

8. English Summary

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Introduction

The Austrian stream sediment geochemistry programme was carried out between 1978 and 2010 by the Geological Survey of Austria (GBA) and the mining companies VOEST-Alpine (VA) and Bleiberg Bergwerksunion (BBU) with the main objective of providing a nation-wide geochemical baseline for metal ore prospection in Austria. The scheelite deposit of Mittersill in Salzburg had been discovered shortly before the onset of the programme and several prospection activities were under way targeting tungsten, molybdenum, lead, zinc and antimony among other elements. The systematic geochemistry programme was meant to provide the basis for focused, local prospection projects. However, from the beginning it was intended to use the analytical results for environmental geochemistry as well. Parallel to sampling and analysing of stream sediments, other studies therefore complemented the programme by analysing rock samples, heavy minerals, surface water, soils and plants. The mineralogical-microchemical phase analysis of heavy minerals in particular proved essential for the distinction between geogenic and anthropogenic effects on the distribution of chemicals in the environment.

Programme structure and organisation

The first phase of the programme (1978–1989) was financed by the Federal Ministries of Science & Research and Trade & Industry, and focused on the Bohemian Massif in northern Austria as well as the Central Alps. While the GBA was responsible for sampling in the Bohemian Massif, VA sampled most of the stream sediments in the Central Alps and BBU worked in the eastern part of the Central Alps. Within their respective sampling areas, the two mining companies had the option to use the analytical results for their own purposes of mineral prospecting. Sampling densities reached on average one sample per km², laboratory analyses were carried out by the Geotechnical Institute of Austrian Research Centre Arsenal in Vienna. The Mining University of Leoben and the Research Institute Joanneum were in charge of digital data processing and quality control. Twelve years after the onset of the programme, the results were published in the form of a geochemical atlas with maps of element concentrations, prepared mainly by VA, and an accompanying text volume (THALMANN et al., 1989a, b).

The second phase of the programme (1991–2010) focused on the remaining areas in Austria, mainly the Southern Alpine units, the Southern and Northern Calcareous Alps, the Flysch zone and the sedimentary basins. For these areas, individual projects were commissioned by each of the nine federal states of Austria together with the Federal Ministry of Science & Research, and were completed over the course of almost 20 years. Except for the sampling in Lower Austria, mining companies were not involved in these projects. Compared to the previous campaign, the objectives shifted from mainly providing the basis for ore prospecting to addressing aspects of environmental geochemistry such as the derivation of natural background values, the delineation of anthropogenic contamination or the as-

essment of the environmental impact of mine waste. The list of elements for geochemical analysis was enlarged to include e.g. cadmium or mercury, which are relevant in environmental studies. However, sampling densities were reduced to approximately 0.1 samples per km². Sampling procedures, sample preparation as well as the laboratory institute carrying out the analyses (Austrian Research Centre Arsenal and its successor ARC Seibersdorf) were kept constant to ensure continuity of the programme and comparability of results. In addition, a certain overlap of sampling areas was planned and control samples were taken at locations from the previous campaign. The final results were published in individual project reports for Lower Austria (KRALIK & AUGUSTIN-GYURITS, 1994; AUGUSTIN-GYURITS & HOLNSTEINER, 1997), Upper Austria (AUGUSTIN-GYURITS et al., 1998), Salzburg (WIMMER et al., 2002a), Tyrol (WIMMER et al., 2002b), Vorarlberg (KLEIN et al., 2005), Carinthia (KLEIN et al., 2006, 2007; SCHEDL et al., 2008), Burgenland (KLEIN et al., 2008), Styria (SCHEDL et al., 2009, 2010a, b), and Vienna (PFLEIDERER et al., 2010).

Sampling methods, sample preparation and chemical analysis – Bohemian Massif and Central Alps

In the Bohemian Massif and the Central Alps, systematic sampling and geochemical analysis of stream sediments were carried out for mineral prospection particularly for metals and metalloids. For this purpose, the grain size fraction to be collected and analysed was set to < 0.18 mm (fine sand and silt), similar to programmes in other European countries and in Canada. The objective was to obtain an integral picture of lithology in the catchment area and to reveal regional element distribution patterns.

Previous experience and methods for stream sediment sampling – gained by the geological surveys of Germany, Sweden and Norway – were adapted to alpine conditions in Austria. These included torrents with highly variable discharge and sediment load, stonewalled channels, constructed stream beds without deposition of fine-grained sediments, slow flowing and deep streams without easy access to river banks, in addition to streams in intensively farmed areas overgrown by plants and carrying abundant organic material. Sampling locations were planned on the basis of topographic maps at the scale of 1:50,000 and targeted all streams and tributaries up to the lowest order. Only large, very high order rivers were occasionally omitted to avoid anthropogenic influence. Where no sample could be taken, as in some of the above-mentioned circumstances, sampling locations were shifted up- or downstream by a distance of up to 50 m. The sample material constituted active sediment, i.e. deposits frequently moved by running water. Stream sediment samples of approximately 1 kg were collected to yield 50 g of material for analysis with a grain size < 0.18 mm. Samples were taken even if the river was dry at the time of sampling. If necessary, samples were dry-sieved in situ to obtain the required amount of fine-grained material. In 1979, the stream sediment sampling procedures were incorporated into the Austrian Standard (ÖNORM) G 1031.

Sample preparation in the field consisted of drying the samples in well aired rooms, followed in the laboratory by weighing, oven drying at 110 °C, renewed weighing to determine the water content, dry-sieving to eliminate grain sizes > 0.18 mm, and finally renewed weighing of the sieved sample.

Chemical analysis of the samples included 35 elements, concentrations were measured using five different methods. Concentrations of the elements Ba, Be, Ca, Ce, Co, Cr, Cu, Fe, Ga, La, Mg, Mn, Na, Ni, P, Sc, Sr, Ti, V and Zn were measured using the method of inductively-coupled plasma optical emission spectrometry (ICP-OES) after dissolving the samples in a mixture of nitric acid, hydrofluoric acid and perchloric acid at a ratio of 5:1:1, respectively. Concentrations of the elements Al, K, Nb, Rb, Th, U, W, Y and Zr were measured using wavelength-dispersive X-ray fluorescence (XRF) spectrometry after producing a compressed powder pellet in a boric acid matrix from the sample. Concentrations of the elements Ag, Mo, Pb and Sn were measured using optical emission spectrography (OES). Concentrations of Sb were measured using atomic absorption spectrometry (AAS), and concentrations of As were measured using the semi-quantitative Gutzeit test.

Analytical results were originally stored in a database in dBase format which, in addition to element concentrations, included sample location number, laboratory number, sample weight, geologic-tectonic unit at the sampling point and within the provenance area, point coordinates, as well as sampling year and team. Presentation of results included 1:50,000 scale maps showing sample locations within geologic-tectonic units, as well as – for each element – univariate point maps and interpolated surface maps. The “Geochemical Atlas of the Republic of Austria 1:1,000,000 – Bohemian Massif and Central Alps” was published by THALMANN et al. (1989a, b). Currently, the GBA holds the data set on SQL servers for further geostatistical and GIS analyses.

Sampling methods, sample preparation and chemical analysis – remaining alpine units and sedimentary basins

For the second phase of the programme, aspects of environmental geochemistry were considered more important than metal ore prospection. The new objectives were to characterize both natural background levels and anthropogenic impacts. Consequently, the grain size fraction < 0.04 mm was sampled in addition to the fraction < 0.18 mm. Large rivers were no longer omitted, and the hydrochemical/hydrophysical conditions of surface water were recorded in addition during sampling. Due to budget constraints, sampling density was reduced on average to one sample per 10 km². In order to still reach the objectives, half the sampling locations were allocated to low order river systems, i.e. small catchment areas, while the other half were placed along larger rivers close to settlements, industrial sites, wastewater treatment plants and other possible emitters of pollution.

Sampling procedures stayed the same as during the first sampling campaign. For the hydrochemical/hydrophysical characterisation of surface water, water temperature, electrical conductivity, pH value and redox potential were

measured in the stream and in the water-saturated sample (before decanting). These measurements were performed at all sampling points except for locations in Lower Austria. For additional quality control, every 50th sample point was sampled twice at the same location.

Due to budget constraints, the grain size fraction < 0.04 mm was analysed only for samples from the states of Lower Austria, Vorarlberg, Carinthia, Styria, Burgenland and Vienna. For the remaining states, the samples are currently kept in storage at the GBA for future analysis. In the case of Upper Austria, samples have been already sieved and prepared for the laboratory. Sample preparation firstly consisted of drying samples at room temperature – to reduce the loss of mercury which results when samples are dried in the oven – for several weeks until the water content was below two weight percent. Subsequently, dried samples were carefully pressed with a porcelain mortar to re-separate grains without grinding them. After weighing, the samples were dry-sieved for 10–20 minutes using stainless steel sieves. Through renewed weighing, the weight percentages of the two grain size fractions were determined. Two 50 ml polyethylene flasks were filled with material from each fraction, one was given to the laboratory for analysis, the other was retained in storage.

Water content was determined by weighing samples before and after oven-drying at 105 °C over night. Subsequent weight loss after oven-drying at 360 °C for two hours and cooling in a desiccator was equated with the amount of (oxidised) organic material although weight change may also be due to iron hydroxide and sheet silicate minerals loosing water at these temperatures. Weight loss after oven-drying at 1,000 °C corresponds to the amount of crystal water and CO₂-loss of carbonates.

The spectrum of elements analysed in the laboratory was enlarged by eight additional elements. These included the main element Si and the trace elements Cd, Cl, F, Hg, Li, S and Se. Only in samples from Lower Austria were Cl and Li concentrations not measured. While Cd and Hg are relevant for environmental studies, and Se and Li are of nutritional interest, Cl and S allow for an improved geological characterization of the sediment as they indicate salt or gypsum deposits or sulphide mineralizations.

Due to significant advances in analytical techniques and improvements in detection limits, the methods were slightly altered compared to the first phase of the programme. This has implications for the comparability of results discussed in the element-specific sections of this publication. Concentrations of the elements Al, Ba, Ca, Cl, Cr, F, Fe, Ga, K, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, S, Si, Sr, Th, Ti, V, Y, Zn and Zr were measured by wavelength-dispersive X-ray fluorescence (XRF) spectrometry, while the trace elements Ag, As, Be, Cd, Ce, Co, Cu, Hg, La, Li, Mo, Sb, Sc, Se, Sn, U and W were determined by inductively-coupled plasma mass spectrometry (ICP-MS).

Analytical results of the second phase of the programme were originally stored as separate data sets for each project. Evaluation and interpretation focus varied among the federal states, with the consequence that 14 individual project reports were published to describe the outcomes. The present publication brings together all data for the first time. The GBA currently holds all data, including the data of the first campaign, as one data set consisting of

sample location number, point coordinates, field measurements, element concentrations and reference to the individual project campaigns.

Quality control, multiple sampling and comparison of methods

At the beginning of the stream sediment programme, the use of machine standards constituted the only quality control and it was carried out internally by the laboratory. However, an external quality control was soon added, using a natural, geological standard ("Danube standard") as well. Additional measures were introduced to examine possible causes of error during sampling, laboratory analysis and data processing. Steps which were undertaken to check for sampling effects included multiple sampling at one location, dividing samples into four or six sub-samples which were separately analysed, simultaneous sampling by different teams, and repeated sampling at the same location after two years. Measures taken to check the quality of analytical results included comparative sampling and analysis by different laboratories, applying different analytical methods to the same sample, and comparing the results of different grain size fractions or between stream sediments, rocks and soils. To test for biases in the geo-statistical data analysis, different methods were applied by different research teams on the same data sets.

Multiple sampling and sample division show only minor deviations with respect to main element concentrations, but significant differences in trace element concentrations. Heterogeneities within the sediment or imperfect sample division may be the cause. These measures of multiple sampling or sample division may be of limited use for quality control of the laboratory. Different sampling methods – carried out by the British Geological Survey (BGS) and the GBA at identical locations – and subsequent analysis by different laboratories, reveal general correlations between element concentrations, but systematic differences remain and results are considered incomparable. This indicates that the GBA's stream sediment geochemical data – obtained by adhering to one constant set of sampling procedures – can be used for relative comparison of element concentrations between different regions in Austria but not for absolute comparison to other data sets. Finally, repeated sampling after two years can be used for laboratory control if the exact same sampling points are revisited, the same sampling procedures are followed, and any natural variability of the sediment over time, due e.g. to changes in hydrological conditions, can be excluded. Comparison between the results of two different sampling years shows minor differences between main element concentrations but large variations for trace elements. It remains unclear whether the cause of these discrepancies lies in sampling team performance, laboratory quality or true variations of sediment composition.

Element-specific results and discussion

For each element, the present publication provides general information on the geogenic and anthropogenic sources of the element, on important carrier minerals, on the abundance in certain minerals, and on the element's behaviour in the environment. Then, the element concentra-

tions in Austrian stream sediments are discussed and presented as diagrams of cumulative distributions and, for most elements, as interpolated surface maps of regional distributions. Due to poor comparability between results of individual sampling campaigns and differing analytical methods, interpolation was performed only for certain elements and in some cases only in certain areas. In the following paragraphs, the discussion of element concentrations of Austrian stream sediment samples will be summarized. Spatial distribution patterns refer to concentrations in the grain size fraction < 0.18 mm, while frequency distributions also include references to the grain size fraction < 0.04 mm.

Ag – Silver: number of analyses: 34,218; number of measurements above quantification limit: 33,033; minimum value: 0.009 ppm, maximum value: 28 ppm.

Concentrations > 1 ppm Ag occur as isolated and disperse data points, some of them associated with anthropogenic emitters such as hospitals or communal sewage water. Geogenic anomalies occur near poly-sulphide Pb-Zn-mineralizations or Au-mineralizations (e.g. in Schladminger Tauern, Kreuzeckgruppe or central Hohe Tauern). Concentrations < 0.9 ppm Ag do not reveal any regional pattern. Interpolation between data points was not performed.

Al – Aluminium: number of analyses: 34,022; number of measurements above quantification limit: 33,993; minimum value: 0.05 %, maximum value: 20.48 %.

The regional distribution reflects the occurrence, or absence, of silicates such as feldspar, mica, amphiboles or clay minerals and therefore describes the lithology of sample provenance areas. Very high concentrations (> 10 % Al) correlate spatially with the occurrence of phyllites or mica schists. In contrast, stream sediments in Weinsberg granite areas of the Bohemian Massif display lower concentrations (< 10 % Al) due to the fact that weathering leads to Al-bearing feldspars accumulating in grain size fractions > 0.18 mm. Carbonate rocks in the Northern and Southern Calcareous Alps produce stream sediments with very low Al concentrations (< 4 % Al). In Neogene and Quaternary sedimentary basins, stream sediments are dominated by quartz minerals and exhibit low to medium Al concentrations (5–8 % Al).

As – Arsenic: number of analyses: 34,333; number of measurements above quantification limit: 19,270; minimum value: 0.1 ppm, maximum value: 1,400 ppm.

Regional patterns of As concentrations are entirely controlled by geogenic factors. Most of the samples in the Bohemian Massif show values < 2 ppm As, in the Molasse basin, Vienna basin, Helvetic zone or Northern Calcareous Alps < 10 ppm As. Values > 100 ppm As are associated either with localised As-mineralizations or with more widely spread sulphide mineralizations within the Drauzug-Gurktal nappe system, the Koralpe-Wölz nappe system or the Semmering-Wechsel region.

Ba – Barium: number of analyses: 34,289; number of measurements above quantification limit: 34,153; minimum value: 5 ppm, maximum value: 19,264 ppm.

The two main sources of barium in stream sediments constitute Ba-bearing silicates, in particular feldspars, and barite veins associated with mineralizations. The first source

is responsible for elevated values (500–1,000 ppm Ba) in the Bohemian Massif and in Austroalpine crystalline units. Even higher concentrations occur in the vicinity of the Pb-Zn-mineralization of Bleiberg-Kreuth (> 6,000 ppm Ba), of barite deposits at Semmering, and in numerous abandoned mining areas (Friesach, Gusswerk and St. Christoph am Arlberg). However, certain occurrences of Pb-Zn-mineralizations are not accompanied by barite veins (Imst, Nassereith and Fernpass) and stream sediments near those areas lack elevated Ba concentrations. In the Northern and Southern Calcareous Alps, concentrations fall below 300 ppm Ba, in Neogene and Quaternary sedimentary basins values range between 300 and 500 ppm Ba.

Be – Beryllium: number of analyses: 34,215; number of measurements above quantification limit: 33,588; minimum value: 0.08 ppm, maximum value: 30 ppm.

Elevated concentrations (> 10 ppm Be) in stream sediments occur in areas of felsic magmatic rocks (granites, granitoids, pegmatites) in the Bohemian Massif, the Austroalpine crystalline units and in the Sub-Penninic nappes. In the Grauwackenzone, the Paleozoic of Graz, in Eastern Tyrol and in the Gurktal Alps, shales and phyllites, which are derived from these granites, also lead to stream sediments enriched in beryllium (5–10 ppm Be). Values < 2 ppm Be are found in the Molasse basin, the Helvetic zone, the Flysch zone, the Northern and Southern Calcareous Alps and in intra-montane basins.

Ca – Calcium: number of analyses: 34,304; number of measurements above quantification limit: 34,302; minimum value: 0.02 %, maximum value: 42.34 %.

High concentrations (> 10 % Ca) in stream sediments coincide with areas made of carbonate rocks, i.e. the Northern and Southern Calcareous Alps. Furthermore, rock suites in Vorarlberg's Molasse zone and Helvetic zone are characterised by carbonates and, consequently, by high Ca concentrations in stream sediments. In areas dominated by crystalline rocks, values correlate with the amount of Ca-bearing silicates (epidote, amphibole, plagioclase) in these rocks. Alternating carbonate and non-carbonate series – as in the Penninic nappes – are traced by alternating Ca concentrations in the stream sediments. Similarly, marble units within crystalline rock suites, and even localised, isolated carbonate occurrences, can be identified in regional stream sediment geochemical patterns. Sediments of rivers originating in the Northern Calcareous Alps, such as the rivers Traun, Alm, Steyr, Ybbs, Traisen, Triesting or Piesting, keep a carbonate matrix along their course until they join the next larger river.

Cd – Cadmium: number of analyses: 4,678; number of measurements above quantification limit: 3,312; minimum value: 0.05 ppm, maximum value: 113.32 ppm.

Until the middle of the 1990's, quantification limits of existing analytical chemistry methods prevented the reliable measurement of natural Cd concentrations in stream sediments (0.1 ppm Cd). During the first phase of the Austrian stream sediment programme (Bohemian Massif and Central Alps), samples were not analysed for Cd. Analytical results of samples collected more recently still exhibit implausible distribution patterns and no interpolated surface map was constructed for this reason. Only anomalies (> 3 ppm Cd) are considered trustworthy and appear asso-

ciated with Pb-Zn-mineralizations in the western Tyrolian and the Southern Calcareous Alps.

Ce – Cerium: number of analyses: 34,306; number of measurements above quantification limit: 34,283; minimum value: 0.22 ppm, maximum value: 3,590 ppm.

Occurrences are linked to the presence of heavy minerals, in particular monazite. Therefore, not only the lithological composition of the catchment area but also the specific circumstances of sediment transport and deposition, control the concentrations of Ce. Enrichment of heavy minerals in stream sediment takes place behind obstacles in the river bed, most notably in the small grain size fraction. With respect to lithological controls, elevated concentrations (> 300 ppm Ce) occur in granite areas of the Bohemian Massif since granites naturally contain abundant Ce-bearing, heavy minerals. In situ weathering of these rocks further increases this abundance as these minerals are strongly resistant to weathering. The lowest concentrations (< 30 ppm Ce) in stream sediments appear in the Northern and Southern Calcareous Alps, followed by slightly higher values (30–100 ppm Ce) in Neogene and Quaternary sedimentary basins, while stream sediments in the Central Alps exhibit values of 100–200 ppm Ce.

Cl – Chlorine: number of analyses: 3,526; number of measurements above quantification limit: 2,827; minimum value: 16 ppm, maximum value: 593 ppm.

Analytical results are not present for the early phases of the Austrian stream sediment programme (Bohemian Massif, Central Alps and Lower Austria) and construction of interpolated surface maps was omitted in these areas. In the data sets of later sampling campaigns, areas with elevated concentrations (> 150 ppm Cl) mark individual massifs in the Northern Calcareous Alps (Schneealpe, Hochschwab, Gesäuse, Dachstein, Tennengebirge and Karwendel). Whether this is caused by different rock types, facies or other factors remains unclear. Within the Neogene and Quaternary sedimentary basins, values range from 30 to 100 ppm Cl. Possible impacts of intensive agriculture still need to be investigated in detail.

Co – Cobalt: number of analyses: 34,304; number of measurements above quantification limit: 34,157; minimum value: 0.5 ppm, maximum value: 226 ppm.

Although 90 % of the data show concentrations within a very narrow range (2–30 ppm Co), the regional distribution patterns can be interpreted in terms of the rock types from which the stream sediments originate. Values above 20 ppm Co are associated with serpentinites and other mafic rocks, as well as with a finely dispersed sulphide content in rocks of the Austroalpine crystalline units.

Cr – Chromium: number of analyses: 34,258; number of measurements above quantification limit: 33,984; minimum value: 2 ppm, maximum value: 3,614 ppm.

Very high concentrations (> 250 ppm Cr) correlate with areas dominated by ultramafic rocks, in particular localised occurrences of serpentinite (Rechnitz in Burgenland, Preg-Kraubath and the areas west of Trieben or north of Heiligenblut). Stream sediments within more widespread areas of mafic rocks exhibit slightly lower values (100–250 ppm Cr). The lowest values (< 50 ppm Cr) are found in the Bohemian Massif and the Northern Calcareous Alps,

although the latter contain local anomalies of high Cr content (> 600 ppm Cr) associated with the Gosau Formation. Concentrations in stream sediment of the Molasse zone and Quaternary/Neogene sediment basins rarely exceed 100 ppm Cr.

Cu – Copper: number of analyses: 34,341; number of measurements above quantification limit: 34,064; minimum value: 0.5 ppm, maximum value: 6,400 ppm.

Approximately 75 % of samples throughout Austria contain less than 30 ppm Cu. In some localised areas, higher concentrations (30–120 ppm Cu) are associated with mafic and ultramafic rocks. Anomalies above 120 ppm Cu are connected to chalcopyrite or polysulphide mineralizations (e.g. at Walchen, Großarl, Kleinfragant, Blindis, Jochberg/Kupferplatte or Röhrerbühel). Isolated sample points in the Weinviertel (north of Vienna) and the southern Vienna basin also show concentrations > 120 ppm Cu. However, these are caused by anthropogenic activity, quite possibly viticulture.

F – Fluorine: number of analyses: 4,678; number of measurements above quantification limit: 3,823; minimum value: 50 ppm, maximum value: 16,302 ppm.

Analytical results are not present for the early phases of the Austrian stream sediment programme (Bohemian Massif and Central Alps). Only for the more recent sampling campaigns (Vorarlberg, Tyrol, Salzburg, Carinthia, Styria, Burgenland and Vienna) do chemical analyses yielded data of sufficient quality to allow interpretation of regional distribution patterns. Construction of interpolated surface maps was therefore only performed in these areas. Sources of fluorine in Austrian stream sediments have not yet been investigated thoroughly. Possible sources include some rock forming minerals such as mica and amphiboles, leading to elevated concentrations in certain crystalline rocks. Fluorite frequently constitutes an accompanying mineral in (poly-) sulphide mineralizations. High values (> 1,000 ppm F) therefore occur in the vicinity of the Pb-Zn-mineralizations of Drauzug. The maximum concentration (16,302 ppm F) was found directly below the former ore processing site of the mining area Bleiberg-Kreuth. Fluorine is also contained in apatite and other phosphate minerals which could account for elevated background levels in areas of intensive agriculture where phosphate fertilizers are used heavily.

Fe – Iron: number of analyses: 34,304; number of measurements above quantification limit: 34,296; minimum value: 0.01 %, maximum value: 29.14 %.

Despite the ubiquitous use of iron in our civilisation, the regional distribution in Austrian stream sediments mostly reflects the geological/geochemical conditions. This is due to the widespread occurrence of Fe-bearing silicates, sulphides (pyrite, marcasite), oxides and hydroxides. Elevated concentrations (> 6 % Fe) in stream sediments mark the presence of mafic rocks, iron-rich paragneiss or mica schists in catchment areas. Iron carbonate deposits (e.g. the Styrian Erzberg or Hüttenberg) do not stand out within these distribution patterns. Very low values (< 1 % Fe) occur in the Southern and Northern Calcareous Alps.

Ga – Gallium: number of analyses: 34,216; number of measurements above quantification limit: 33,662; minimum value: 0.5 ppm, maximum value: 91 ppm.

The overall range of Ga concentrations in stream sediments is very narrow (5–90 ppm Ga). Within the Central Alps, the highest values occur in the area of polysulphide mineralizations south of Wörgl (> 60 ppm Ga) and west of Hermagor (> 40 ppm Ga). The presence of gallium is possibly connected to sphalerite in those cases. Values above 30 ppm Ga also appear in catchment areas with rock types containing Al-rich feldspars and micas. Noticeably, stream sediments near Pb-Zn-mineralizations in Bleiberg or in the western Tyrolean Alps do not show elevated Ga concentrations. The Southern and Northern Calcareous Alps as well as the Neogene and Quaternary sedimentary basins are characterised by low concentrations (< 16 ppm Ga).

Hg – Mercury: number of analyses: 4,677; number of measurements above quantification limit: 4,497; minimum value: 0.005 ppm, maximum value: 8.7 ppm.

Analytical results are not present for the early phase of the Austrian stream sediment programme (Bohemian Massif and Central Alps) and construction of interpolated surface maps was omitted in these areas. For later sampling campaigns, over 99 % of analyses show Hg concentrations below 1 ppm. The distribution of higher values points to geogenic as well as anthropogenic sources. Mercury can be contained in sulphide copper ore (e.g. in the Kitzbühel Alps, Tennengebirge and the eastern Grauwackenzone at Radmer and Mürzzuschlag), leading to 3–8.7 ppm Hg in stream sediments, while cinnabar can be associated with siderite deposits (e.g. 4 ppm Hg in stream sediments at the Styrian Erzberg). The former mercury mining site at Bad Vellach/Kotschnatal in southern Carinthia also shows up as an anomaly (1 ppm Hg). Concerning anthropogenic emitters, the siderite smelting at Donawitz contributes to elevated Hg concentrations (8 ppm Hg) in the stream sediments of Vordernberger Bach. The anthropogenic sources of Hg concentrations in Marchfeld (east of Vienna) and the southern Vienna basin (> 1 ppm Hg) still need to be investigated in detail.

K – Potassium: number of analyses: 33,992; number of measurements above quantification limit: 33,949; minimum value: 0.013 %, maximum value: 7.11 %.

The spatial distribution of K concentrations in Austrian stream sediments directly correlates with the presence, or absence, of rock types containing K-bearing feldspars, micas and clay minerals. Although potassium is also introduced into the environment by humans through the use of fertilisers, the distribution patterns are mainly due to natural background levels. Thus, K concentrations are low (< 1 %) in stream sediments of the Southern and Northern Calcareous Alps, as well as in areas of marbles, calc-mica schists and calcareous phyllites.

La – Lanthanum: number of analyses: 34,306; number of measurements above quantification limit: 34,110; minimum value: 0.5 ppm, maximum value: 6,732 ppm.

As for the element cerium, the occurrence of La is linked to the presence of heavy minerals, in particular monazite and orthite. The physics of heavy minerals transport leads to preferred deposition behind obstacles in the river bed, most notably in the smaller grain size fraction (< 0.04 mm).

With respect to the coarser grain size fraction (< 0.18 mm), high La concentrations (> 400 ppm La) are restricted to samples from the Bohemian Massif, due to the fact that granites and migmatites abundantly contain La-bearing heavy minerals and in situ weathering increases this abundance in stream sediments. The lowest concentrations appear in stream sediments of the Southern and Northern Calcareous Alps (< 12 ppm La), followed by the Neogene and Quaternary sedimentary basins (13–36 ppm La). Sediments in large rivers of the Central Alps show intermediate values (37–102 ppm La).

Li – Lithium: number of analyses: 3,526; number of measurements above quantification limit: 3,423; minimum value: 0.99 ppm, maximum value: 117 ppm.

Analytical results are not present for the early phases of the Austrian stream sediment programme (Bohemian Massif, Central Alps and Lower Austria) and construction of interpolated surface maps was omitted in these areas. In the data sets of later sampling campaigns, stream sediments of the Southern and Northern Calcareous Alps show the lowest concentrations (< 16 ppm Li), samples from the Neogene and Quaternary sedimentary basins exhibit intermediate values (16–52 ppm La). Since lithium can substitute potassium, sodium and magnesium in the lattice of feldspars, micas and amphiboles, rock types dominated by these minerals lead to stream sediments with higher Li concentrations. Spodumene-bearing pegmatites in the Austroalpine crystalline units do not manifest themselves in the stream sediment geochemical distribution due to insufficient sampling densities.

Mg – Magnesium: number of analyses: 34,304; number of measurements above quantification limit: 34,268; minimum value: 0.05 %, maximum value: 20.84 %.

Elevated Mg concentrations in stream sediments (> 4 % Mg) indicate dolomitic rocks in the catchment areas of the Southern and Northern Calcareous Alps. Rock suites in Vorarlberg's Molasse and Helvetic zones are also characterised by carbonates and, consequently, by high Mg concentrations in stream sediments. Alternating carbonate and non-carbonate series – as in the Penninic nappes – are traced by alternating Mg concentrations in the stream sediments. Even localised, isolated carbonate occurrences (e.g. Mesozoic of Brenner, carbonates in Radstädter Tauern and the Mesozoic east of Krappfeld) can be identified in regional stream sediment geochemical patterns. Sediments of rivers originating in the Northern and Southern Calcareous Alps, such as the rivers Traun, Alm, Steyr, Ybbs, Traisen, Triesting or Piesting, keep a carbonate matrix along their course until they join the next larger river. In non-carbonate, crystalline units, mafic rocks with abundant Mg-bearing minerals, such as amphiboles, pyroxenes, micas, or clay minerals, lead to stream sediments with slightly elevated Mg concentrations (> 1.7 % Mg).

Mn – Manganese: number of analyses: 34,303; number of measurements above quantification limit: 34,044; minimum value: 0.002 %, maximum value: 2.776 %.

The geochemical nature and distribution of Mn is very similar to that of Fe. Elevated Mn concentrations in stream sediments (0.4–0.6 % Mn) are found near siderite deposits (at Eisenerz and Radmer) or Fe-bearing dolomites (in the Grauwackenzone). Localised anomalies (0.15 % Mn) oc-

cur in the Northern Calcareous Alps in catchment areas containing Mn-rich Jurassic rocks which in former times were mined for Mn (e.g. at Osterhorngruppe or northwest of Lofer).

Mo – Molybdenum: number of analyses: 34,219; number of measurements above quantification limit: 33,002; minimum value: 0.1 ppm, maximum value: 542.1 ppm.

Elevated Mo concentrations in stream sediments are associated with several geogenic sources. Mafic rocks in the Austroalpine crystalline units tend to yield stream sediments with slightly elevated values (2–5 ppm Mo), although this correlation needs to be investigated further. Carbonate rocks in the Northern Calcareous Alps of Upper and Lower Austria as well as of western Tyrol exhibit equally elevated values. Again, further studies are required to substantiate this association. In the vicinity of Pb-Zn-mineralizations in Drauzug, stream sediments contain very high concentrations (> 200 ppm Mo). Carbonate rocks in Drauzug, in the Lienzer Dolomites and the Karawanks give rise to 5–30 ppm Mo in stream sediments. A small anomaly at Kalkkögel near Fulpmes shows values of 40 ppm Mo. Finally, anthropogenic emitters (steel production and processing) exist along the river Mürz which cause values in sediments to rise to 10–40 ppm Mo.

Na – Sodium: number of analyses: 34,304; number of measurements above quantification limit: 34,086; minimum value: 0.004 %, maximum value: 5.04 %.

Since Na is mainly bound to albite and microcline, the spatial distribution of Na concentrations in stream sediments reflects that of crystalline rocks containing these minerals. Elevated values (> 2 % Na) are linked to the presence of granites, granitoids, migmatites and orthogneiss in the respective provenance areas. In Neogene and Quaternary sedimentary basins, stream sediments contain 0.5–1 % Na, while within the Southern and Northern Calcareous Alps values drop to < 0.5 % Na.

Nb – Niobium: number of analyses: 34,256; number of measurements above quantification limit: 33,139; minimum value: 0.5 ppm, maximum value: 243 ppm.

As for the elements cerium and lanthanum, the abundance of heavy minerals reflects Nb concentrations in Austrian stream sediments. Carrier minerals for Nb are mainly rutile and ilmenite. High values (> 30 ppm Nb) occur in the Bohemian Massif and in the Austroalpine crystalline units. In contrast, stream sediments in the Northern and Southern Calcareous Alps exhibit low values (< 10 ppm Nb), while the Flysch zone and the Molasse zone are characterised by 10–20 ppm Nb in stream sediments. In the eastern Styrian basin where sediments are derived from the Central Alps, Nb content in stream sediments ranges between 20 and 30 ppm Nb.

Ni – Nickel: number of analyses: 34,304; number of measurements above quantification limit: 33,954; minimum value: 2 ppm, maximum value: 2,471 ppm.

Similarly to chromium, very high concentrations (> 500 ppm Ni) correlate with areas dominated by ultramafic rocks, in particular localised occurrences of serpentinite (Rettenbach/Redlschlag in Burgenland, Preg-Kraubath, the areas west of Trieben or north of Heiligenblut). Stream sediments within more widespread areas of mafic rocks

exhibit slightly lower values (50–200 ppm Ni). Small anomalies with elevated concentrations (> 250 ppm Ni) in the Northern Calcareous Alps are linked to Cretaceous sedimentary rocks (Gosau Formation) which contain chromite.

P – Phosphorus: number of analyses: 34,303; number of measurements above quantification limit: 33,059; minimum value: 0.004 %, maximum value: 1.444 %.

Within crystalline rocks, phosphorus is contained in heavy minerals such as apatite, monazite and xenotime. Stream sediments in the Bohemian Massif therefore contain P in high concentrations (> 0.2 % P). Phosphorus is also contained as a trace element in amphiboles, pyroxenes, micas and feldspars which may explain elevated concentrations in certain stream sediments in the Central Alps (> 0.15 % P). However, rock geochemical data are needed to identify the rock types responsible for these stream sediment geochemical distribution patterns. High P concentrations (> 0.2 % P) also occur in areas of intensive agriculture (e.g. Weinviertel, Marchfeld and the southern Vienna basin) and result from the use of fertilisers.

Pb – Lead: number of analyses: 34,217; number of measurements above quantification limit: 34,198; minimum value: 3 ppm, maximum value: 11,662 ppm.

High Pb concentrations in stream sediments (300–11,600 ppm Pb) appear near polysulphide (and in particular Pb-Zn-) mineralizations. Among the former are the mineralizations at Walchen, Schladminger Tauern, in Kreuzeckgruppe and the Kitzbühel Alps, among the latter, deposits in the Paleozoic of Graz, in Drauzug, in the Karawanks, and in the western part of the Northern Calcareous Alps in Tyrol. At Sonnblickgruppe, galena mineralization in veins leads to slightly elevated levels (90 ppm Pb) in stream sediments. Except for these anomalies, lead contained as a trace element in feldspars results in low natural background levels (< 50 ppm Pb) in stream sediments. Anthropogenic contamination causes elevated levels in the southern Vienna basin (80–800 ppm Pb).

Rb – Rubidium: number of analyses: 34,039; number of measurements above quantification limit: 33,934; minimum value: 4 ppm, maximum value: 597 ppm.

Concentrations of Rb in stream sediments correlate closely with those of K since rubidium, just like potassium, is contained in feldspars and, to a lesser degree, in micas. Values are low (< 50 ppm Rb) in stream sediments of the Southern and Northern Calcareous Alps while in the Flysch zone and the Neogene and Quaternary sedimentary basins values range between 50 and 100 ppm Rb. Crystalline rocks in the Bohemian Massif and the Central Alps give rise to elevated values (100–590 ppm Rb) in stream sediments.

S – Sulfur: number of analyses: 4,678; number of measurements above quantification limit: 4,327; minimum value: 13 ppm, maximum value: 110,365 ppm.

Analytical results are not present for the early phases of the Austrian stream sediment programme (Bohemian Massif and Central Alps). Only for the more recent sampling campaigns (Vorarlberg, Tyrol, Salzburg, Carinthia, Styria, Burgenland and Vienna) did chemical analyses yield data of sufficient quality to allow interpretation of regional distribution patterns. Construction of interpolated surface

maps was therefore only performed in these areas. Natural sources for high S concentrations (> 1,000 ppm S) in stream sediments are on one hand sulphides associated with polysulphide mineralizations or finely dispersed pyrite, and on the other hand sulphates in gypsum/anhydrite deposits in the Northern Calcareous Alps. In Burgenland and northern Vorarlberg many samples show elevated values (2,500–7,500 ppm S) which could be caused by anthropogenic activities.

Sb – Antimony: number of analyses: 34,366; number of measurements above quantification limit: 6,382; minimum value: 0.025 ppm, maximum value: 180 ppm.

90 % of analytical results show Sb concentrations below the quantification limit. Therefore, no interpolated surface map was constructed. Values exceeding 8 ppm Sb in stream sediments (only 1 % of data) can be ascribed to stibnite deposits (at Schläining, Obertilliach, Rabant or Falggasanerbachtal) or to polysulphide mineralizations containing Sb-bearing sulphide copper ore.

Sc – Scandium: number of analyses: 34,304; number of measurements above quantification limit: 34,252; minimum value: 0.1 ppm, maximum value: 77 ppm.

Scandium is contained as a trace element in amphiboles, pyroxenes and biotite, and therefore associated with mafic rocks. Stream sediments originating from these rocks display concentrations of > 30 ppm Sc. Other crystalline rocks in the Austroalpine and Sub-Penninic nappes give rise to 15–30 ppm Sc in stream sediments. While samples from the Southern and Northern Calcareous Alps show the lowest values (< 5 ppm Sc), stream sediments from the Neogene and Quaternary sedimentary basins contain 5 to 15 ppm Sc.

Se – Selenium: number of analyses: 4,678; number of measurements above quantification limit: 4,375; minimum value: 0.025 ppm, maximum value: 22.1 ppm.

No data exist for the first phase of the Austrian stream sediment programme (Bohemian Massif and Central Alps) and construction of interpolated surface maps was omitted in these areas. Results from later sampling campaigns show Se concentrations ranging from 0.02 to 22 ppm Se. The spatial distribution of these values does not reveal any clear correlation with rock types or mineralizations. Elevated values (> 1.5 ppm) occur mainly in areas of intensive agriculture which could indicate a connection with fertiliser usage or other anthropogenic inputs.

Si – Silicon: number of analyses: 4,678; number of measurements above quantification limit: 4,678; minimum value: 0.09 %, maximum value: 39.36 %.

No data exist for the first phase of the Austrian stream sediment programme (Bohemian Massif and Central Alps). Results from later sampling campaigns show Si as the most abundant of all elements in stream sediments (up to 39 % Si). This is due to the fact that, except for carbonate areas, quartz constitutes the most common mineral. The spatial distribution shows the reciprocal patterns of calcium, i.e. low concentrations (< 15 % Si) in stream sediments from the Southern and Northern Calcareous Alps and high values (> 25 % Si) in samples from the Neogene and Quaternary sedimentary basins.

Sn – Tin: number of analyses: 34,219; number of measurements above quantification limit: 33,254; minimum value: 0.4 ppm, maximum value: 285 ppm.

Within the Bohemian Massif, high Sn concentrations (> 20 ppm Sn) in stream sediments are associated with greisen formation, i.e. hydrothermal alterations of granite intrusions in the northern Weinviertel. Spatial distribution patterns in stream sediments from crystalline rocks of the Austroalpine and Sub-Penninic nappes are not easily explained and will require additional rock geochemical data for interpretation. Isolated occurrences of small anomalies (> 20 ppm Sn) along major rivers (e.g. in the southern Vienna basin) may be the result of anthropogenic inputs.

Sr – Strontium: number of analyses: 34,304; number of measurements above quantification limit: 34,278; minimum value: 10 ppm, maximum value: 8,695 ppm.

Strontium appears as a trace element in calcite, gypsum and feldspars. High concentrations (> 500 ppm Sr) in stream sediments therefore occur in carbonate areas, even higher values (> 750 ppm Sr) are reached near gypsum/anhydrite deposits (e.g. Klostertal/Montafon, Grundlsee and western Drauzug). Moreover, some Austroalpine crystalline units give rise to elevated Sr concentrations (200–500 ppm Sr) in stream sediments if these units contain limestone or marble or rock types with Sr-bearing feldspars and mica.

Th – Thorium: number of analyses: 34,039; number of measurements above quantification limit: 21,441; minimum value: 2 ppm, maximum value: 1,919 ppm.

Since geogenic Th is mainly contained in heavy minerals, it correlates with cerium and lanthanum and elevated concentrations (30–150 ppm Th) in stream sediments are linked to catchments consisting of granites, granitoids and migmatites within the Bohemian Massif. In some granite areas, small anomalies even show concentrations of 150–650 ppm Th. In stream sediments of the Central Alps, generally low background values (< 25 ppm Th) are present and only occasionally do values reach 70 ppm Th.

Ti – Titanium: number of analyses: 34,341; number of measurements above quantification limit: 34,217; minimum value: 0.002 %, maximum value: 7.582 %.

This element is contained in rutile and titanite and as a trace element in amphiboles, pyroxenes and mica and therefore associated with mafic rocks. Consequently, elevated concentrations (1 %, occasionally even 2 % Ti) in stream sediments occur in catchment areas dominated by these rock types. Very low values (< 0.5 % Ti) are found in the Flysch zone, the Helvetic zone and the Southern and Northern Calcareous Alps. Equally low values occur in stream sediments originating from carbonate rocks in Engadin, Hohe Tauern and the Paleozoic of Graz.

U – Uranium: number of analyses: 34,042; number of measurements above quantification limit: 12,192; minimum value: 0.1 ppm, maximum value: 172 ppm.

75 % of uranium measurements of the first phase of the Austrian stream sediment programme (Bohemian Massif and Central Alps) fall below the quantification limit of that time (5 ppm U). Values are not comparable to data from subsequent sampling campaigns and interpolation

between data points was therefore not performed. Uranium is mainly associated with the heavy minerals xenotime, monazite and zircon. Elevated concentrations (up to 19 ppm U) in stream sediments in orthogneiss-dominated regions of the Austroalpine basement (in particular the Silvretta-Seckau and Ötztal-Bundschuh nappe systems). Within the Sub-Penninic nappes, local mineralizations in the central gneiss can give rise to high concentrations (up to 80 ppm U) in stream sediments. “Permoskythian” clastic rocks in the eastern Grauwackenzone also represent sources of uranium, yielding stream sediments with up to 20 ppm U. Finally, bituminous intercalations in the Hauptdolomit and its equivalent in the Gailtal Alps can cause elevated concentrations (up to 13 ppm U). Among the known uranium deposits, only the one in Forstau is manifested by elevated uranium concentrations in stream sediments (15 ppm U).

V – Vanadium: number of analyses: 34,306; number of measurements above quantification limit: 34,200; minimum value: 0.5 ppm, maximum value: 927 ppm.

This element occurs as a trace element in amphiboles, pyroxenes and mica and is therefore associated with mafic and ultramafic rocks. The spatial distribution of vanadium concentrations in stream sediments shows elevated values (90–150 ppm V) correlating with the occurrence of mafic rock types, and even higher values (> 200 ppm V) in catchment areas dominated by ultramafic rocks. Neogene sediments in the Northern Weinviertel or in the Styrian basin are derived from these rock types and therefore give rise to equally elevated values (up to 150 ppm V) in stream sediments. In the Southern and Northern Calcareous Alps as well as in carbonate areas within Austroalpine crystalline units, stream sediments contain low concentrations (< 50 ppm V).

W – Tungsten: number of analyses: 34,042; number of measurements above quantification limit: 15,567; minimum value: 0.1 ppm, maximum value: 2,693 ppm.

This element is predominantly contained in scheelite. If stream sediment samples are collected at places within the current where this mineral is particularly accumulated due to its high specific weight, the tungsten content can be overestimated. This is the case in the Austroalpine crystalline units and the Sub-Penninic nappes, where isolated anomalies with very high concentrations (> 70 ppm W) and areas with values below the quantification limit (1 ppm W) are juxtaposed. Furthermore, in areas sampled more recently no plausible spatial distribution was found. Therefore, no interpolated surface map of tungsten concentrations in stream sediments was constructed.

Y – Yttrium: number of analyses: 34,039; number of measurements above quantification limit: 33,019; minimum value: 4 ppm, maximum value: 2,055 ppm.

The occurrence of yttrium is linked to the presence of heavy minerals, in particular xenotime. The physics of heavy minerals transport leads to preferred deposition behind obstacles in the river bed, most notably in the smaller grain size fraction (< 0.04 mm). With respect to the coarser grain size fraction (< 0.18 mm), high yttrium concentrations (> 170 ppm Y) are restricted to samples from the Bohemian Massif, due to the fact that granites and migmatites abundantly contain Y-bearing heavy minerals and in situ

weathering increases this abundance in stream sediments. The lowest concentrations appear in stream sediments of the Southern and Northern Calcareous Alps (< 20 ppm Y), followed by the Molasse zone and intramontane basins (20–40 ppm Y). Sediments in large rivers of the Central Alps also show these values. In the Weinviertel and certain regions of the Upper Austrian Molasse Zone, where Neogene sediments are derived from the Bohemian Massif, concentrations can exceed 40 ppm Y in stream sediments.

Zn – Zinc: number of analyses: 34,340; number of measurements above quantification limit: 34,225; minimum value: 5 ppm, maximum value: 25,468 ppm.

Crystalline rocks of the Austroalpine nappes and the Bohemian Massif yield stream sediments containing very low concentrations (< 140 ppm Zn). Small areas with elevated values (up to 800 ppm Zn) are associated with sulphide deposits or Zn-bearing amphiboles, pyroxenes, micas or garnets in the catchments areas. Very high Zn concentrations in stream sediments appear in the vicinity of Pb-Zn-mineralizations in the Paleozoic of Graz (Frohnleiten – 4,200 ppm Zn), the Northern Calcareous Alps (Annaberg/Türnitz – 1,680 ppm Zn), in Drauzug (Bleiberg/Kreuth – 25,500 ppm Zn), in the Karawanks (2,600 ppm Zn) and the western part of the Northern Calcareous Alps in Tyrol (2,400 ppm Zn). Anthropogenic emission from industrial sites causes high values (up to 2,400 ppm Zn) in sediments of the rivers Ager, Traun and Traisen, as well as in stream sediments within Marchfeld and south of Vienna (up to 1,400 ppm Zn). Smelting and metal processing near Arnoldstein also affects Zn content in stream sediments (13,500 ppm Zn).

Zr – Zirconium: number of analyses: 34,039; number of measurements above quantification limit: 33,953; minimum value: 10 ppm, maximum value: 9,820 ppm.

The occurrence of Zr is linked to the presence of heavy minerals, in particular zircon. The physics of heavy minerals transport leads to preferred deposition behind obstacles in the river bed, most notably in the smaller grain size fraction (< 0.04 mm). With respect to the coarser grain size fraction (< 0.18 mm), high Zr concentrations (> 750 ppm Zr) are restricted to samples from the Bohemian Massif, due to the fact that granites and migmatites abundantly contain Zr-bearing heavy minerals and in situ weathering increases this abundance in stream sediments. The lowest concentrations appear in stream sediments of the Southern and Northern Calcareous Alps (< 100 ppm Zr), followed by slightly higher values in the Molasse zone and in intramontane basins (100–400 ppm Zr, occasionally rising to 3,000 ppm Zr). Sediments in large rivers of the Central Alps also show these slightly higher values.

Results and discussion of accompanying measurements and analyses

During the second phase of the Austrian stream sediment geochemistry programme, measurements of temperature, electrical conductivity, pH and redox potential in the stream and in the water-saturated sample accompanied the sampling. The data can be used to check whether stream and sediment were interacting, or were uncoupled, at the time of sampling. In the latter case, readings in the stream and the sediment of e.g. pH or redox potential dif-

fer significantly, indicating that the sample does not represent active sediment but material deposited during the last flood event. Analytical results in this case still reflect the chemical make-up of the provenance area but the potential of contaminant emission can be modified due to rapid changes of pH and redox potential during flooding. Particularly in the Upper Austrian Molasse zone, the Weinviertel and the Vienna basin, this uncoupling occurs in many rivers and leads to negative values of redox potential in the sediment while the stream water shows positive values.

Despite variable weather conditions during sampling, the spatial distribution of electrical conductivity coincides with known trends in surface water hydrochemistry. A low degree of mineralization, or a small value of electrical conductivity (< 250 $\mu\text{S}/\text{cm}$), is typical for stream waters in the Central Alps, slightly more elevated values (250–400 $\mu\text{S}/\text{cm}$) appear in the Southern and Northern Calcareous Alps. The Upper Austrian Molasse zone and the Styrian Neogene basin exhibit yet higher values (400–900 $\mu\text{S}/\text{cm}$) while the highest degrees of mineralization exist in Weinviertel and Northern Burgenland (900–3,000 $\mu\text{S}/\text{cm}$).

Applications of results

The present publication constitutes a documentation of the Austrian stream sediment geochemistry programme, including project organisation, sampling and analytical methods, and presentation of the data which resulted from this programme. The data can now serve for further environmental or geochemical studies. It can be combined with other data sets, e.g. soil geochemistry, hydrochemistry or mineralogical analyses to study the source and fate of chemicals in the environment. Future statistical or regional analyses of the data can assist in discriminating between natural occurrences of elements and human-induced contamination. The following paragraphs summarise five examples of data applications in the field of environmental geochemistry, described in detail in chapters 7.1–7.5.

Chapter 7.1 presents a discussion of several methods to estimate litho-geochemistry and derive natural background levels from stream sediment data. Methods of constructing surface maps of element concentrations through interpolation between sampling points are shown to be useful for visualising regional trends but not for quantifying element concentrations of specific rock types in the catchment areas. The GIS method of spatially joining sampling points to polygons on digital geological maps is shown here to be an easy way to link stream sediment data to rock units, but this method will yield correct results only where catchment areas are composed entirely of the rock type identified by the point-polygon superposition. The best results are shown to be gained when catchment areas are delimited for each sampling point through the use of GIS and only lithologically homogeneous areas are used for attributing stream sediment geochemistry to rock types. This method yields adequate estimates of whole rock geochemistry and is, in the absence of anomalies due for example to mineral deposits or anthropogenic contamination, well suited to deriving natural background levels. As an application of this method, examples are given from Carinthia (SCHEDL et al., 2008) and Styria (SCHEDL et al., 2010b).

Chapter 7.2 gives an example of multivariate logratio statistics performed on a subset of stream sediment geochemical data in the Weinsberg granite area of the Bohemian Massif. Variability of element logratios is shown to reflect changes in the chemical composition due to weathering, transportation and sedimentation processes. K-feldspars appear to better withstand chemical weathering since Al to K logratios show very small variability among all samples (variance of $\ln(\text{Al}/\text{K})$: 0.044). In contrast, plagioclase is less resistant to weathering and Ca to K logratios vary widely (variance of $\ln(\text{Ca}/\text{K})$: 0.409). Subsequently, robust principal component analysis (PCA) of compositional data was performed on main and trace element concentrations and presented using compositional biplots. Among the main elements, principle components were dominated by K, Al, Mg and Ti, while among the trace elements Ce, La and Zr represent dominant vectors on the biplot. The latter three elements also emerged when PCA was performed on all elements combined. This was interpreted as an indication that the concentrations of these trace elements result more from transport and sedimentation processes than from the mineral composition of the parent rock. Finally, principal component scores were imported into a GIS and plotted as point symbol maps. Within the distribution of the second principle component of main element PCA, a regional pattern appears whereby negative factor loadings (low Mg concentrations) are concentrated in the central part of the Weinsberg granite area where relief energy is high.

Chapter 7.3 presents examples from studies which combined stream sediment data with data from soil monitoring programmes, hydrochemical analyses of stream and spring waters and whole rock geochemistry to develop models for element exchange between rocks, soils and groundwater. One such study (PIRKL, 1993) combined soil geochemistry, stream sediment geochemistry and hydrochemical data to reveal transfer pathways of chromium in Krappfeld (Carinthia) where naturally elevated Cr concentrations were overprinted by emissions from a metal recycling plant. Micro-chemical – mineralogical phase analysis of chromium minerals allowed the differentiation of geogenic and anthropogenic sources. A second study (PIRKL, 1999) identified specific element fluxes between the atmosphere, vegetation, soil, aquifer and spring water in an area of the Northern Calcareous Alps, resulting in a qualitative model of the main transfer pathways. With respect to heavy metals, Pb and Cd were shown to be introduced into the soil at least partly through atmospheric deposition, while transfer into the groundwater was demonstrated for Pb, Cd, Cr, Cu and Ni. A third study (NEINAVAIE et al., 2001) focussed on the sources and transfer of heavy metals in the area of an abandoned mining site in the Kitzbühel Alps. Due to natural mineralization, the elements Ag, As, Cu, Hg, Ni, Sb and Zn are highly concentrated in this area.

While As and Cu were shown to resist weathering, Hg, Ni, Sb and Zn dissolve easily and end up contaminating the soils and groundwater. Milk and cheese derived from cows grazing on contaminated soils are however not affected. Finally, a nation-wide study on mine waste (SCHEDL et al., 2012) combined mining and mine waste data with environmental geochemistry data, and issued a list of heavy metal emission risks for specific abandoned mining areas in Austria.

Chapter 7.4 compares spatial distribution patterns of element concentrations in the stream sediments, overbank sediments and soils of Carinthia and Styria. In data from the Carinthian soil inventory, high lead content (> 120 ppm Pb) in soils appears in approximately the same areas as anomalies in stream sediments, and are either locally associated with former mining areas or situated along river valleys downstream of mining areas. Additional sampling and chemical analyses of overbank sediments along the rivers Gailitz, Gail and Drau corroborate these patterns. Even though these data are derived from different material using different analytical methods, the emerging regional patterns still coincide to a great extent. Regarding the Styrian soil inventory, data of cadmium concentration in soils display the same spatial distributions as those of stream sediments, concerning areas of low values (in the Central Alps) as well as local anomalies with elevated values (e.g. near Pb-Zn-mineralizations of the Paleozoic of Graz and in regions of the Northern Calcareous Alps).

Chapter 7.5 presents micro-chemical – mineralogical phase analyses of the heavy mineral fraction of stream sediments to pinpoint the source minerals of e.g. tungsten, but also analyses of soil or dust samples to distinguish between geogenic and anthropogenic sources of trace elements. Using incident and transmitted light microscopy as well as microprobe and reflection electron microscope, these analyses can assess trace element concentration and mobility. In addition to purely geochemical investigations, they are applied in environmental studies around industrial sites, assessments of old waste sites, risk evaluation of mine waste sites and for the identification of emitters. A digital atlas of mineral phases has been published (NEINAVAIE et al., 2008) which contains 546 geogenic and technogenic mineral phases documented by 4,729 photos. Chapter 7.5 gives examples of mineral phase analyses of stream sediment samples which prove particle emissions of the iron and steel industry along the rivers Mürz and Mur in Styria, or near Hüttenberg and Friesach-Olsa in Carinthia. Typical particles represent sinter, slag or cast iron particles, or globular particles from high-temperature applications. Other particles originate from coal-fired power stations, glass production plants, sinter plants or cement factories as emission sources. A compilation of mineral phases and their possible trace element content, published previously by PIRKL & NEINAVAIE (2002), is given.