefiles are projected in UTM/WGS84.

   (CD: Rosia Montana\GIS database\fluvio2002/3/4\*.shp)

4. As an ARCMAP project (Rosia Montana.mxd) which integrates all the shapefiles (Table 8-11) into a single GIS layout. Each shapefile has been converted into a number of layer files (*.lyr) with each layer file representing the symbology (proportional circles) for a given geochemical parameter (e.g. Cd concentration). Figures 9.6-9.8, 9.10-9.12, and 9.14-9.15 show hardcopy outputs of the shape/layer files; the geochemical patterns they show are discussed in section 3 of this report.

   (CD: \GIS database\Rosia Montana.mxd)
3 Objective 2: Identification of the Geochemical Footprint

Identification of the geochemical footprint associated with past and present mining activity in the Abrud/Arieş catchment

Identification of the geochemical footprint associated with mining activity in the Abrud/Arieş catchment has been investigated using three approaches. First, spatial and temporal patterns of water and sediment quality, as shown by fluvio’s geochemical database, are discussed and interpreted. Second, a composite sediment fingerprinting technique/sediment mixing model is employed to statistically determine the downstream extent of sediment-associated contamination arising from mining operations at Roşia Montana. Finally, Pb isotope ratios in river channel, catchment and mine waste samples are determined to evaluate their potential role in ‘fingerprinting’ specific sources of contamination within the Abrud/Arieş catchment.

3.1 Contamination Patterns in River Water and River Sediment

An initial assessment of the geochemical footprint associated with mining activity in the Abrud/Arieş catchment has been made by investigating spatial and temporal patterns in water and sediment quality recorded in fluvio’s geochemical database. Initially, spatial patterns are described in detail for the July 2002 data and then comparisons made with the July 2003 and March 2004 data. Section 2.2 of this report discussed the various environmental guidelines available for assessing water and sediment quality; in the absence of a unified set of values, and to aid clarity in the discussion, all water quality data are compared with EU (75/440/EEC) target and imperative values (Table 8-5), and all sediment quality data are compared with Dutch target and intervention values (Table 8-9).

3.1.1 River Water

July 2002 As, Cd, Cu, Pb, and Zn concentrations in river waters, and pH, are plotted in the form of proportional circles on a series of drainage network maps (Figure 9.6a-f); higher concentrations are shown by the larger circles. To evaluate if metal concentrations in river water exceed levels considered to be safe, proportional circles have been colour coded to show where values fall above, or below target or imperative metal concentrations required for the abstraction of drinking water (75/440/EEC). Red denotes where metal concentrations exceed imperative levels (As 10 µg/l; Cd 5 µg/l; Cu 50 µg/l; Pb 50 µg/l; Zn 3,000 µg/l), orange denotes where metal concentrations exceed target values (As 5 µg/l; Cd; 1 µg/l; Cu 20 µg/l; Zn 500 µg/l), and green denotes where metal values comply with the EC water quality directive (Table 8-5).

With the exception of Pb and As, metal concentrations in the River Abrud are highest immediately downstream of the EM Bucium mine (Figure 9.6), with Cd, Cu and Zn exceeding EU imperative values by 7.6, 58 and 1.8 times, respectively. Solute metal concentrations decline with distance downstream, however, some tributary streams act as point sources of metal contaminants. Cd and Cu concentrations are elevated above imperative values downstream of the Rivers Izbiţa, Abrudului and Roşia, whilst Zn exceeds the target value downstream of the Rivers Izbiţa and Roşia. The Valea Saliste and the Valea Corna (which is not currently subjected to metal mining activity but would be dammed for waste disposal in the event of exploitation at Roşia Montana) are not significantly enriched in metals and do not cause a degradation in water quality. Although As concentrations exceed target and imperative values in the Saliste and Roşia rivers, respectively, As levels remain below target levels in the Abrud downstream of both river confluences.
In the River Arieş, despite having generally higher solute metal concentrations in its mining affected tributary streams, As, Cd, Pb, Zn concentrations all comply with EU directive 75/440/EEC. Cu concentrations fall below target levels at 81% of sites, but exceed target levels at sites up to 16 km downstream of the Arieş’ confluence with the Valea Sartaş, which contains the Sartaşului tailings pond. Whilst increases in solute metal concentration are generally evident downstream of tributary streams and the town of Baia de Arieş, the river water environment of the River Arieş, unlike that of its principal tributary the Abrud, is generally not as polluted by mining activity. Four factors are believed to account for this. First, unlike the River Abrud, there is no direct hydrological coupling between mine sites and the Arieş river channel. Second, a large number of unmined tributary streams within the Arieş basin deliver uncontaminated water to the river and dilute contaminants from active mine sites. Third, the high natural buffering capacity of the local, limestone rich, bedrock, creates a high pH in the River Arieş system (7.3 – 8.7), promoting dissolution of solute metals. Finally, a number of the ore deposits within the Arieş system, such as Baia de Arieş and Iara, have been shown to contain appreciable amounts of carbonate gangue (Udubasa et al., 1992; Dallmeyer et al., 1999), limiting widespread production of metal-rich AMD.

Figures 9.7 and 9.8 show river water As, Cd, Cu, Pb, and Zn concentrations, along with pH, in July 2003 and March 2004, respectively. In addition, for the main channel of the Abrud and Arieş rivers, As and metal concentrations are plotted on a downstream basis with imperative and target values shown by red and green horizontal lines, respectively (Figure 9.9). Although the overall pattern of water quality remained generally stable over the three sampling periods, two points are worthy of note. First, solute metal and As concentrations were generally lower in March 2004 than in either of the two summer sampling periods; it is likely that high river flows generated by rainfall and snowmelt led to solute dilution (Figure 9.9). Second, in all three years solute metal and As concentrations generally increase downstream in the River Roşia. This increase in element levels is almost certainly being caused by a combination of direct inputs to the River Roşia of metal and As rich sediment from spoil tips on the south side of the Valea Roşia, and acidic river water (c. 2.5 to 3.0) bringing the metals into solution. Although As is generally regarded as being more soluble in alkaline rather than acidic water, recent experimental studies by Sanchez et al. (2004) have shown that solubility can also increase at pH values less than 5.

In summary, the EM Bucium mine grossly pollutes the River Abrud but within 2.5 km downstream metal concentrations decline by 98.9%. In both the upper 15 km and lower 5.5 km of the River Abrud, mining-affected tributaries (e.g. Roşia) cause a local reduction in aqueous pH and elevation in solute metal concentrations. Although Cd, Cu, Zn and As concentrations exceed EU imperative values in the River Roşia, concentrations generally fall below target values after the confluence of the Abrud with the Arieş.

3.1.2 River Sediment

As, Cd, Cu, Pb, and Zn concentrations in river sediment are plotted in the form of proportional circles on a series of drainage network maps (Figure 9.10 a-e); higher concentrations are shown by the larger circles. To evaluate if metal concentrations in river sediment exceed levels considered to be safe, proportional circles have been colour coded to show where values fall above, or below Dutch target or intervention metal values. Red denotes where metal concentrations exceed intervention levels (As 55 mg/kg; Cd 12 mg/kg; Cu 190 mg/kg; Pb 530 mg/kg; Zn 720 mg/kg), orange denotes where metal concentrations exceed target values (As 29 mg/kg; Cd 0.8 mg/kg; Cu 36 mg/kg; Pb 85 mg/kg; Zn 140 mg/kg) and green denotes where metal values comply with Dutch target values (Table 8-9).

In the River Abrud, peak Cd, Cu, and Zn concentrations in river sediment (similar to metal levels in river waters) occur downstream of the EM Bucium mine, however, peaks are not found at the mine site itself but occur between 2 km (Cu, Zn) and 5 km (Cd) downstream. Downstream of the River Izbija, peak sediment-metal concentrations occur further downstream than peak solute metal levels. It is possible that this reflects changes in the
state-partitioning of metals between solute and sediment-bound forms in response to changes in pH. Cd, Cu and Zn concentrations exhibit marked reductions (mean = 98%) in the vicinity of the Izbiţa confluence probably as a result of physical dilution by relatively clean sediments. Cu concentrations exceed the Dutch intervention value at 77% of sample sites as opposed to 15 and 38% for Cd and Zn, respectively, with Pb levels falling below the intervention value at all sites. Cu contamination of river sediments is more widespread than for other heavy metals, and may be explained by the Cu-rich mineralogy of local bedrock associated with the local Roşia Poieni ore deposit. This is supported by the fact that concentrations of Cu and Zn in the presently un-mined Valea Corna, which drains the Roşia Poieni and Roşia Montana ore deposits, exceed intervention and target values, respectively.

In a pattern similar to river waters, As concentrations exceed intervention values in the Valea Roşia, in the Salişte (where tailings from Roşia Montana are stored), and in the Abrud immediately downstream of the Roşia confluence. Geochemical analysis of samples taken from open cast pits at Roşia Montana, spoil tips on the south side of the Valea Roşia, and the Roşia Montana tailings ponds located in the Salişte valley and at Gura Rosiei, show that they all contain As concentrations that exceed Dutch target values, and 13 out of the 15 samples exceeded Dutch intervention values. It is likely, therefore, that elevated As levels in river sediments in the River Roşia and Abrud are being sourced from the Roşia Montana mine site and waste storage facilities.

In July 2002 there was widespread Cu pollution in River Arieş channel sediments with 67% of sites exceeding the Dutch imperative value. Cd and Zn concentrations both exceeded Dutch target values at 93% of sites and Pb exceeded the target value at 40% of sites. Metal concentrations in tributary streams of the River Arieş, downstream of the Abrud confluence, vary considerably. In the Rivers Sesei and Iara all metal concentrations fall below target values with the exception of Cu. The Valeas Muşcanilor and Sartăş are more polluted, with all metal concentrations (except Pb in the Muşcanilor) exceeding target values and Cu in the Muşcanilor exceeding the imperative value. The downstream extent of sediment-bound metal dispersal is considerable and even at river km 140 (just upstream of Arieş/Mureş confluence) Cu concentrations exceed imperative intervention values and Cd and Zn levels exceed target values despite being 48 km downstream of the nearest mined tributary.

Figures 9.11 and 9.12 show concentrations of As, Cd, Cu, Pb, and Zn in river sediment in July 2003 and March 2004. In addition, for the main channel of the Abrud and Arieş rivers, As and metal concentrations are plotted on a downstream basis with intervention and target values shown by red and green horizontal lines, respectively (Figure 9.13). Although the overall pattern of river sediment quality remained generally stable over the three sampling periods, two points are worthy of note. First, levels of Cu in the Abrud and Arieş (down to Turda) remain consistently above target, and generally above intervention, values in all three years (Figure 9.13). However, in March 2004 Cu concentrations in the Abrud generally only exceeded target values, whereas in the Arieş they exceeded intervention values downstream to Moldovenesti (10 km upstream of Turda). This suggests that during the floods of March 2004, not only was Cu-rich sediment being supplied from the Muscanilor and Sesei tributaries, but that Cu concentrations were not significantly diluted by uncontaminated sediment sourced from un-mined tributary catchments. Second, in July 2002 Zn concentrations were highest in the Abrud and generally exceeded the intervention value (Figure 9.10e), but in July 2003 and March 2004, by contrast, Zn concentrations were highest in the Arieş, especially downstream of Baia de Arieş. This changing pattern of Zn in river sediment may reflect changes in the location of sediment-associated Zn within the catchment, or it may be a function of chemical interactions between river water and river sediment leading to Zn in solution adsorbing onto river sediment.
3.1.3 Catchment and Mine Waste

In order to provide an indication of naturally occurring (background) metal concentrations in soils and sediments in the Abrud catchment, 16 samples of catchment material from actively eroding slopes and road cuttings were collected (Figure 9.4). Figure 9.14 plots metal and As concentrations as proportional circles; the circles have been colour-coded to show where metal concentrations fall above, or below, Dutch target or intervention metal values. Red denotes where metal concentrations exceed intervention levels (As 55 mg/kg; Cd 12 mg/kg; Cu 190 mg/kg; Pb 530 mg/kg; Zn 720 mg/kg), orange denotes where metal concentrations exceed target values (As 29 mg/kg; Cd 0.8 mg/kg; Cu 36 mg/kg; Pb 85 mg/kg; Zn 140 mg/kg) and green denotes where metal values comply with Dutch target values (Table 8-9).

Cadmium and Zn concentrations fall below Dutch target values in all samples, with mean concentrations in the Roșia catchment being 0.1 and 35 mg kg⁻¹, respectively (Table 8-12). Pb concentrations only exceed the 85 mg kg⁻¹ target value at one site, situated on the southern side of the catchment. Arsenic levels in the Roșia catchment also fall below target values at all but one site, with the one exceptional value (100 mg kg⁻¹) exceeding the Dutch intervention value. In addition to the lower Roșia, As levels in two samples from the Corna catchment exceed target and intervention values.

Copper concentrations, by contrast, exceed target values at a number of sites, not only in the Roșia catchment, but in the Abrud catchment as a whole. The peak concentration in the Roșia catchment is 69 mg kg⁻¹, with a mean of 40 mg kg⁻¹ that exceeds Dutch target values. It is apparent that the relatively high Cu concentrations in the Abrud catchment, including river sediments, reflect the general importance of Cu in the mineralogy of the region.

Given that stores of mine spoil and tailings comprise potentially significant sources of sediment to local river channels, it is also important to evaluate metal levels in mine waste. Figure 9.15 plots metal and As concentrations as proportional circles; the circles have been colour-coded to show where metal concentrations fall above, or below, Dutch target or intervention metal values. Red denotes where metal concentrations exceed intervention levels (As 55 mg/kg; Cd 12 mg/kg; Cu 190 mg/kg; Pb 530 mg/kg; Zn 720 mg/kg), orange denotes where metal concentrations exceed target values (As 29 mg/kg; Cd 0.8 mg/kg; Cu 36 mg/kg; Pb 85 mg/kg; Zn 140 mg/kg) and green denotes where metal values comply with Dutch target values (Table 8-9).

Cadmium concentrations fall below target values in all samples, with the exception of 3 sites. First, mine spoil (2 sites) on the south side of the Roșia river valley contains up to 6 mg kg⁻¹, whilst mine spoil on a tributary of the upper Bucium contains 0.9 mg kg⁻¹ Cd. Zn concentrations in mine waste also fall below target values in the majority of samples, exceeding target values at only one site (470 mg kg⁻¹), a site where Cd levels are also at their highest. The percentage of Cu concentrations exceeding target values in mine waste (36%) is lower than in background/catchment samples (58%); peak Cu concentrations in mine waste in the Roșia catchment (200 mg kg⁻¹) occur in spoil located in the headwaters of the catchment above Taul Mare lake. Pb concentrations in mine waste exceed target values in 31 % of samples, including tailings in the Izbita valley, spoil in the upper Bucium catchment and material in the Gura Rosiei tailings pond. Peak Pb concentrations (500 mg kg⁻¹) occur in spoil on the south side of the Roșia valley that also contains the highest Cd and Zn levels.

Arsenic is the element that shows the most widespread elevation above target and intervention values, with only 23 % of samples containing concentrations less than Dutch target values. Of the 6 samples falling below target values, four were collected from the River Izbita and upper Bucium and the remaining two from spoil above Taul Mare. Peak As concentrations (240 mg kg⁻¹), which exceed the intervention value, occur in spoil from the north bank of the Upper Roșia, however, elevated levels (up to 220 mg kg⁻¹) also occur in spoil present in the Corna catchment, this spoil is believed to be sourced from the Cirnic open cast pit.
Figure 9.16 compares Cd, Cu Pb and Zn concentrations in mine waste stored in the Abrud catchment with mine waste stored in other Romanian river catchments (Certej, near Deva, and in Maramureș County), and in other European countries (Bulgaria, Spain and the UK). The graph shows that metal levels in mine waste, particularly mean concentrations, in the Abrud catchment are generally lower than in other parts of Romania, and are significantly lower than levels found elsewhere in Europe. Lower metal levels in Abrud mine waste may be a function of bedrock geology or may reflect more efficient metal extraction procedures, however, it should be remembered that As levels exceed Dutch intervention values in the majority of mine waste samples taken from the Valea Roșia.

### 3.1.4 Speciation of Sediment-Associated Metals

Particulate-bound metals present in the fluvial system are distributed among different physico-chemical phases (Lopez-Sanchez et al., 1993). It is widely reported that the partitioning of metals between phases, or metal speciation, is of critical importance to the potential toxicity and mobility of contaminant metals released into the fluvial environment through either natural or anthropogenic processes (Förstner et al., 1981). Given the importance of metal speciation, it has been widely argued that the nature of metal partitioning in the sedimentary environment may be of more importance than the total concentrations of heavy metals (Ma and Rao, 1997). Indeed, Mester et al. (1998) argued that determining the total content of heavy metals is insufficient to assess the potential environmental impact of contaminated sediments. This is because only a small proportion of the metal present may take part in short-term geochemical processes and(or) be bio-available.

Metal speciation is usually determined using a sequential extraction procedure (SEP), whereby a sediment sample is subjected to a series of increasingly strong, phase-specific reagents under controlled conditions (Nirel and Morel, 1990), giving metal concentrations in a number of operationally-defined physico-chemical phases. In this report, the Community Bureau of Reference (BCR) procedure (Quevaullier et al., 1993) has been followed for the SEP. Sequential extraction procedures provide an insight into the chemical associations of metals with specific sedimentary phases whereby the bio-availability, environmental mobility and environmental significance of metals may be estimated (Dawson and Macklin, 1998).

The chemical partitioning of Cd, Cu, Pb and Zn in July 2002 river sediment between the exchangeable (≡ bio-available), Fe/Mn oxides, sulphide/organic matter and residual phases determined by the SEP in the Rivers Abrud and Arieș (and tributary streams) is plotted on a downstream basis in Figure 9.17 (for sample site locations see Figure 9.1). Cd is largely associated with the exchangeable phase (50-70%), especially in the upper Abrud and in the Arieș (except between sites AR6 and AR9). The pattern for Zn is similar, but the percentage partitioning in the exchangeable phase is generally lower (20-60%). Pb in both the Rivers Abrud and Arieș is largely associated with the Fe/Mn oxide and residual phases. Metals associated with the residual phase are generally incorporated into the lattice structure of resistant minerals and are likely to be generally unavailable for chemical or biochemical interaction within the aquatic environment.

Statistically significant correlations exist in the River Abrud between the percentage partitioning of the exchangeable phase and summed total metal concentrations in river sediments (Table 8-13). Exchangeable Cu, Pb and Zn correlations are significant at the 99 % confidence level, whilst that for Cd is significant at 95 %. This indicates that in the River Abrud, the proportion of metal in the exchangeable phase is related to the total metal concentration, which in turn has been shown in this study to be related to metal mining activity. By contrast, in the River Arieș (with the exception of Cu) the relationship between total metal concentrations and metal levels in the exchangeable form is not statistically significant. This indicates that in the River Arieș, where mine-river coupling is more restricted, metal speciation patterns may reflect background geochemical conditions more closely than in the River Abrud.
3.1.4.1 Environmental significance of sediment-bound metals

It is increasingly being recognized that total concentrations alone are not sufficient for assessing the environmental significance of heavy metals in river systems (Bird et al., 2003). In this report an SEP has been used to evaluate metal speciation with the most environmentally significant metals; that is, those associated with the exchangeable phase. Cd, Cu and Zn concentrations in the exchangeable phase are plotted using environmental quality guidelines in the form of coded circles identifying sites in the Arieş system where metal concentrations in the exchangeable phase fall above or below target, or exceed intervention values (Figure 9.18). Exchangeable Pb concentrations at all sites fall below target values and are not shown.

In the Rivers Abrud and Arieş, Cd concentrations in the exchangeable phase exceed target and intervention values at 19 and 2 sites, respectively. The two sites where exchangeable phase concentrations exceed imperative values are AB4 and AB5 in the River Abrud, immediately downstream of the Bucium mine. This also occurs with Cu (sites AB3, AB4 and AB5) and Zn (sites AB4 and AB5). These sites can be identified as ‘exchangeable metal hotspots’ (Bird et al., 2003) and with high metal concentrations in the acetic acid-soluble phase, are locations of particular environmental concern.

With respect to Cd and Zn, no other sites in the Rivers Abrud and Arieş have exchangeable metal concentrations in river sediments that exceed Dutch intervention values, although 19 and 45 % of sites exceed target values for Cd and Zn, respectively. However, exchangeable Cu concentrations fall above the intervention value at a further four sites in the Rivers Abrud and Arieş. Exchangeable hotspots for Cu occur in the lower Arieş at sites AR7 and AR2, more than 60 km downstream of the nearest mine.

Cadmium, and to a lesser extent Zn, offer the greatest potential for chemical remobilization via re-solution given the tendency of both metals to associate strongly with the exchangeable phase of the sediment. In the River Arieş, this may be mitigated by the relatively high river water pH, but, in the upper Abrud, where pH is lower due to the direct effect of metal mining, the potential for remobilization may be greater.

3.1.5 Summary

In summary, Cd, Cu and Zn contamination in river water is most serious immediately downstream of the EM Bucium mine in the Abrud catchment. Arsenic concentrations are generally highest in the waters, river and spoil sediments of the River Roşia, and there are elevated levels of solute Cu in much of the River Arieş. To assess the overall impact of As and metal contamination in river water and river sediment, all fluvio samples taken in July 2002, July 2003 and March 2004 have been compared with the three sets of water quality values and the two sets of sediment quality values presented in section 2.2 of this report (Tables 8-14 and 8-15).

The percentage of river water and river sediment samples complying with, or exceeding, the quality guidelines values has remained remarkably stable over the three sampling periods, suggesting that a dynamic equilibrium may exist between the physical and chemical processes controlling the rates of contaminant sediment supply and dispersal in the fluvial system. However, sites designated as exchangeable ‘hotspots’ by the SEP method should be monitored closely as they pose the greatest potential risk to human and ecosystem health.
3.2 Composite Sediment Fingerprinting and Sediment Mixing Model

Figures 9.6 to 9.15 are an effective means of showing spatial and temporal variations in river sediment and river water quality in the Abrud/Arieş river system, and provide clear indications of where the principal contaminant sources are located in the catchment. However, metal concentrations at a particular site give little, or no, indication of the original source or provenance of the contaminants. Therefore, techniques have been developed which enable sediment to be 'fingerprinted' permitting sources of contamination and to be distinguished and mapped on a downstream basis. In this report a sediment fingerprinting technique and a multivariate mixing model have been used in combination to statistically determine the geochemical footprint of mining activity at Roşia Montana. Prior to running the fingerprinting and sediment mixing models, discrete sediment source groups were identified which represent the principal sources of sediment in the Abrud/Arieş catchment.

Eight sediment source groups were identified based on bedrock geology, mining activity and geographical location (Figure 9.19). First, the Bucium group contains river sediment samples from the Abrud upstream of the Valea Roşia and represents a mix of contaminated and uncontaminated sediments from mining-affected (Izbita, Abrudzel, Corna and Salişte) and unmined (Cerbul and Cernit) tributaries, respectively. Second, the Roşia group contains river sediment samples from the Valea Roşia and represents material from present mining activity at Roşia Montana. Third, the Upper Arieş group contains river sediment samples from the Arieş upstream of the Abrud confluence and represents the first major sediment source downstream of the Valea Roşia. Fourth, the Stefanca, Musca, Sesei and Iara source groups contain river sediment samples from mining affected tributaries of the Arieş and represent point contamination sources downstream of Valea Roşia. Finally, the 'uncharacterised' source group represents sediment supplied from catchments in the middle and lower Arieş valley whose geochemistry has not been determined.

3.2.1 Composite Fingerprinting Technique

The fingerprinting approach is relatively simple in principle (Rowan et al., 2000), and is founded on the assumption that one or more properties of transported sediment is reflected in the sources involved (Collins et al., 1997b). Two basic steps underpin the application of sediment fingerprinting: first, selection of diagnostic physical and chemical properties that are capable of discriminating potential sediment source groups in an unequivocal manner, and second, comparison of the fingerprint properties obtained for downstream sediment samples with those for source group materials (Oldfield et al., 1979; Walling and Woodward, 1992; Collins et al., 1997a). The fingerprinting procedure employs a two-step statistical selection procedure to create a composite fingerprint, containing the fewest number of diagnostic parameters capable of discriminating between different source materials.

Step 1: significant difference analysis

In the first stage of the procedure a non-parametric significant difference analysis (Kruskal-Wallis H-Test) was used in order to establish which of the geochemical parameters in the all element geochemical database displayed significant difference between each source group. A null hypothesis was adopted stating that any difference between the mean rank of each group was due to chance; each successful geochemical parameter was then entered into a multivariate discriminant function analysis.
Step 2: Multivariate discriminant function analysis (MDA)

The second stage of the fingerprinting procedure identifies the fewest number of diagnostic parameters that are able to distinguish between source groups. The procedure adopts a MDA using the minimisation of Wilks’ lambda ($\Lambda$):

$$\Lambda = \frac{\sum (X_{Di} - X_{DG})^2}{\sum (X_{Di} - X_{DT})^2}$$   (equation 1)

Where $X_{Di}$ is the score for observation $i$ on the discriminant function $D$, $X_{DG}$ is the mean score on discriminant function $D$ for the observations in the group of which $i$ is a member, and $X_{DT}$ is the mean score on discriminant function $D$ for all observations (Johnston, 1978).

The procedure constructs a predictive model of group membership based upon the observed characteristics of each group. Diagnostic geochemical parameters were removed from the analysis leaving the optimum number required to provide a fingerprint of the source material. Both step 1 and step 2 of the composite fingerprinting procedure were carried out using the SPSS 12.0 statistical software package.

### 3.2.2 Multivariate Mixing Model

Whilst sediment provenance was determined using the composite fingerprinting technique, a multivariate mixing model (cf Walling et al., 1999) was employed in order to determine the relative contribution of each sediment source group to samples of trunk stream sediment. In the model, performed using the Solver optimisation tool present within Microsoft Excel 2003™, a set of linear equations is produced that ascribes (i.e. un-mixes) the concentrations of each fingerprint parameter in the river sediment sample to the combined contributions of the potential source groups. A linear equation is generated for each property in the fingerprint and, using the least squares method, the proportion of material derived from each source group is established by minimising the sum of the squares of the residuals (equation 2) for all diagnostic properties included in the model:

$$R_{es} = \sum_{i=1}^{s} \left( \frac{C_{gi} - (C_{si}P_s)}{C_{gi}} \right)^2 W_i$$   (equation 2)

Where $R_{es}$ is the sum of the squares of the residuals, $C_{gi}$ is the concentration of diagnostic property $i$ in the fluvial sediment sample, $C_{si}$ is the mean concentration of tracer property $i$ in source group $s$, and $P_s$ is the relative proportion from source groups (Walling et al., 1999).

### 3.2.3 Results

The multivariate mixing model was applied to samples in the River Abrud, downstream of the River Roșia confluence, and in the River Arieș, downstream of the Abrud confluence (Figure 9.19). At each sample site, the relative contribution (%) of sediment from each defined source groups in the Abrud/Arieș catchment was calculated and is shown on a downstream basis in Figure 9.20. Not all potential source groups in the Arieș were geochemically characterised, especially downstream of the Sesei (Figures 9.19 and 9.20). To account for this, the percentage contribution of the uncharacterised source groups was estimated as being proportional to their respective catchment areas. Although this is not an unreasonable
assumption to make, it does introduce an artefact into the modelling procedure which is discussed below.

The multivariate mixing model suggests that 300 m downstream of the Abrud/Roşia confluence (Figure 9.20; GF64), up to 44 % of river sediment is sourced from the Roşia catchment; this reduces to 42 % a further 3 km downstream of the confluence (Figure 9.20; GF87). At the first sample site in the River Arieş (Figure 9.20; GF88), the percentage contribution of sediment from the River Roşia is diluted by sediment inputs from the upper Arieş catchment; the upper Arieş is estimated to contribute over 30 % of sediment present at the Abrud/Arieş confluence. Downstream of the Abrud/Arieş confluence, the relative proportion of River Roşia sediment steadily declines to 27% at site GF90, and then reduces to 21% downstream of the Arieş/Stefanca confluence (GF91). Downstream of the Arieş/Muscaniilor confluence (site GF92) a maximum of 8 % of the sediment is estimated to come from the River Roşia, indicating substantial dilution by sediment sourced from elsewhere within the catchment.

Downstream of the River Sesei (GF69-GF102) the predicted contribution of the River Roşia sediment to the Arieş sediment remains relatively stable (8.6 - 12.5%). This is due to the fact that, downstream of the Sesei, no other tributary systems have been geochemically characterised. Although catchment area has been used as a surrogate for sediment supply for these potential source groups, and the mixing model has been scaled accordingly (Figure 9.20), the uncharacterised source groups have clearly introduced an artefact into the mixing model. Further sampling and geochemical characterisation of potential source groups in the River Arieş would almost certainly result in a more marked reduction in the predicted contribution of the Roşia catchment.

Figure 9.21 plots the percentage contribution of River Roşia sediment, along with error bars, for the 17 sample sites used in the mixing model analysis. A sharp decline in the relative proportion of River Roşia sediment over the first six sites is clearly evident (these sites are unaffected by the mixing model artefact discussed above), and a regression line plotted through these points yields a statistically significant (P = 0.05) correlation coefficient ($r^2 = 0.94$). The gradient of the line generated by the regression equation suggests that, at the modelled rate of reduction, the percentage contribution of the Roşia catchment would fall to below 1% at a point 28 km downstream of the Roşia/Abrud confluence; that is at Baia de Arieş. By determining regression line gradients for the error bar minima and maxima as well (Figure 9.21), it is possible to estimate the reach on the Arieş where the proportion of River Roşia sediment falls to below 1%. Using this error bar approach indicates that geochemical footprint of River Roşia sediments in March 2004, extended between 24 km and 30 km downstream of the Roşia/Abrud confluence; that is between Valea Lupsei and Brazeşti.

It should be stressed that the significant difference analysis and the multivariate mixing model are only statistical procedures and are subject to errors (Figure 9.21). However, these techniques have defined a geochemical footprint for Roşia Montana that is logical in terms of sediment supply dynamics. Downstream of the Abrud/Arieş confluence, sediment sourced from Roşia Montana will be physically diluted by contaminated and uncontaminated sediment inputs from tributary catchments. The calculated Roşia Montana geochemical footprint extends to a reach which lies between Valea Lupsei and Brazeşti, and in this reach there are further significant sources of both contaminated (Sesei and Baia de Arieş) and uncontaminated sediment from geochemically uncharacterised tributaries which will dilute the Roşia Montana geochemical signal to an undetectable level.

The Roşia Montana geochemical footprint has only been determined using the March 2004 geochemical data; further sampling and analysis would be required to ascertain if the footprint is stable, or if its downstream extent varies on a seasonal basis, for example. We strongly recommend that additional geochemical footprint determinations are undertaken, before, during and after exploitation of the Roşia Montana gold reserve, so that downstream dispersal of contamination from Roşia Montana can be monitored, and waste control measures adjusted if necessary.
3.3 Pb Isotope Analysis

Recent research has demonstrated that metal isotopes (particularly those for Pb) can be used to ‘fingerprint’ sources of contamination and to distinguish contamination arising from human activity (e.g., mining) from naturally occurring sources (Hudson Edwards et al., 1999; Miller et al., 2002). This is possible because the isotopic composition of Pb varies between separate ore deposits, and also differs between mineralised and unmineralised areas.

Isotope analysis, coupled with the composite sediment fingerprinting and sediment mixing models outlined above, provides further potential for accurately identifying and characterising point contaminant sources, and tracking their downstream dispersal.

Mean isotope ratios for $^{208/206}\text{Pb}$, $^{207/206}\text{Pb}$ and $^{208/207}\text{Pb}$ in river sediment and catchment material were calculated based upon the analysis of 15 repeat ICP-MS analyses. Ratios were calibrated using the ratio between $^{205/203}\text{Tl}$, which is known to be constant within the terrestrial environment.

3.3.1 Pb Isotope Ratios in Mine Material

Figure 9.22 plots bivariate Pb isotope ratios ($^{208/206}\text{Pb}$, $^{207/206}\text{Pb}$, $^{208/207}\text{Pb}$) for sediment samples taken from open cast pits (Cetate, Cîrnic, Napolean), mine spoil (Roşia Poieni, Izbita, Bucium, Roşia Montana) and tailings (Saliste, Izbita, Gura Rosiei) within the Abrud catchment. Three point clusters can be identified on all three bivariate isotope ratio plots. First, there appears to be a similarity in the isotopic signature of material in the Cetate open cast pit with mine tailings stored in the Gura Rosiei and Saliste tailings ponds; this is not surprising since these two tailings ponds store material originally mined from the Valea Roşia.

A second point cluster contains samples collected from a variety of locations within the Abrud catchment. Within this group, samples of material from the Cîrnic and Napolean pits exhibit a consistently similar isotopic signature, and interestingly can be clearly distinguished from material taken from the Cetate pit, even though the two sites are geographically very close. A consistent outlier to this second cluster is a sample of Roşia Poieni spoil collected from the headwater of the Abrudzel and Roşia river valleys; this is likely to reflect differing mineralisation (largely porphyry diorite) of the Roşia Poieni deposit compared to Roşia Montana.

Finally, whilst mining waste from Roşia Montana stored in the Saliste and Gura Rosiei tailings ponds has been shown to have similar isotopic signatures to actively mined ore in the Cetate deposit, mine spoil situated on the south bank of the Roşia river valley has a very different isotopic signature based upon bivariate isotope relationships (Figure 9.22). Given that it is unlikely that the difference in isotopic signature between Roşia Montana spoil and tailings is due to chemical changes that occurred during ore processing, it is possible that the spoil may have been sourced from an ore deposit that has not been sampled. It is interesting to note that spoil present in a tributary valley of the upper Bucium at Lupulesti, has a similar Pb isotope signature to that in the Roşia valley. Information regarding the original sources of this spoil is required to establish whether it was sourced from geologically similar areas within the catchment.

3.3.2 Pb Isotope Ratios in River Sediment

Given that tailings pond and spoil tips act as potentially important sources of sediment to local river channels, isotope ratios for Pb in river sediment samples, collected downstream of mine spoil and tailings ponds, are plotted in Figure 9.23. In general, no clear associations occur between isotope patterns in river sediment and those in mine waste or tailings, with a majority of points falling between the two largest isotope ratio clusters identified above (Figure 9.22). However, Pb isotope ratios in river sediment collected immediately
downstream of the Gura Rosiei (site GF54) and Salişte (site GF49) tailings ponds, respectively, closely match the signatures of tailings collected from the two ponds, suggesting in-wash of tailings into local river channels.

Whilst it is apparent that the isotopic signature of Roşia Montana-derived mine waste can be detected in the River Abrud immediately downstream of the Gura Rosiei and Salişte tailings ponds, the same clear association does not occur in the River Roşia itself. Instead, samples from the River Roşia generally lie between the two largest sample clusters, suggesting that the river sediments comprise a mixture of material from geologically different areas within the catchment.

Figure 9.24 plots Pb isotope ratios on a downstream basis for river sediment sampled from the Rivers Abrud and Arieş, and selected tributaries, between the River Roşia confluence and Buru. The data show that, given the errors bars associated with the isotope analyses, no consistent and clear differentiation exists between Pb isotope ratios in trunk and tributary streams, and there is no systematic downstream change in isotope ratios. Although the Pb isotope ratios determined in this report have not enhanced the determination of the Roşia Montana geochemical footprint, they have been able to distinguish between material from open cast pits and material from mine spoil in the Roşia Montana catchment.

Even given the patterns described above, we believe that there are two pieces of evidence to indicate that Pb isotope ratios are potentially an extremely powerful tool for characterising contamination sources and mapping their downstream transport pathways. First, the isotope ratios presented in this report were determined using UWA’s ICP-MS and have relatively high errors associated with them (Figure 9.24). However, UWA have recently invested in a new magnetic sector instrument which reduces isotope measurement errors by over an order of magnitude, thus permitting more statistically robust delineation of isotopic ratio clusters. Second, preliminary isotope ratio determinations for river sediment samples taken from the Vişeu River (Maramureş County), using UWA’s new magnetic sector instrument, not only show the significantly reduced isotope error bars, but also show that the Vişeu sediment has a significantly different isotopic signature. Given this evidence, we believe that detailed magnetic-sector based isotopic determinations not only have the potential of significantly enhancing determination of the Roşia Montana geochemical footprint, but will also enable whole basin (e.g. Tisa) sediment fingerprinting procedures to be undertaken. Information of this type will form a critical part of the ongoing environmental impact assessment in the lead-up to developing the Roşia Montana gold deposit.
4 Objective 3: Additional Sampling Sites

Identification of areas within the Abrud/Arieş catchment which may require additional environmental monitoring and collection of suspended sediment samples

The geochemical GIS database was analysed prior to the March 2004 sampling programme to identify geochemical hotspots and areas where incomplete or no geochemical data existed in the Abrud/Arieş catchment. As a result of this analysis, water and sediment samples were collected in March 2004 from i) sites common to both RMGC and fluvio sampling networks, ii) sites sampled by fluvio in July 2002 and July 2003, and iii) 51 new sites on the Rivers Izbita, Corna, Cerbul, Abrudzel, Cernit, Roşia, Abrud, Stefanca, Musca, Sesei and Arieş (Figure 9.3). Collection of geochemical data at these additional sites improved delineation of the Roşia Montana geochemical footprint (Objective 2), as well as considerably enhancing the baseline geochemical survey in the Abrud/Arieş catchment (Objective 1).

Between them, the RMGC and fluvio sampling networks provide comprehensive spatial coverage of the Abrud catchment, allowing contamination hotspots to be identified and monitored. Although sample sites are more widely spaced on the Arieş, it has still been possible to identify point contamination sources (e.g. tributaries, Baia de Arieş) and track patterns of downstream contaminant dispersal from them.

To ascertain if RMGC need to integrate additional sites within their sampling network, two geochemical hotspot maps have been produced (Figures 9.26 and 9.27). These maps show sites where EU imperative (water), and Dutch intervention (sediment) values, were exceeded for at least one element (As, Cd, Cu, Pb, Zn) in every sample taken from the site; these maps integrate data from both the RMGC and fluvio databases. It should be noted that these maps only show the most seriously, and persistently, contaminated sites; many sites were excluded from these maps because just one sample had an element concentration which fell below a particular imperative/intervention value. For river water (Figure 9.26), three hotspots were identified, all in the Abrud catchment: 1) in the headwaters of the Abrudzel (RMGC - SO21), 2) in the upper Corna valley (RMGC - SO32), and 3) in the River Roşia immediately upstream of the Abrud confluence (RMGC - SO10). For river sediment (Figure 9.27), five hotspots were identified, of which two fell in the Abrud catchment: 1) on the Bucium upstream of the Abrudzel confluence (fluvio - BU7), 2) on the Bucium downstream of the Abrudzel confluence (fluvio – BU8), 3) on the Arieş downstream of Salciua de Jos (fluvio – AR7), 4) on the Arieş at Ocolis (fluvio – AR6), and 5) on the Arieş upstream of the Iara confluence (AR5).

It is interesting to note that persistent and serious river water contamination only occurs in the Abrud catchment, and only one of these sites is in the Valea Roşia. Furthermore, persistent and serious sediment contamination is more widespread in the Arieş; the significant enrichment of sediment by contaminant metals and As, especially downstream of Baia de Arieş, suggests that the majority of the contamination must be sourced locally in the Arieş valley. However, it should be recognised that floodplain sediments can act as a significant store of contaminant metals, and it may be that river bank erosion in this part of the Arieş valley is remobilising this material. Detailed sampling of floodplain sediments would not only determine the potential threat that river bank erosion might pose to water and sediment quality, but would also establish the magnitude and provenance of historical floodplain contamination in the Abrud/Arieş catchment.
4.1 Additional Sampling Sites

In the light of the catchment contamination maps (Figures 9.6-9.8, 9.10-9.12), and the two hotspot maps (Figures 9.26 and 9.27), we recommend that RMGC integrate the following fluvio (March 2004) sites within their sampling network:

1. GF87 – on the Abrud between Gura Roşia and Cimpeni (site adjacent to a suspension footbridge). With the exception of RMGC site SO11, immediately downstream of the Roşia/Abrud confluence, this site provides the only opportunity to assess mixing between river water draining from Roşia Montana with river water from the upper Abrud.

2. GF88 – on the Arieş c. 1.5 km downstream of the Abrud confluence. This site provides the earliest opportunity to assess mixing between river water draining from the Abrud with river water draining from the upper Arieş catchment. Data from this site will complement data from RMGC site SO14 (GF90; fluvio March 2004) located upstream of the Stefanca tributary.

3. GF92, GF76, GF69, GF93, GF94, GF67, GF95 and GF96 – all on the Arieş. These sites encompass the area of the calculated Roşia Montana geochemical footprint, and as such should be routinely monitored as mining operations develop at Roşia Montana.

In addition to collecting water samples at these sites, we would recommend that RMGC also collect river sediment samples at these sites and all the other sites in their sampling network. This report has highlighted differences in water and sediment contamination patterns in the Abrud/Arieş catchment, and routine analysis of sediment samples from these sites (which fluvio can undertake) will provide the opportunity to update the Roşia Montana geochemical footprint as mining operations develop.

4.2 Suspended Sediment Samples

At present no information exists within the Roşia Montana area on levels of contaminant metals being transported in streams as suspended load, which, on the basis of studies elsewhere in mining-affected catchments, is likely to be quite large. To address this issue, all water samples collected in March 2004 by fluvio (n = 60) and by Analist Service SRL (n = 45) were filtered with the aim of geochemically analysing the sediment retained on the filter papers. Unfortunately, insufficient sediment was collected on any of the filter papers for reliable geochemical determinations. We recommend, however, that a further targeted suspended sediment programme is undertaken in the Abrud/Arieş catchment; this will not only help to quantify solute metal loadings, but will also provide data relating to the physical dilution of Roşia Montana sediment in the Abrud and Arieş rivers.
5 Summary and Conclusions

This report has addressed three objectives and provided the stipulated contract deliverables in terms of hard copy maps and electronic data files. A comprehensive river water and river sediment geochemical database has been developed (Objective 1) using RMGC (n = 272) and fluvio (n = 421) sample data; it accompanies this report in the form of Excel spreadsheets, database files (dbf IV) and ARC shapefiles. The geochemical footprint of Roşia Montana (Objective 2) was determined through a combination of i) catchment contamination maps, ii) composite sediment fingerprinting and sediment mixing models, and iii) Pb isotope analysis. By using these approaches it is estimated that the maximum downstream extent of the geochemical footprint associated with mining activity in the Roşia Montana catchment lies between 24 km and 30 km downstream of the Roşia/Abrud confluence; that is between Valea Lupsei and Brazeşti. Finally, additional sites have been identified on the Abrud and Arieş which RMGC should integrate within their existing sampling network (Objective 3). Water and sediment samples should be taken routinely at all river sites within the RMGC network so that contaminant dispersal patterns can be fully monitored, evaluated and modelled.

Throughout the course of the report, recommendations have been made with regards to improving the Roşia Montana geochemical database and enhancing the delineation of the geochemical footprint. In summary, these are:

- Determination of the geochemical properties of river sediment in the uncharacterised catchments of the Arieş valley. This will help reduce the statistical anomaly present in the existing sediment mixing model that was used to determine the Roşia Montana geochemical footprint.

- Sampling and analysis of floodplain bank sections / floodplain cores to establish the magnitude and pattern of contamination in the Abrud/Arieş catchment arising from historical metal mining.

- A targeted suspended sediment programme in the Abrud/Arieş catchment to quantify solute metal loadings and provide data relating to the physical dilution of Roşia Montana sediment in the Abrud and Arieş rivers.

- Regular monitoring of sites designated as exchangeable ‘hotspots’ by the SEP method, as these pose the greatest potential risk to human and ecosystem health.

- Undertake additional sampling of catchment material to enhance the statistical determination of background metal and As concentrations in the Abrud/Arieş catchment. This information will be of direct relevance to implementing the EU water framework directive and, furthermore, it will enable the magnitude of contamination to be more realistically compared between catchments with differing patterns of mineralisation and degrees of mining activity.

Fluvio have the field, analytical and modelling expertise, and firsthand experience, to undertake these tasks, which dovetail with monitoring currently being undertaken by RMGC in the Abrud/Arieş catchment.
6 References


7 Statement of Liability

Whilst the University will use all reasonable endeavours to ensure the accuracy of the work performed and any information given, the University makes no warranty, express or implied, as to accuracy and will not be held responsible for any consequence arising out of any inaccuracies or omissions unless such inaccuracies or omissions are the result of negligence on the part of the university or its agents.

The parties agree and declare that the obligations of the University and its agents shall cease upon delivery of the reports and that no liability whatsoever either direct or indirect shall rest upon them for the effects of any product, process or action that may be produced, adopted and/or taken by the Sponsor or any other party, notwithstanding that the formulation of such product, process or action may be based upon the findings of the Project.

Neither party shall be liable to the other for any death or injury unless it is caused by the negligence of that party or its agents, nor shall it be liable to the other for any other loss or damage whatsoever unless it is caused by its wilful default or that of its agents.
8 Tables

Table 8-1. Summary of river water and river sediment samples

<table>
<thead>
<tr>
<th>Sample type</th>
<th>July 2002</th>
<th>July 2002</th>
<th>March 2004</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>53</td>
<td>53</td>
<td>60</td>
<td>166</td>
</tr>
<tr>
<td>River sediment</td>
<td>49</td>
<td>53</td>
<td>104</td>
<td>206</td>
</tr>
<tr>
<td>Catchment</td>
<td>-</td>
<td>-</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>102</strong></td>
<td><strong>106</strong></td>
<td><strong>213</strong></td>
<td><strong>421</strong></td>
</tr>
</tbody>
</table>

Table 8-2. Maximum and minimum concentrations (µg l⁻¹) of selected metals in river water from the Rivers Roșia and Abrud.
Data adapted from Forray (2002).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Minimum concentration</th>
<th>Maximum concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>150</td>
<td>260,000</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>130</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>260</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>1,100</td>
</tr>
<tr>
<td>Fe</td>
<td>170</td>
<td>204,200</td>
</tr>
<tr>
<td>Mn</td>
<td>39</td>
<td>80,400</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>290</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>163</td>
</tr>
<tr>
<td>Zn</td>
<td>12</td>
<td>42,600</td>
</tr>
</tbody>
</table>

Table 8-3. Chemical composition of river water collected during winter from the River Arieş between Baia de Arieş and Cheia.
Data adapted from Forray and Hallbauer (2000).

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>EC</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Sr</th>
<th>Mn</th>
<th>Ba</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.5</td>
<td>486</td>
<td>73,000</td>
<td>8,600</td>
<td>15,600</td>
<td>4,500</td>
<td>164</td>
<td>207</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>323</td>
<td>47,000</td>
<td>6,300</td>
<td>7,400</td>
<td>3,200</td>
<td>147</td>
<td>216</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>7.4</td>
<td>328</td>
<td>49,000</td>
<td>7,100</td>
<td>7,300</td>
<td>1,000</td>
<td>147</td>
<td>229</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>7.4</td>
<td>343</td>
<td>46,000</td>
<td>6,200</td>
<td>7,000</td>
<td>2,500</td>
<td>148</td>
<td>251</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>7.1</td>
<td>348</td>
<td>49,000</td>
<td>6,900</td>
<td>8,200</td>
<td>1,500</td>
<td>148</td>
<td>274</td>
<td>-</td>
<td>175</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>7.1</td>
<td>332</td>
<td>47,000</td>
<td>7,200</td>
<td>6,100</td>
<td>1,600</td>
<td>148</td>
<td>279</td>
<td>-</td>
<td>172</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>7.4</td>
<td>333</td>
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<td>1,600</td>
<td>147</td>
<td>278</td>
<td>-</td>
<td>181</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>6.2</td>
<td>334</td>
<td>43,000</td>
<td>5,500</td>
<td>8,500</td>
<td>1,500</td>
<td>145</td>
<td>264</td>
<td>-</td>
<td>196</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>6.0</td>
<td>361</td>
<td>44,000</td>
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<td>7,300</td>
<td>1,800</td>
<td>149</td>
<td>261</td>
<td>-</td>
<td>236</td>
<td>227</td>
</tr>
<tr>
<td>16</td>
<td>5.8</td>
<td>393</td>
<td>45,000</td>
<td>7,400</td>
<td>7,300</td>
<td>2,700</td>
<td>147</td>
<td>272</td>
<td>174</td>
<td>235</td>
<td>319</td>
</tr>
<tr>
<td>18</td>
<td>5.8</td>
<td>417</td>
<td>46,000</td>
<td>6,600</td>
<td>7,200</td>
<td>2,700</td>
<td>145</td>
<td>280</td>
<td>190</td>
<td>213</td>
<td>340</td>
</tr>
<tr>
<td>19</td>
<td>5.5</td>
<td>420</td>
<td>43,000</td>
<td>6,600</td>
<td>4,400</td>
<td>3,000</td>
<td>146</td>
<td>284</td>
<td>-</td>
<td>237</td>
<td>350</td>
</tr>
<tr>
<td>20</td>
<td>5.3</td>
<td>426</td>
<td>40,000</td>
<td>7,000</td>
<td>4,000</td>
<td>1,800</td>
<td>147</td>
<td>1,000</td>
<td>-</td>
<td>256</td>
<td>406</td>
</tr>
<tr>
<td>21</td>
<td>5.3</td>
<td>431</td>
<td>42,000</td>
<td>7,200</td>
<td>4,300</td>
<td>2,300</td>
<td>142</td>
<td>2,000</td>
<td>-</td>
<td>236</td>
<td>324</td>
</tr>
</tbody>
</table>

Section 8: Tables
Table 8-4. Sample sites common to both the RMGC and fluvio sampling programmes, listing site identification numbers and geographic locations.

<table>
<thead>
<tr>
<th>River</th>
<th>RMGC sampling programme</th>
<th>Fluvio sampling programme</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site ID</td>
<td>Stereo 70 E</td>
</tr>
<tr>
<td>Abrudzel</td>
<td>S002</td>
<td>355852</td>
</tr>
<tr>
<td>Bucium</td>
<td>S003</td>
<td>352946</td>
</tr>
<tr>
<td>Corna</td>
<td>S004</td>
<td>352905</td>
</tr>
<tr>
<td>Saliste</td>
<td>S006</td>
<td>350819</td>
</tr>
<tr>
<td>Abrud</td>
<td>S008</td>
<td>350367</td>
</tr>
<tr>
<td>Abrud</td>
<td>S011</td>
<td>350666</td>
</tr>
<tr>
<td>Abrud</td>
<td>S012</td>
<td>352163</td>
</tr>
<tr>
<td>Arieș</td>
<td>S014</td>
<td>357619</td>
</tr>
<tr>
<td>Arieș</td>
<td>S016</td>
<td>357617</td>
</tr>
<tr>
<td>Bucium</td>
<td>S017</td>
<td>359367</td>
</tr>
<tr>
<td>Bucium</td>
<td>S019</td>
<td>358072</td>
</tr>
<tr>
<td>Izbita</td>
<td>S020</td>
<td>358079</td>
</tr>
<tr>
<td>Abrud</td>
<td>S023</td>
<td>350442</td>
</tr>
<tr>
<td>Arieș</td>
<td>S025</td>
<td>364279</td>
</tr>
<tr>
<td>Sesei</td>
<td>S024</td>
<td>364279</td>
</tr>
</tbody>
</table>
Table 8-5. EU directive concerning the quality required of river water for the abstraction for drinking water (75/440/EEC).
Values in μg l⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>target value</th>
<th>imperative value</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Cd</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Pb</td>
<td>none</td>
<td>50</td>
</tr>
<tr>
<td>Zn</td>
<td>500</td>
<td>3000</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 – 8.5</td>
<td>None</td>
</tr>
</tbody>
</table>

Table 8-6. Romanian STAS values concerning the quality required of river water for the abstraction for drinking water.
Values in μg l⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>STAS 4706/1988 (Levels I, II &amp; III)</td>
<td>10</td>
<td>3</td>
<td>50</td>
<td>50</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 8-7. Romanian Ministerial Order limits regarding permissible As and metal concentrations in river water (MO1146/2002).
Values in μg l⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>Limit I</th>
<th>Limit II</th>
<th>Limit III</th>
<th>Limit IV</th>
<th>Limit V</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Background</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>&gt; 5</td>
</tr>
<tr>
<td>Cd</td>
<td>Background</td>
<td>0.1</td>
<td>0.2</td>
<td>0.5</td>
<td>&gt; 0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>Background</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>&gt; 8</td>
</tr>
<tr>
<td>Pb</td>
<td>Background</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>&gt; 5</td>
</tr>
<tr>
<td>Zn</td>
<td>Background</td>
<td>5</td>
<td>10</td>
<td>25</td>
<td>&gt; 25</td>
</tr>
</tbody>
</table>
### Table 8-8. Background metal concentrations (μg l⁻¹) determined for the Arieş catchment.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 2002</td>
<td>1.0</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>6.0</td>
</tr>
<tr>
<td>July 2003</td>
<td>1.0</td>
<td>0.1</td>
<td>0.5</td>
<td>0.1</td>
<td>6.0</td>
</tr>
<tr>
<td>March 2004</td>
<td>0.2</td>
<td>0.1</td>
<td>1.5</td>
<td>0.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Weighted mean</td>
<td>0.6</td>
<td>0.1</td>
<td>1.1</td>
<td>0.6</td>
<td>5.0</td>
</tr>
</tbody>
</table>

### Table 8-9. Target values and soil remediation intervention values for selected metals

Target values and soil remediation intervention values for selected metals from the Dutch Ministry of Housing, Spatial Planning and Environment. Values have been expressed as the concentration in a standard soil (10% organic matter, 25% clay). Guideline values, supplied by RMGC, for the physical-chemical determination of sediment are also shown. All values in mg kg⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>Target value</th>
<th>Intervention value</th>
<th>RMGC value</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>29</td>
<td>55</td>
<td>17</td>
</tr>
<tr>
<td>Cd</td>
<td>0.8</td>
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<td>3.5</td>
</tr>
<tr>
<td>Cu</td>
<td>36</td>
<td>190</td>
<td>200</td>
</tr>
<tr>
<td>Pb</td>
<td>85</td>
<td>530</td>
<td>90</td>
</tr>
<tr>
<td>Zn</td>
<td>140</td>
<td>720</td>
<td>300</td>
</tr>
</tbody>
</table>
Table 8-10. A list of elements analysed on the ICP-MS for fluvio’s river water and river sediment samples.

NB It should be noted that the quality of sediment geochemical data is strongly dependant upon the type of acid-extraction procedure used. A sealed tube digestion procedure for river sediments was not used by fluvio and hence Hg concentrations are probably considerably under-estimated.

<table>
<thead>
<tr>
<th>Alkaline metals</th>
<th>Transition metals</th>
<th>Other metals</th>
<th>Rare Earth elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Sc</td>
<td>Al</td>
<td>La</td>
</tr>
<tr>
<td>Rb</td>
<td>Ti</td>
<td>Ga</td>
<td>Ce</td>
</tr>
<tr>
<td>Cs</td>
<td>V</td>
<td>In</td>
<td>Pr</td>
</tr>
<tr>
<td>Cr</td>
<td>Sb</td>
<td>Sm</td>
<td></td>
</tr>
<tr>
<td>Alkaline earth metals</td>
<td>Ni</td>
<td>Sn</td>
<td>Eu</td>
</tr>
<tr>
<td>Be</td>
<td>Co</td>
<td>Ti</td>
<td>Gd</td>
</tr>
<tr>
<td>Sr</td>
<td>Zn</td>
<td>Pb</td>
<td>Tb</td>
</tr>
<tr>
<td>Ba</td>
<td>Y</td>
<td>Bi</td>
<td>Dy</td>
</tr>
<tr>
<td>Zr</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Metalloids</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>As</td>
<td>Mo</td>
<td>Yb</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Pd</td>
<td>Lu</td>
<td></td>
</tr>
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<td>Cd</td>
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</tr>
<tr>
<td>Hg</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8-11. Summary of shapefile contents in the geochemical database.

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<thead>
<tr>
<th>Shapefile name</th>
<th>Shapefile contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>XYfluvio_2002_river_water.shp</td>
<td>fluvio 2002 river water data</td>
</tr>
<tr>
<td>XYfluvio_2002_channel_sediment.shp</td>
<td>fluvio 2002 river sediment data</td>
</tr>
<tr>
<td>XYfluvio_2003_river_water.shp</td>
<td>fluvio 2003 river water data</td>
</tr>
<tr>
<td>XYfluvio_2003_channel_sediment.shp</td>
<td>fluvio 2003 river sediment data</td>
</tr>
<tr>
<td>XYfluvio_2003_mine_waste.shp</td>
<td>fluvio 2003 mine waste data</td>
</tr>
<tr>
<td>XYfluvio_2004_river_water.shp</td>
<td>fluvio 2004 river water data</td>
</tr>
<tr>
<td>XYfluvio_2004_channel_sediment.shp</td>
<td>fluvio 2004 river sediment data</td>
</tr>
<tr>
<td>XYfluvio_2004_mine_waste.shp</td>
<td>fluvio 2004 mine waste data</td>
</tr>
<tr>
<td>XYfluvio_2004_'catchment'.shp</td>
<td>fluvio 2004 catchment sample data</td>
</tr>
</tbody>
</table>
Table 8-12. Range and mean heavy metal and as concentrations in Roşia and Abrud catchment material.
NB Abrud data includes Roşia catchment. *contains one non-detectable concentration.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
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<td><strong>Roşia catchment</strong></td>
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<tr>
<td>Range</td>
<td>0.5 - 100</td>
<td>0.06* – 0.3</td>
<td>8.2 - 69</td>
<td>2.4 - 109</td>
<td>4.5 – 72</td>
</tr>
<tr>
<td>Mean</td>
<td>10</td>
<td>0.1</td>
<td>40</td>
<td>24</td>
<td>35</td>
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<tr>
<td><strong>Abrud catchment</strong></td>
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<td></td>
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</tr>
<tr>
<td>Range</td>
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<td>0.04* – 0.4</td>
<td>8.2 - 240</td>
<td>2.4 - 109</td>
<td>4.6 - 100</td>
</tr>
<tr>
<td>Mean</td>
<td>11</td>
<td>0.2</td>
<td>50</td>
<td>24</td>
<td>40</td>
</tr>
</tbody>
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Table 8-13. Non-parametric Spearman Rank correlation coefficients
Non-parametric Spearman Rank correlation coefficients for the relationship between % metal partitioning in the ‘exchangeable’ (P1), ‘Fe/Mn oxide’ (P2), ‘organic matter/sulphide’ (P3) and ‘residual’ (P4) phases and summed total metal concentration in river sediment. * and ** denote correlation significant at the 95 and 99 percent confidence limits, respectively.

<table>
<thead>
<tr>
<th></th>
<th>River Abrud</th>
<th></th>
<th></th>
<th>River Arieş</th>
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<th></th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P1 %</td>
<td></td>
<td></td>
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<tr>
<td>Cd</td>
<td>0.57*</td>
<td>0.14</td>
<td>-0.31</td>
<td>-0.39</td>
<td>0.09</td>
<td>-0.07</td>
</tr>
<tr>
<td>Cu</td>
<td>0.74**</td>
<td>0.20</td>
<td>-0.41*</td>
<td>-0.50*</td>
<td>0.59**</td>
<td>0.25</td>
</tr>
<tr>
<td>Pb</td>
<td>0.78**</td>
<td>-0.39</td>
<td>0.36</td>
<td>-0.03</td>
<td>-0.27</td>
<td>-0.65**</td>
</tr>
<tr>
<td>Zn</td>
<td>0.85**</td>
<td>0.08</td>
<td>-0.51*</td>
<td>-0.65**</td>
<td>0.36</td>
<td>0.28</td>
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### Table 8-14. Percentage of fluvio river water samples which exceeded EU, STAS and MO water quality thresholds

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<tbody>
<tr>
<td></td>
<td>T = target; I = imperative</td>
<td>T = target</td>
<td>L1 – L4 = levels</td>
</tr>
<tr>
<td></td>
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<td>Cd</td>
<td>Cu</td>
</tr>
<tr>
<td>2002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; T</td>
<td>96</td>
<td>68</td>
<td>69</td>
</tr>
<tr>
<td>&gt; T &lt; I</td>
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<td>14</td>
<td>6</td>
</tr>
<tr>
<td>&gt; I</td>
<td>2</td>
<td>18</td>
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<td></td>
<td></td>
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<tr>
<td>&lt; T</td>
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<td>55</td>
<td>64</td>
</tr>
<tr>
<td>&gt; T &lt; I</td>
<td>2</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>&gt; I</td>
<td>9</td>
<td>30</td>
<td>32</td>
</tr>
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<td></td>
</tr>
<tr>
<td>2004</td>
<td></td>
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</tr>
<tr>
<td>&lt; T</td>
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<td>70</td>
<td>60</td>
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<tr>
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<td>3</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>&gt; I</td>
<td>5</td>
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<td>28</td>
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<td></td>
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</table>
Table 8-15. Percentage of fluvio river sediment samples which exceed Dutch and Romanian guideline values.

<table>
<thead>
<tr>
<th></th>
<th>vs. Dutch guidelines</th>
<th>vs. Romanian guidelines</th>
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<td></td>
<td>As</td>
<td>Cd</td>
</tr>
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<td></td>
<td></td>
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<tr>
<td>&lt; T</td>
<td>71</td>
<td>35</td>
</tr>
<tr>
<td>&gt; T</td>
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<td>60</td>
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<tr>
<td>&gt; I</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; T</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>&gt; T</td>
<td>13</td>
<td>70</td>
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<tr>
<td>&gt; I</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; T</td>
<td>71</td>
<td>70</td>
</tr>
<tr>
<td>&gt; T</td>
<td>11</td>
<td>30</td>
</tr>
<tr>
<td>&gt; I</td>
<td>18</td>
<td>0</td>
</tr>
</tbody>
</table>
9 Figures

Figure 9.1. The Abrud/Arieș catchment showing the location of river water and river sediment sampling sites in July 2002.
Figure 9.2. The Abrud/Arieş catchment showing the location of river water and river sediment sampling sites in July 2003.
Figure 9.3. The Abrud/Arieș catchment showing the location of river water and river sediment sampling sites in March 2004.
Figure 9.4. The Abrud/Arieș catchment showing the location of catchment sediment sampling sites in March 2004.

a: location of catchment (slope) sediment sampling sites
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a: Arsenic
Figure 9.6. Colour coded proportional circles showing where July 2002 Cd concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieş catchment.

b: Cadmium
Figure 9.6. Colour coded proportional circles showing where July 2002 Cu concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative values for drinking water abstraction in the Abrud/Arieş catchment.

c: Copper
Figure 9.6. Colour coded proportional circles showing where July 2002 Pb concentrations in river water fell either below or above EC the imperative value for drinking water abstraction in the Abrud/Arieș catchment.

d: Lead
Figure 9.6. Colour coded proportional circles showing where July 2002 Zn concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieş catchment.

e: Zinc
Figure 9.6. Colour coded proportional circles showing where July 2002 river water pH fell either below or above the EC target value for drinking water abstraction in the Abrud/Arieş catchment.

f: pH
Figure 9.7. Colour coded proportional circles showing concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Aries catchment (July 2003)

a: Arsenic
Figure 9.7. Colour coded proportional circles showing where July 2003 Cd concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieș catchment.

b: Cadmium
Figure 9.7. Colour coded proportional circles showing where July 2003 Cu concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative values for drinking water abstraction in the Abrud/Ariș catchment.

c: Copper
Figure 9.7. Colour coded proportional circles showing where July 2003 Pb concentrations in river water fell either below or above EC the imperative value for drinking water abstraction in the Abrud/Aries catchment.

d: Lead
Figure 9.7. Colour coded proportional circles showing where July 2003 Zn concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieş catchment.

e: Zinc
Figure 9.7. Colour coded proportional circles showing where July 2003 river water pH fell either below or above the EC target value for drinking water abstraction in the Abrud/Arieș catchment.

f: pH
Figure 9.8. Colour coded proportional circles showing where March 2004 concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieş catchment.

a: Arsenic
Figure 9.8. Colour coded proportional circles showing where March 2004 Cd concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieș catchment

b: Cadmium
Figure 9.8. Colour coded proportional circles showing where March 2004 Cu concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative values for drinking water abstraction in the Abrud/Arieş catchment.

c: Copper
Figure 9.8. Colour coded proportional circles showing where March 2004 Pb concentrations in river water fell either below or above EC the imperative value for drinking water abstraction in the Abrud/Ariëş catchment.

d: Lead
Figure 9.8. Colour coded proportional circles showing where March 2004 Zn concentrations in river water fell either below or above the EC target value, or where they exceeded the imperative value for drinking water abstraction in the Abrud/Arieş catchment.

Zinc
Figure 9.8. Colour coded proportional circles showing where March 2004 river water pH fell either below or above the EC target value for drinking water abstraction in the Abrud/Arieş catchment.

f: pH
Figure 9.9. Downstream changes in river water heavy metal and As concentrations in the Abrud/Arieș catchment.
Figure 9.10. Colour coded proportional circles showing where July 2002 concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Ariş catchment.

a: Arsenic
Figure 9.10. Colour coded proportional circles showing where July 2002 Cd concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment

b: Cadmium
Figure 9.10. Colour coded proportional circles showing where July 2002 Cu concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Ariş catchment.

c: Copper
Figure 9.10. Colour coded proportional circles showing where July 2002 Pb concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment.

d: Lead
Figure 9.10. Colour coded proportional circles showing where July 2002 Zn concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment.

e: Zinc
Figure 9.11. Colour coded proportional circles showing where July 2003 concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment.

a: Arsenic
Figure 9.11. Colour coded proportional circles showing where July 2003 Cd concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Arieş catchment.

b: Cadmium
Figure 9.11. Colour coded proportional circles showing where July 2003 Cu concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment.

c: Copper
**Figure 9.11.** Colour coded proportional circles showing where July 2003 Pb concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment.

d: Lead
Figure 9.11. Colour coded proportional circles showing where July 2003 Zn concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Arieș catchment.

**e: Zinc**
Figure 9.12. Colour coded proportional circles showing where March 2004 concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Arieş catchment.

a: Arsenic
Figure 9.12. Colour coded proportional circles showing where March 2004 Cd concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Ariş catchment.

b: Cadmium
Figure 9.12. Colour coded proportional circles showing where March 2004 Cu concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Aries catchment.

c: Copper
Figure 9.12. Colour coded proportional circles showing where March 2004 Pb concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Arieş catchment.

d: Lead
Figure 9.12. Colour coded proportional circles showing where March 2004 Zn concentrations in river sediment fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud/Arieş catchment.

e: Zinc
Figure 9.13. Downstream changes in river sediment heavy metal and As concentrations in the Abrud/Arieș catchment.
Figure 9.14. Colour coded proportional circles showing where March 2004 concentrations in catchment samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

a: Arsenic
**Figure 9.14.** Colour coded proportional circles showing where March 2004 Cd concentrations in catchment samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

b: Cadmium
Figure 9.14: Colour coded proportional circles showing where March 2004 Cu concentrations in catchment samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

c: Copper
Figure 9.14. Colour coded proportional circles showing where March 2004 Pb concentrations in catchment samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

d: Lead
Figure 9.14. Colour coded proportional circles showing where March 2004 Zn concentrations in catchment samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

e: Zinc
Figure 9.15. Colour coded proportional circles showing where March 2004 concentrations in mine waste samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

a: Arsenic
Figure 9.15. Colour coded proportional circles showing where March 2004 Cd concentrations in mine waste samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

b: Cadmium
Figure 9.15. Colour coded proportional circles showing where March 2004 Cu concentrations in mine waste samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

c: Copper
Figure 9.15. Colour coded proportional circles showing where March 2004 Pb concentrations in mine waste samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

d: Lead
Figure 9.15. Colour coded proportional circles showing where March 2004 Zn concentrations in mine waste samples fell either below or above the Dutch target value, or where they exceeded the intervention value in the Abrud catchment.

e: Zinc
Figure 9.16. **Comparison of minimum, mean and maximum metal concentrations in mine waste**

Comparison of minimum, mean and maximum metal concentrations in mine waste from the Abrud catchment and from a number of other mining-affected regions in Romania and Europe.
Figure 9.17. Metal speciation patterns in river sediments

Metal speciation patterns in river sediments of the Rivers Abrud and Arieş and major mining affected tributaries. Samples IZ1 (Izbiţa), ABR1 (Abrudului), SI1 (Sălişte) and RO1 (Roşia) are samples taken from tributary streams. No speciation data is available for sample AR11.
Figure 9.18. Exchangeable concentrations of Cd, Cu and Zn in the Arieş catchment plotted relative to Dutch target and intervention values.
Figure 9.19. Geographical extent of the source groups used in the composite sediment fingerprinting/sediment mixing model.

The location of the river sediment samples used to determine the geochemical footprint of Roșia Montana are shown as open circles.
Figure 9.20. Percentage sediment contribution of each source group to downstream river sediment samples in the Abrud/Arieş catchment.

Figure 9.21. Percentage contribution of River Roşia catchment material to downstream river sediment samples

Percentage contribution (with error bars) of River Roşia catchment material to downstream river sediment samples in the Abrud/Arieş catchment. The solid black regression line relates to the data points for the six upstream sites, the upper and lower dashed regression lines relate to the maximum and minimum error bars, respectively.
Figure 9.22. Bivariate Pb isotope ratios

Bivariate Pb isotope ratios (\(^{208}/^{206}\text{Pb},^{207}/^{206}\text{Pb},^{208}/^{207}\text{Pb}\)) for sediment samples taken from open cast pits (Cetate, Cirnic, Napolean), mine spoil (Roşia Poieni, Izbita, Bucium, Roşia Montana) and tailings (Saliste, Izbita, Gura Rosiei) in the Abrud catchment.
Figure 9.23. Pb isotope ratios for mine spoil, tailings and river sediment samples in the Abrud catchment.
Figure 9.24. Pb isotope ratios plotted on a downstream basis for river sediment sampled from the Rivers Abrud and Arieș, between the River Roșia confluence and Buru.
Figure 9.25. A comparison of Pb isotope ratios plotted on a downstream basis for river sediment

A comparison of Pb isotope ratios plotted on a downstream basis for river sediment sampled from the Rivers Abrud and Arieș, between the River Roșia confluence and Buru, with Pb isotope ratios from the River Vișeu (Maramureș County).
Figure 9.26. River water geochemical hotspots showing sites where EU imperative values were exceeded

River water geochemical hotspots showing sites where EU imperative values were exceeded for at least one element (As, Cd, Cu, Pb, Zn) in every RMGC and fluvio sample taken from the site.
Figure 9.27. River sediment geochemical hotspots showing sites where Dutch intervention values were exceeded

River sediment geochemical hotspots showing sites where Dutch intervention values were exceeded for at least one element (As, Cd, Cu, Pb, Zn) in every RMGC and fluvio sample taken from the site.

NB the two hotspot sites on the Bucium overlap one another and hence only one circle is shown.