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Modern fluvial sediment provenance and pollutant tracing: a case study from the Dřevnice River Basin (eastern Moravia, Czech Republic)

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Abstract: Modern fluvial deposits of a small fluvial system were studied in the area of eastern Moravia (Czech Republic) with the aim of determining the provenance of the deposits and weathering processes. Identification of the source rocks and their alongstream variations were used for the evaluation of the natural or anthropogenic source of the heavy metals. Paleogene flysch sandstones, flysch mudstones and Quaternary loesses represent source rocks and reflect both the role of recycling and local sources. Provenance from sandstones dominate upstream whereas mudstones represent dominant source rock in the downstream part of the fluvial system. The contents of Pb and Zn are highly enhanced when compared with the natural background in the entire study area. Their anthropogenic source is connected with the rubber/shoe manufacturing industry and traffic. The contents of Cr, Co, Cu, Ni and V are usually lower in modern deposits than in the identified source rocks.

Key words: Quaternary, heavy metals, natural and anthropogenic source, small river system.

Introduction

Fluvial deposits are the principal source of information regarding terrestrial processes. Modern fluvial sediments particularly in industrial areas provide numerous data about the impact of human activities on natural systems. Changes in fluvial and sediment discharge, the availability and character of eroded material and anthropogenic material production are obliterating natural environments and their characteristics. The content of hazardous components/pollutants represents strategic information for the quality of environment and sediment management. Whereas some of these components (DDT, POP's) are clearly anthropogenic in origin, certain others (heavy metals) can be both natural and anthropogenic. In such cases, not only the information on concentration of components but also their source, represent the principal information for environmental studies.

The provenance of clastic sediments includes all aspects of the drainage area (source lithology, topographic relief, climate, transport energy and deposition environment hydrodynamics), although the source lithology is the most important parameter (Johnsson 1993; Sensarma et al. 2008). The data obtained by the provenance analysis of the sediments is mainly used for: i) information about weathering processes, ii) discriminating the paleogeographic and tectonic context of the deposition, iii) describing diagenesis conditions, iv) highlighting differences between individual depositional units (McLennan et al. 1993; Young & Nesbitt 1998; Singh & Rajami 2001; Zimmermann & Bahlburg 2003; Passchier & Whitehead 2006; Borges & Huh 2007; Barbera et al. 2009). In addition, the application of the techniques and methods of provenance analysis can be used for the evaluation of the natural or anthropogenic origin of possible mineral components and their fate in the deposition system.

The majority of provenance studies are focused on large river deposits. Since large rivers often drain highly variable source rocks and their deposits reveal a complicated reworking history, the precise recognition of the source rocks could not be obtained unequivocally (White & Blum 1995; Nesbitt et al. 1996; Sensarma et al. 2008). For this reason the presented study is oriented to a small river system that drains few rock types, so that the nature of the source material is better constrained. The textural, mineralogical and geochemical composition (major and trace elements) of the modern fluvial sediments were compared with possible source rocks in order to obtain information about: i) the provenance of the modern deposits, ii) the weathering processes in the source area, iii) the distribution/redeposition of the eroded material within the fluvial system, iv) the natural vs. anthropogenic source of the heavy metals.

Geological and geomorphological settings

The study area is located in the eastern part of the Czech Republic in the broader surroundings of the city of Zlín (Fig. 1). The area is strongly affected by both agriculture and industry. The area is mainly formed by deposits of the Rača Unit of the

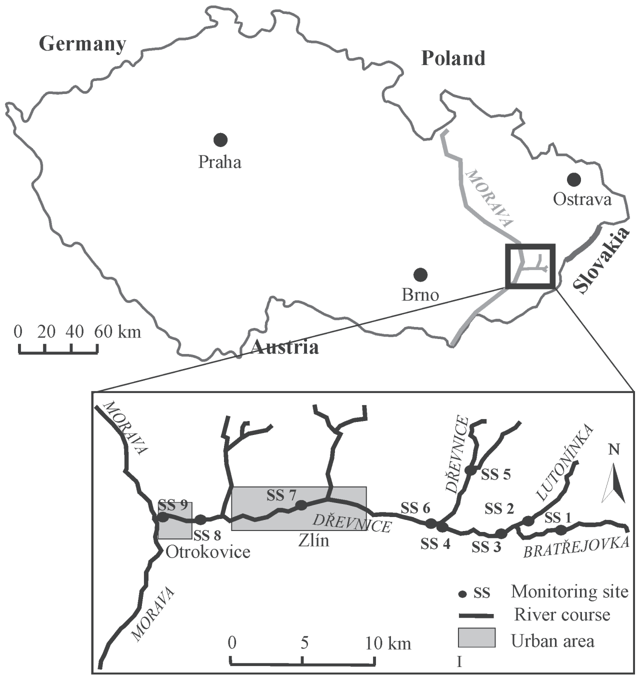

Fig. 1. Schematic map of the area under study with the location of the monitoring sites.

Magura Group of Nappes (Western Carpathian Flysch Belt see Fig. 2). The Rača Unit (Upper Cretaceous to Oligocene) is represented predominantly by the Zlín Formation, whereas the deposits of the Soláň and Belověž Formations play a minor role. The Zlín Formation can be subdivided into the Újezd and Vsetín Member. The Újezd Member (Late Eocene–Early Oligocene) is characterized as rhythmic flysch with predominance of arcosic sandstones and subordinate beds of grey-green mudstones. The Vsetín Member (Middle Eocene–Early Oligocene) is rhythmic flysch with dominance of grey, calcareous mudstones with subordinate beds of fine-grained glauconitic sandstones (Pesl 1968; Stráník et al. 1993). The Soláň Formation (Senonian–Paleocene) can be subdivided into the Ráztoka and Lukov Member. Rhythmic alternations of sandstone and mudstone beds are typical for the Ráztoka Member. Rhythmic flysch with absolute dominance of sandstones (arcoses, greywackes) and conglomerates represents the Lukov Member. The Belověž Formation (Paleocene–Middle Eocene) is represented by rhythmic deposits with a predominance of green-grey and reddish mudstones. Flysch rocks are often covered by younger deposits. The areal extent of the Neogene clays is extremely limited. The Quaternary sediments are more abundant, being represented by a wider spectrum of rocks. Loesses, blown sands, sandy alluvial fans, anthropogenic, fluvial (muddy sands, sands, sandy gravels), deluviofluvial, deluvial (muddy sandstones), proluvial deposits (muddy gravels) have all been documented (Pesl 1982; Novák 1994; Havlíček 2001).

The erosive-denudation relief of the Zlínska vrchovina Highland (the average height above sea level 354.2 m, the average angle of the slope 6° 11′) was formed within the substrate. Broad flat elevations and shallow widely open asymmetric depressions are typical (Demek 1987). The relatively broad river valleys are cut by numerous transverse erosive short depressions with active small alluvial fans, ravines, and slope instabilities (Jinochová 1996; Kašpárek 1997). The Dřevnice, Bratřejovka and Lutonínka Rivers drain the area. The smallest of them is the Bratřejovka River which springs at an altitude of 520 m a.s.l. Its river basin has an extent of 32.1 km^2 with the average discharge at the river mouth being 0.31 m^3/s. The Bratřejovka River flows into the Lutonínka River at an altitude of 290 m a.s.l. The Lutonínka River springs at an altitude of 540 m a.s.l. Its river basin has an extent of 89.3 km^2 and a course length of 15.3 km. The average discharge at the river mouth is 0.89 m^3/s. The Lutonínka River flows into the Dřevnice River at an altitude of 245 m a.s.l. The Dřevnice River springs at an altitude of 510 m a.s.l. Its river basin has an extent of 434.6 km^2. The length of the river course is 42.3 km and the average discharge at the river mouth is 3.15 m^3/s. The Dřevnice River flows into the Morava River at an altitude of 182 m a.s.l. (Vlček 1984).

Maximum discharges during the 10-year period were 195 m^3/s for the Dřevnice and 21.7 m^3/s for the Lutonínka Rivers. The minimum discharge values were 0.14 m^3/s and 0.02 m^3/s, average discharge values 2.4 m^3/s and 0.54 m^3/s, respectively. The actual daily values vary in orders of magnitude of 3 to 4 during year. Daily discharge measurements from the 10-year period (1997–2006) were acquired from the Czech Hydrological Institute. The gauging stations are at Zlín (Dřevnice River, close to the sampling site 8) and Vizovice (Lutonínka River, close to the sampling site 3). Strong seasonal trends and variability in discharges with similar seasonal trend, that is noticeable differences between spring and autumn periods can be found (see Fig. 3). Arrows show sampling events in spring and autumn 2005 and 2006 that fall into typical periods with higher (spring) and low (autumn) discharge stages. The differences between spring and autumn periods are typical for rivers in drainage basins in a humid climate, with maximum discharge values appearing in longer periods following snow melting and in short periods following summer thunder storm events.

Sampling and analytical techniques

Modern fluvial deposits were sampled at 9 sampling sites (SS) located within the courses of the rivers Bratřejovka, Lutonínka and Dřevnice (Fig. 1). The uppermost bottom layers of the river bed (max. 10 cm thick) within the active river channel were sampled manually over four successive sampling seasons (i.e. May and September 2005 and 2006).

Combined sieving and laser methods were used for the grain size analysis. A Retch AS 200 sieving machine analysed the coarser grain fraction (4 mm–0.063 mm, wet sieving), whereas a Cilas 1064 laser diffraction granulometer was used for the finer one (0.0004–0.063 mm). Ultrasonic dispersion, distilled water and sodium polyphosphate were used prior to analyses in order to avoid a flocculation of particles. The graphic mean (Mz) and inclusive standard deviation (σI) were used to demonstrate the average grain size and sediment sorting (Folk & Ward 1957).

Fig. 2. Simplified geological map and stratigraphic chart of the area under study — according to Novák (Ed.) (1994), Pesl (Ed.) (1982), and Müller (2001).

The gravel mineral composition (the grains >2 mm in diameter) was studied under a binocular microscope. Geochemical methods were used for the bulk-rock composition of a finer fraction. Dry sediments were homogenized, ground with a pestle and mortar and sieved using a 2 mm sieve. The sample was melted with a lithium tetraborate/metaborate mixture (Spectromelt A12, Merck) and dissolved in diluted nitric acid. The main oxide components of silicate matrix (Li_2O, Na_2O, K_2O, MgO, CaO, Fe_2O_3, TiO_2, Al_2O_3, SiO_2, P_2O_5 and SO_3) were determined by ICP-OES (Jobin-Yvon 170 Ultrace, JY-Horiba, France). The total heavy metal content (As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V, Zn) was determined by sample dissolution and by analysing the solution obtained. The ISO 14869-1 procedure was used for the silicate matrix decomposition in an open vessel system by a mixture of hydrofluoric and perchloric acid. 1 g of the pulverized sample was used for the dissolution and the sample solution was diluted adequately prior to analysis. ICP-MS (Agilent 7500ce, Agilent Technologies, Japan) was used for the determination of heavy metals. The elements suffering from polyatomic interferences were measured in a He collision mode using the Octopole Reaction System. Internal standards (Ge, In, Bi) were applied in order to eliminate the matrix effect. The total content of mercury was determined by the thermooxidation method using an AMA-254 analyser (Altec, Czech Republic). The accuracy of the methodology was verified by an analysis of the soil certified reference materials (ANA 7001–7004, Analytika Prague, Czech Republic).

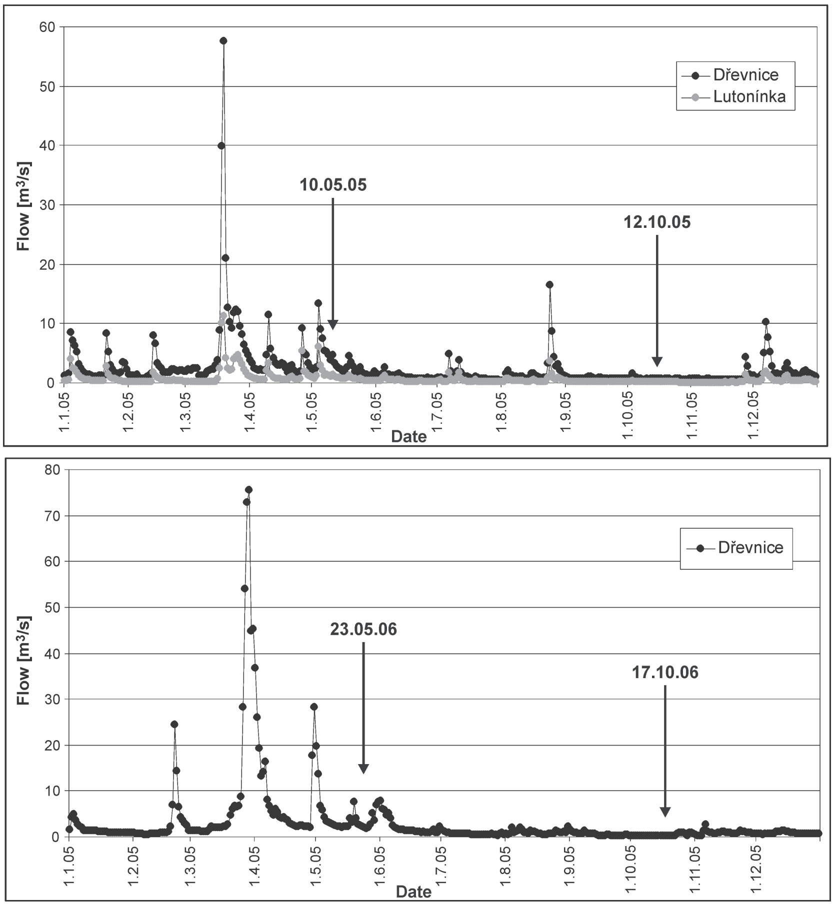

Fig. 3. Fluvial discharge for Dřevnice and Lutonínka Rivers in the years 2005 and 2006. Arrows show sampling events in spring and autumn 2005 and 2006, respectively.

The mineralogy of the clay fraction of modern deposits was evaluated by RTG diffraction at Stoe Stadi P. diffractometer. Measurement conditions: Co-Kα_1 radiation (1.78896 Å), accelerating voltage 40 kV, beam 30 mA, reflection mode, linear PSD detector, step in 0.01 2Θ, counting time of 3 s. Low content of clay fraction in the studied sediment led to RTG quantitative phase analyses.

The source rock samples were analysed in the laboratories of the Czech Geological Survey Prague. The complete silicate analysis (oxides of major elements and certain minor elements) and a standard set of trace elements were determined by X-ray fluorescence (fm. Philips PW1410) and emission spectral analysis (spectrograph fm. Zeiss). The mineral composition was determined by X-ray diffraction analysis (complemented by automatic diffraction phase analyses); the results were compared with those obtained by a differential thermal analysis. Due to the highly varying carbonate content and absence of CO_2 data, a precise correction for the carbonate CaO was difficult for the chemical index of alternation (CIA index — Young & Nesbitt 1998). After correcting for P_2O_5 (apatite), the value of CaO is consequently accepted if the mole fraction of $CaO \leq Na_2O$. However, if $CaO \geq Na_2O$, then it was assumed that the moles of $CaO = Na_2O$ (McLennan 1993; Bock et al. 2008). The Vsetín, Újezd, Ráztoka, and Lukov Flysch Sandstones are denoted as VFS, UFS, RFS, and LFS, respectively. The Vsetín, Újezd, Ráztoka, Lukov, and Bělověž Flysch Mudstones are denoted as VFM, UFM, RFM, LFM, and BFM, respectively. Quaternary Loesses are denoted as QL.

Results

Grain size

The distribution of the individual particle size classes of the studied samples is presented in Table 1. Sand and silt predominate in the majority of the studied samples. Based on Folk (1968), the sediments were classified as sands (33.3 %), silty sands (27.8 %) or sandy silts (22.2 %). Sandy gravels (11.1 %) and silts (5 %) are less frequent. The gravel content is mostly negligible apart from some SS (typically 3). The content of clay fraction is relatively low and slightly rises downstream. The graphic mean varies between –1.5 and 6.3 ϕ, but mostly between 2.8 and 4.9 ϕ (72.2 %). The σI values varied between 1.3 and 3.5 ϕ, which indicates poor to extremely poor sorting. The samples with a higher value of Mz are generally better sorted than the samples with a lower value. The grain size of samples from the spring and autumn seasons are usually similar with respect to individual SS. The along stream variation is better developed in the spring samples when slightly finer grained spring sediments were recognized in most upstream SS and coarser grained deposits in most downstream SS. The downstream fining of the studied deposits can be accepted when taking into account the confluences (Fig. 4). Additional/transverse sources of material (bank erosion, transport from the adjacent slopes or ravines) to the main axial fluvial drainage are supposed close to the monitoring sites 3, 9. Deposits of Holocene alluvial fans were recognized adjacent to these monitoring sites. Additional provenance from these deposits and so an important role of local sources is supposed. Torrential water from the summer storms can transport the coarser material from adjacent slopes to the river course and accentuate the additional/transverse source of sediment at selected localities.

Gravel petrography

Three different types of material were recognized: (i) anthropogenic material (fragments of glass, bricks, concrete, asphalt, plastics), (ii) organic material (plant detritus, seeds), and (iii) rock debris (predominantly sandstones, conglomerates, quartzes, limestones, mudstones, exceptionally gneisses or granitoids). The content of these materials differs both areally and seasonally (Fig. 5). The organic material completely predominates in certain SS (typically 1, 6, 7, 8) and is usually more common during the autumn. A higher content of anthropogenic material is typical for downstream samples (usually SS 6–9) and its content seems to be enhanced in the spring. An absolute dominance of rock debris can usually be observed in SS 3 and 5, whereas it is absent or very low downstream (particularly SS 6–8). The content of the organic material is generally higher in finer-grained fraction, whereas a coarser content typically reveals a higher presence of rock debris and anthropogenic material (Fig. 6A,B,C).

Clay mineralogy

Significant differences in mineralogy existed between the results from individual monitoring sites from the single sampling season and also different seasons. Semiquantitative evaluation of all studied samples is presented in the Table 2. Individual minerals were evaluated by numbers to reflect their relative occurrences (0 — not present, 1 — very rare, 2 — rare, 3 — medium, 4 — abundant, 5 — very abundant).

Quartz is the most abundant mineral. Content of illite and kaolinite is relative stable. Significant variations can be followed in the role of smectite. Significant differences can also be followed for the content of chlorite. The content of feldspar also varies. Presence of feldspar is in general relatively lower in the autumn samples (compared with the spring ones). Presence of plagioclase is usually more important than the presence of feldspar (Dosbaba 2008).

Major elements

The major elements for the sediments are given in Table 3. The SiO_2 content ranges widely from 60.7 to 83.7 wt. % and is consistent with site lithologies (Fig. 7A). The main element content reveals both areal and seasonal variations with an inverse dependence on grain size (particularly for K_2O, Na_2O, MgO, Al_2O_3, Fe_2O_3, and TiO_2 — Fig. 7B–D). The grain size effect on chemical composition suggests SiO_2/Al_2O_3–Na_2O/K_2O diagram (Fig. 7E) (see Ohta 2008).

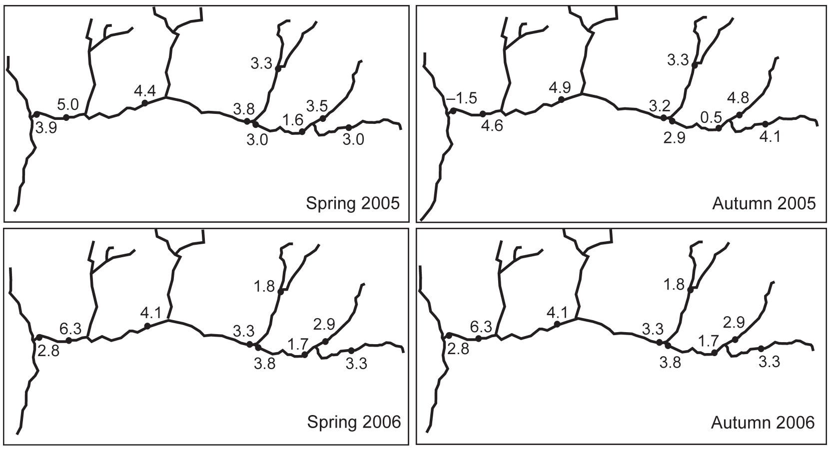

Fig. 4. Areal distribution of the graphic mean (Mz) for the deposits in the studied monitoring sites. The values are in Φ units.

Table 1: Characteristics of sites — grain-size characteristics of the studied modern fluvial deposits.

Site code	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Mud (%)	Mz (Φ)	(σI)
	Median (Minimum–Maximum)						
SS 1	4.3 (3.6–7.4)	59.2 (55.5–70.1)	30.9 (20.2–31.9)	5.6 (4.0–7.5)	35.8 (25.5–39.4)	3.4 (3.0–4.1)	2.6 (2.4–2.8)
SS 2	1.4 (0.1–4.5)	69.7 (39.8–72.6)	23.1 (18.5–52.0)	5.9 (4.4–7.9)	29.0 (22.9–59.8)	3.2 (2.8–4.8)	2.4 (2.0–3.4)
SS 3	19.4 (4.2–30.4)	71.8 (64.6–85.1)	7.3 (4.1–8.6)	1.5 (0.9–2.1)	8.8 (5.0–10.7)	1.0 (0.0–1.7)	2.0 (1.3–2.2)
SS 4	3.1 (1.1–3.9)	61.4 (43.9–74.2)	30.3 (18.6–48.4)	5.0 (3.8–6.6)	35.3 (22.4–55.0)	3.4 (2.9–4.3)	2.4 (2.3–2.7)
SS 5	10.1 (0.1–49.8)	67.4 (39.9–75.7)	18.0 (8.3–22.5)	3.4 (1.6–4.0)	21.8 (9.9–25.7)	2.6 (–0.1–3.3)	2.4 (1.9–3.4)
SS 6	1.4 (0.4–2.4)	68.6 (62.3–72.2)	23.5 (18.6–32.9)	3.4 (3.3–4.4)	26.8 (22.1–37.3)	3.4 (3.2–3.8)	2.2 (2.0–2.3)
SS 7	1.0 (0.5–1.5)	48.2 (32.2–59.7)	45.6 (35.7–60.2)	4.7 (4.0–7.1)	50.4 (39.7–67.3)	4.3 (3.8–4.9)	2.0 (1.9–2.1)
SS 8	0.2 (0.0–0.8)	23.6 (13.3–40.9)	66.3 (50.9–72.6)	8.7 (6.9–16.9)	76.2 (58.3–86.7)	5.3 (4.6–6.3)	1.9 (1.8–2.2)
SS 9	9.4 (1.2–62.2)	38.1 (31.7–64.0)	36.4 (5.6–47.5)	4.9 (0.6–9.8)	41.4 (6.1–57.3)	3.4 (–1.5–3.9)	2.5 (2.1–3.5)

Table 2: Semiquantitative mineralogy of the clay fraction of the studied sediments.

Mineral	Spring 2005	Autumn 2005	Spring 2006	Autumn 2006
Smectite	3.3	4.3	2.1	2.4
Chlorite	1.7	1.3	2.2	1.4
Illite	4.0	3.5	3.9	3.7
Kaolinite	3.0	3.2	2.8	2.9
Quartz	5.0	4.7	5.0	5.0
Feldspar	2.3	1.2	2.1	1.4
Plagioclase	2.0	1.8	3.0	2.6

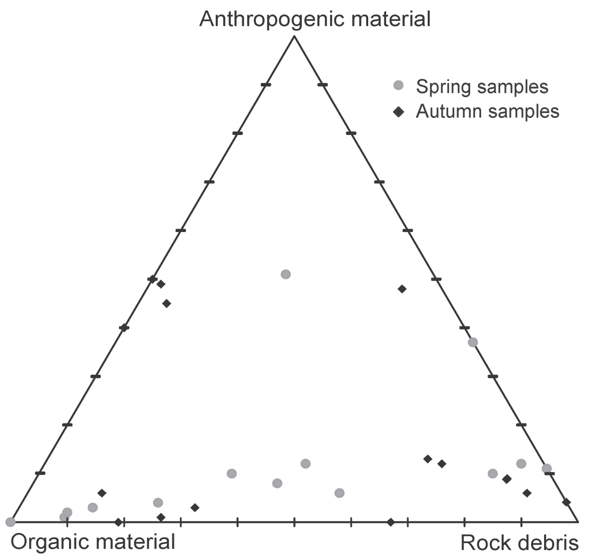

Fig. 5. Composition of the gravelly grain size fraction (2–8 mm) of the studied sediments.

The positive inter-relationship amongst Al_2O_3 and TiO_2 is well developed (Fig. 8A). A diagram of Al_2O_3 vs. TiO_2 and the Ti : Al ratio were used for studies of the provenance and weathering extent (Young & Nesbitt 1998). The Ti : Al ratio for the studied samples varies between 0.12 to 0.17 and is generally higher downstream. A negative correlation between TiO_2 and SiO_2 is generally supposed (Fig. 8B). K_2O/Al_2O_3 ratio is between 0.17–0.29 and its relation to grain size is complex (Fig. 8C). The coarser samples (Mz below 3 ϕ) and the finer ones (Mz above 3 ϕ) seem to form two subpopulations in the diagram.

The deposits can be classified as lithic arenites, apart from several which are sublithic arenites and wacke (see Fig. 8D according to Herron 1988). The content of total alkali is relatively low. Alongstream, irregular variations in the content of the major elements are developed (Fig. 8E–H). A decline in the SiO_2 content can usually be observed between the SS 3–4 and 6–8 and an increase at SS 3, 5 and 8. The opposite trend, namely a rise between the SS 3–4 and 6–8 and a decline at SS 3 and 9 can often be seen in the content of K_2O, Na_2O, CaO, MgO, Al_2O_3, TiO_2 and Fe_2O_3. These trends are slightly obliterated by seasonal variations. The upstream sediments could be slightly higher with an abundance of K_2O, Na_2O, CaO, MgO, Al_2O_3, TiO_2 and Fe_2O_3, and lower in SiO_2. An inverse relation between the grain size and the Ti : Al ratio can be observed (Fig. 9).

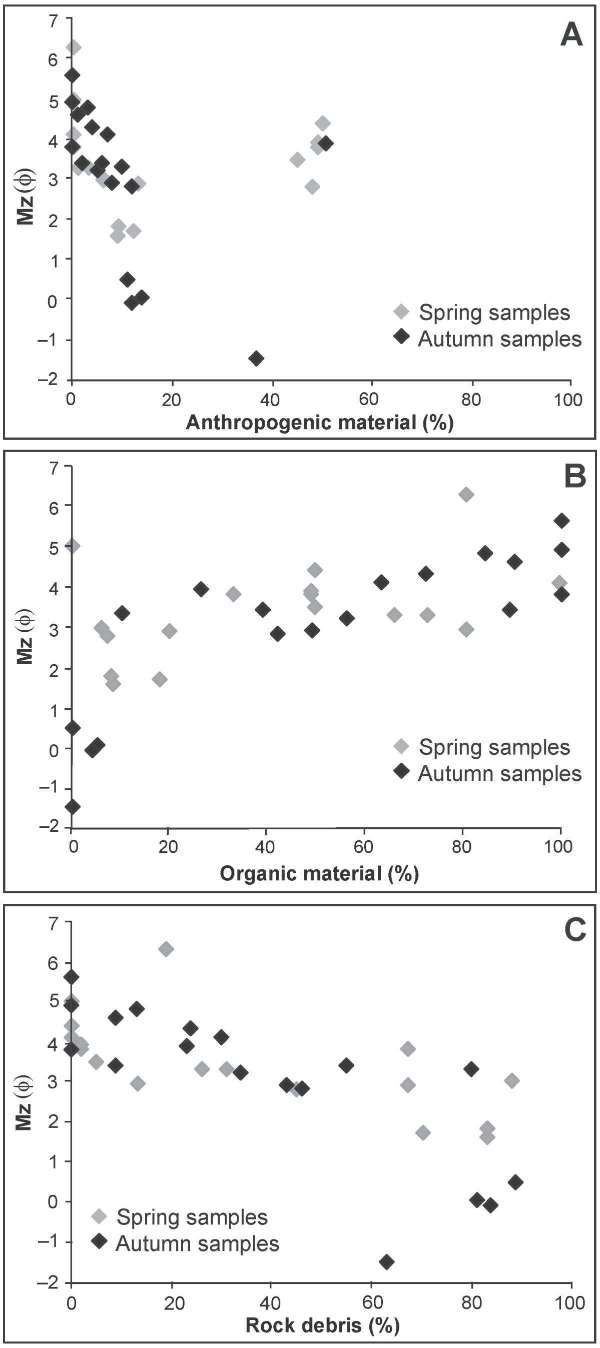

Fig. 6. Relations of the graphic mean Mz and: **A** — the content of anthropogenic material in gravel fraction, **B** — the content of organic material in gravel fraction, **C** — the content of rock debris in gravel fraction.

Provenance

The chemical composition of clastic sediments is a result of a number of geological factors (source rock composition, chemical weathering intensity, sediment supply rate, and textural/mineralogical/hydraulic sorting) (Johnsson 1993; Cox & Lowe 1995; Sensarma et al. 2008).

The value of the ratio K_2O/Na_2O (Roser & Korsch 1986) for the studied sediments varies between 2.55 and 4.71. This

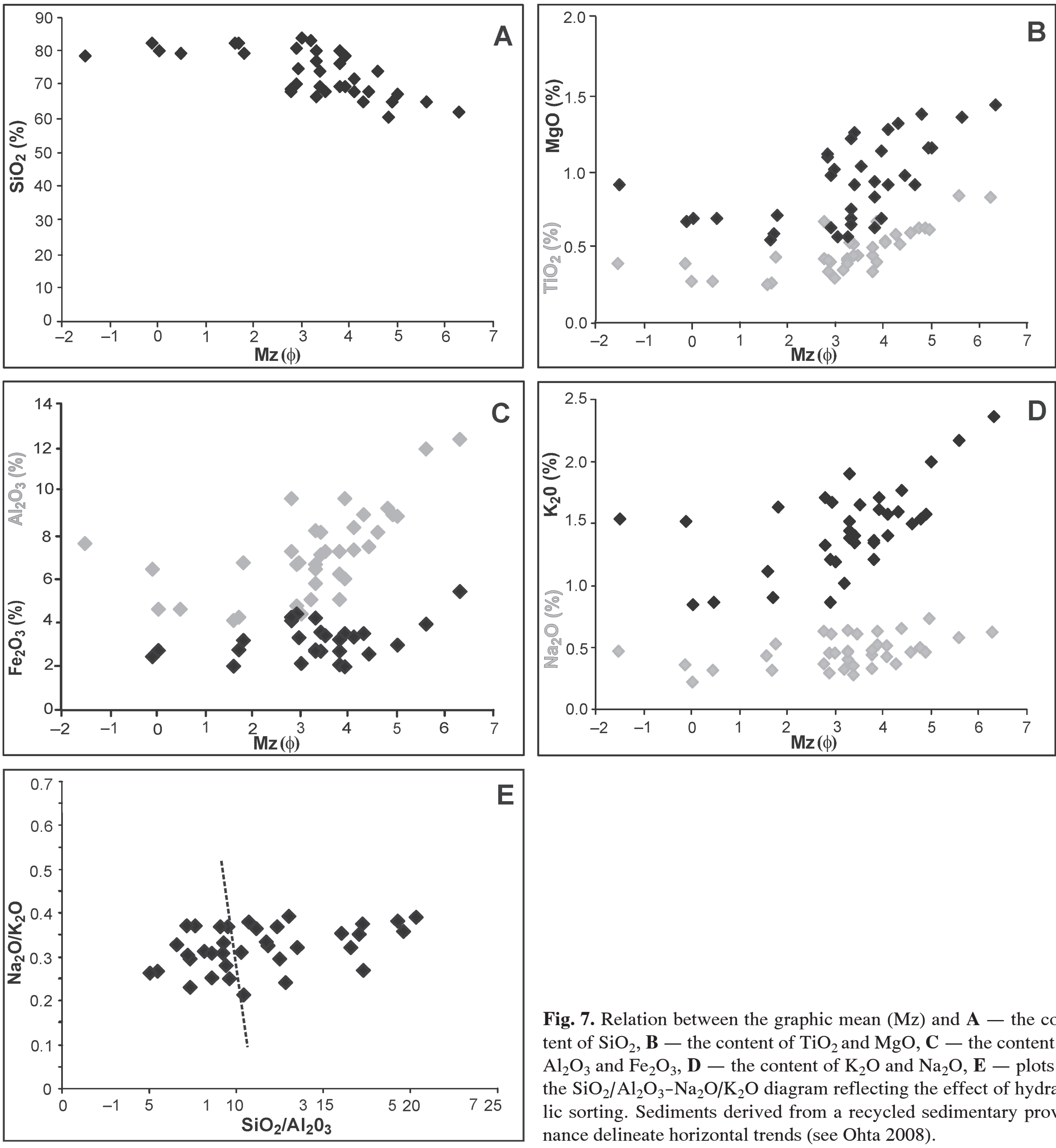

Fig. 7. Relation between the graphic mean (Mz) and **A** — the content of SiO_2, **B** — the content of TiO_2 and MgO, **C** — the content of Al_2O_3 and Fe_2O_3, **D** — the content of K_2O and Na_2O, **E** — plots of the SiO_2/Al_2O_3–Na_2O/K_2O diagram reflecting the effect of hydraulic sorting. Sediments derived from a recycled sedimentary provenance delineate horizontal trends (see Ohta 2008).

high value reflects a derivation from the recycled sedimentary sources (McLennan et al. 1993; Bock et al. 1998).

A multivariate cluster analysis (Ward's method as an algorithm) was applied to compare the chemical composition of the source rocks and the sediments (Fig. 10). Ten major/minor elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and seven trace elements (Cr, Cu, Ni, Pb, Zn, V, Co) were considered. Based on the analysis, the samples were clustered into two principal groups. The first one (see the group on the left side in Fig. 10) linked 12 sediments to the source flysch mudstones (RFM, BFM, LFM, VFM, UFM). The second group linked the remaining 24 sediment samples to the source flysch sandstones (VFS, UFS, RFS, LFS). Of these 24 samples, 11 sediments were more tightly associated with the source Quaternary loeses (QL), see the subgroup separated from the second group on the right side of Fig. 10. In the single groups, the sediments of all the seasons were mixed (Table 4). The chemical compositions of the potential source rocks are presented in Table 5a,b.

With respect to the SS, the sediments of the first group with the source mudstones were particularly dominant downstream (particularly on SS 7 and 8). The sediments with the source sandstones mainly predominate upstream (SS 1, 2 and also 5). The loesses source is typical for the middle part of the area (SS 3, 6, 4).

The studied sediments were plotted onto the Al_2O_3–$(CaO+Na_2O)$–K_2O diagram (Fig. 11A), the A–CN–K in the

Table 3: Characteristics of sites — sediment major element composition.

Site code	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	LiO_2 (%)	MgO (%)	MnO (%)	Na_2O (%)	TiO_2 (%)	P_2O_5 (%)	SiO_2 (%)
	Median (Maximum–Minimum)										
SS 1	7.81 (6.71–8.31)	3.72 (4.08–3.23)	3.73 (4.25–3.23)	1.50 (1.68–1.41)	0.01 (0.02–0.01)	1.19 (1.27–1.00)	0.17 (0.20–0.11)	0.47 (0.61–0.35)	0.50 (0.54–0.40)	0.14 (0.18–0.10)	70.67 (74.88–66.56)
SS 2	7.55 (9.14–6.61)	6.86 (7.75–6.30)	4.00 (4.45–3.43)	1.43 (1.66–1.21)	0.01 (0.02–0.01)	1.11 (1.37–0.97)	0.12 (0.17–0.09)	0.49 (0.61–0.37)	0.48 (0.62–0.41)	0.15 (0.20–0.11)	66.93 (70.70–60.70)
SS 3	4.38 (4.62–4.06)	4.10 (4.91–3.25)	2.52 (4.91–3.25)	0.93 (1.11–0.85)	0.01 (0.01–0.01)	0.62 (0.68–0.55)	0.09 (0.09–0.08)	0.33 (0.43–0.23)	0.27 (0.28–0.25)	0.09 (0.11–0.05)	81.19 (82.53–79.71)
SS 4	6.04 (8.89–4.34)	3.28 (4.11–2.62)	2.99 (4.11–2.62)	1.21 (1.60–0.86)	0.02 (0.02–0.01)	0.84 (1.31–0.57)	0.11 (0.12–0.08)	0.39 (55.5–70.1)	0.42 (0.59–0.30)	0.15 (0.27–0.08)	76.62 (83.70–65.29)
SS 5	6.54 (6.71–6.40)	2.03 (2.89–1.37)	2.82 (2.89 –1.37)	1.61 (1.91–1.38)	0.01 (0.02–0.01)	0.71 (0.75–0.67)	0.09 (0.13–0.05)	0.69 (0.46–0.30)	0.42 (0.43–0.39)	0.09 (0.11–0.08)	79.84 (82.25–77.37)
SS 6	5.72 (7.09–5.01)	2.83 (3.34 –2.11)	2.54 (3.34–2.11)	1.29 (1.44–1.02)	0.01 (0.02–0.01)	0.69 (0.91–0.56)	0.09 (0.11–0.06)	0.39 (0.64–0.36)	0.38 (0.45–0.39)	0.16 (0.29–0.06)	78.89 (83.47–74.12)
SS 7	7.71 (8.87–7.20)	4.90 (5.58–4.60)	2.90 (5.58–4.60)	1.56 (1.78–1.34)	0.01 (0.02–0.01)	0.99 (1.14–0.90)	0.09 (0.12–0.06)	0.49 (0.48–0.29)	0.54 (0.63–0.5)	0.24 (0.28–0.22)	67.56 (69.29–65.36)
SS 8	10.26 (12.29–8.06)	3.06 (3.65–2.58)	4.14 (3.65–2.58)	2.01 (2.37–1.5)	0.01 (0.03–0.01)	1.21 (1.44–0.92)	0.12 (0.14 –0.09)	0.60 (0.66–0.46)	0.72 (0.84–0.60)	0.29 (0.36–0.22)	67.28 (74.27–62.06)
SS 9	8.21 (9.60–6.01)	3.01 (3.36–2.80)	3.28 (3.36–2.80)	1.64 (1.72–1.53)	0.01 (0.02–0.01)	0.96 (1.13–0.69)	0.12 (0.14–0.09)	0.57 (0.63–0.47)	0.53 (0.67–0.37)	0.28 (0.39–0.20)	73.74 (78.34–68.87)

Table 4: Results of cluster analysis: Numbers of individual sediment samples in single groups of sources rocks in single seasons and mean position of sampling point.

	mudstone group	sandstone-loess group	sandstone subgroup	loess subgroup
spring	5	13	7	5
autumn	7	11	5	6
2005	5	13	5	7
2006	7	11	7	4
sampling point mean number	7	4	3.6	4.7

next text, and the CIA index was calculated. The weathering indices reflect in this case a variation in possible parent rock composition rather than the degree of weathering (Borghes & Huh 2007). The samples follow a trend of increasing Al_2O_3 and K_2O with decreasing $CaO+Na_2O$. The CIA index ranges between 54 and 74, with the majority of samples ranging between 64 and 73. The annual CIA variations are larger than the areal ones, although the downstream samples show a slightly higher CIA index.

The possible source rocks were plotted in the A–CN–K diagram (Fig. 11B). The similar pattern can be followed in both modern and possible source rocks, that is, the contents of Al_2O_3 and K_2O increase when $CaO+Na_2O$ decreases. The CIA index for the flysch sandstones varies between 61 and 68, and for the flysch mudstones between 71 and 80. Neogene clays and Quaternary loesses show mean values in the CIA index of about 83 and 74, respectively. The Ti:Al ratio for the flysch sandstones varies between 0.07 and 0.15, and for the flysch mudstones between 0.10 and 0.12. Neogene clays have an average value of the CIA of about 0.11 and Quaternary loesses of about 0.16.

Trace elements/heavy metals

The heavy metal contents in the studied samples are given in Table 6. They vary highly, both areally and seasonally. High seasonal variations were recognized in particular for Pb and V. The contents of Pb, Ni, V, Cr, Cd, Zn, Cu, and Sb are influenced by lithology (Fig. 12A–E), the finer grained samples usually reveal a higher content of the metals. However, a lack of a simple linear pattern (particularly for Pb, Zn, Cd and Sb) also indicates further factors influencing the content of these elements.

Alongstream irregular variations in the content of heavy metals are visible (Fig. 13A–E) similarly to major elements. The highest concentrations were usually most apparent downstream (SS 7 and 8), with the exception of Ni, and Pb. The samples from the furthest upstream SS 1 and 2 often revealed enhanced concentrations of metals (particularly Ni). The content of all the heavy metals decreased at SS 3 and increased (often rapidly) at SS 7. A downstream increase in the content of Ni, Cr and V was recognized between SS 3–4 and 7–8. The opposite trend, namely a decrease between the same SS, was recognized for Sb, Zn, Pb and Cd.

The content of the heavy metals in potential source rocks is demonstrated in Table 5B. Flysch sandstones contain remarkably lower contents of heavy metals than their mudstone "counterparts" as well as in comparison with Quaternary

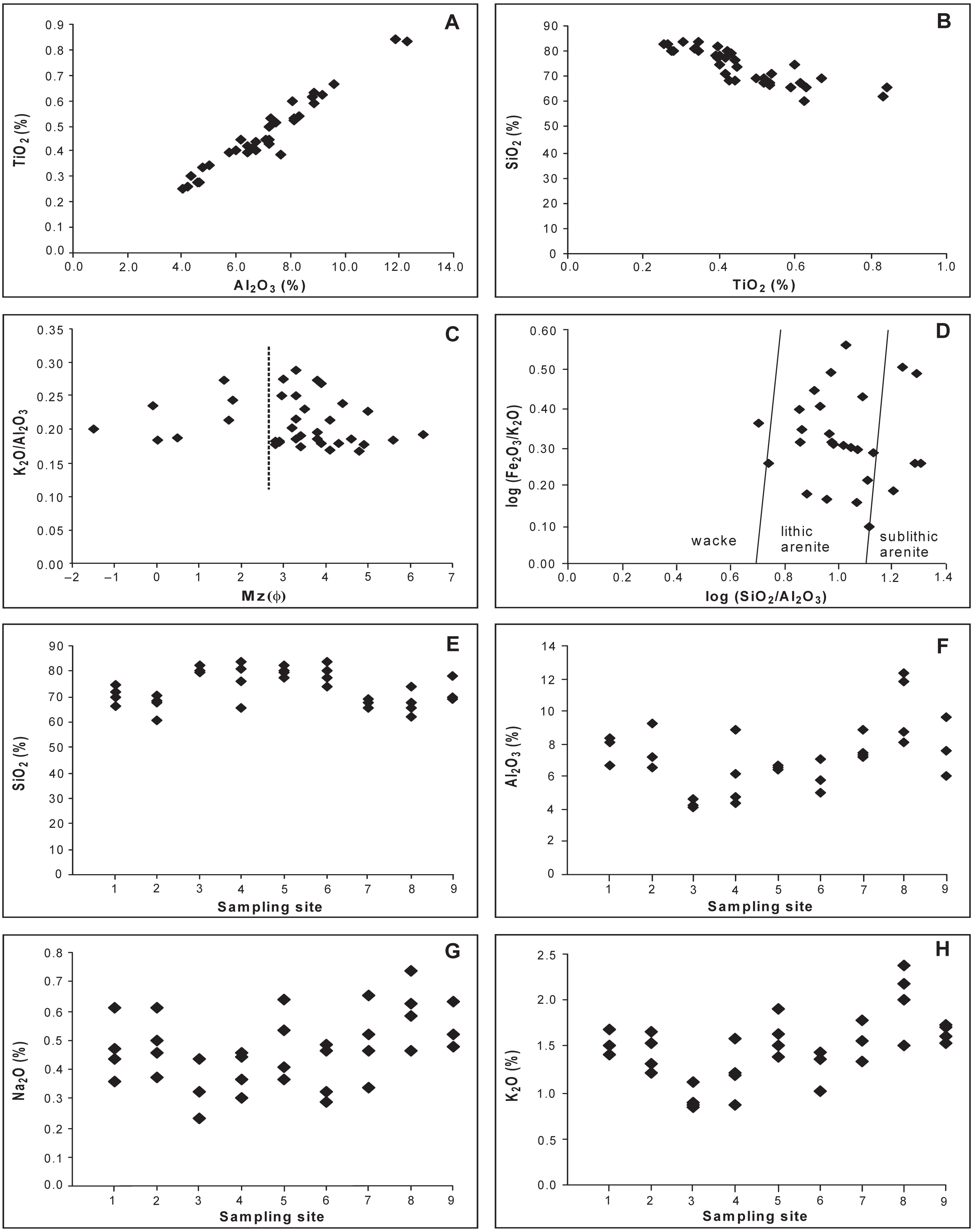

Fig. 8. Relation between: **A** — the content of TiO_2 and Al_2O_3, **B** — the content of SiO_2 and TiO_2, **C** — K_2O/Al_2O_3 and the graphic mean (Mz), **D** — Compositional maturity of studied sediments (Herron 1988). The alongstream distribution of major oxides: **E** — Si_2O, **F** — Al_2O_3, **G** — Na_2O, **H** — K_2O.

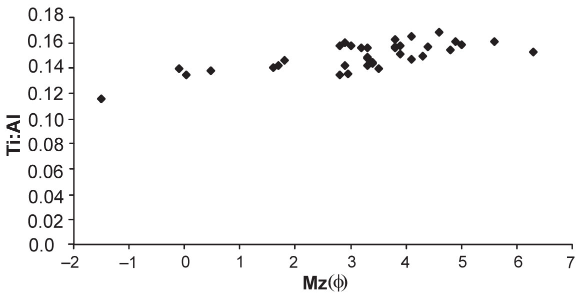

Fig. 9. Relations of the graphic mean (Mz) and Ti/Al.

loesses. A comparison of sediments and their possible provenance rocks with respect to the content of heavy metals is presented in Fig. 14.

Relatively immobile trace elements, Cr and, Ni, are generally believed to undergo the least fractionation during sedimentary processes (Hassler & Lowe 2006). The Cr/Ni ratio of the studied samples varies between 1.03 and 2.09 (1.37 on average). In comparison with the source rocks, the ratio was less than for flysch sandstones (2.2–3.4), partly for flysch mudstones (1.6–3.9) and Quaternary loesses (1.9 on average).

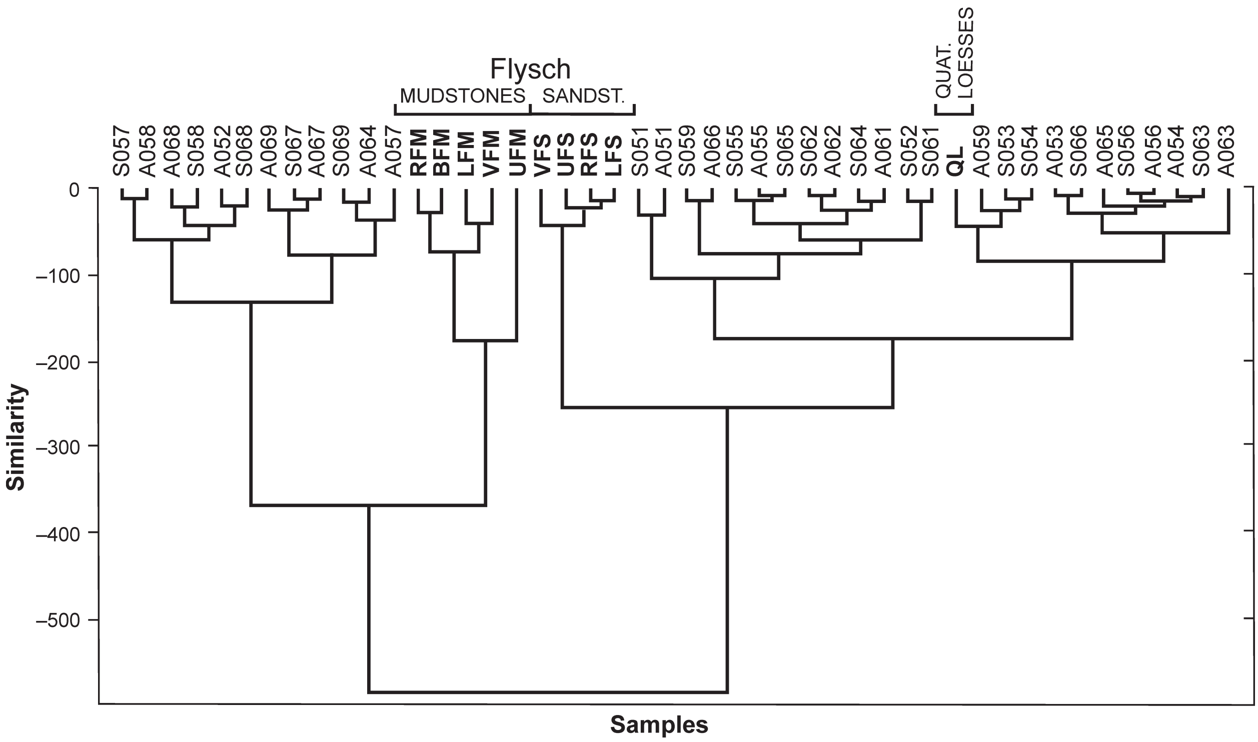

Fig. 10. Multivariate data cluster analysis based on chemical composition of sediments and source rocks (Vard's method). The source rocks are highlighted (Vsetín, Újezd, Ráztoka, and Lukov Flysch Sandstones are denoted as VFS, UFS, RFS, and LFS. Vsetín, Újezd, Ráztoka, Lukov, and Bělověž Flysch Mudstones are denoted as VFM, UFM, RFM, LFM, and BFM. Quaternary Loesses are denoted as QL. Modern sediment samples are denoted as A or S: autumn or spring season, 05 or 06: 2005 or 2006 year of sampling, and 1–9: number of sampling site).

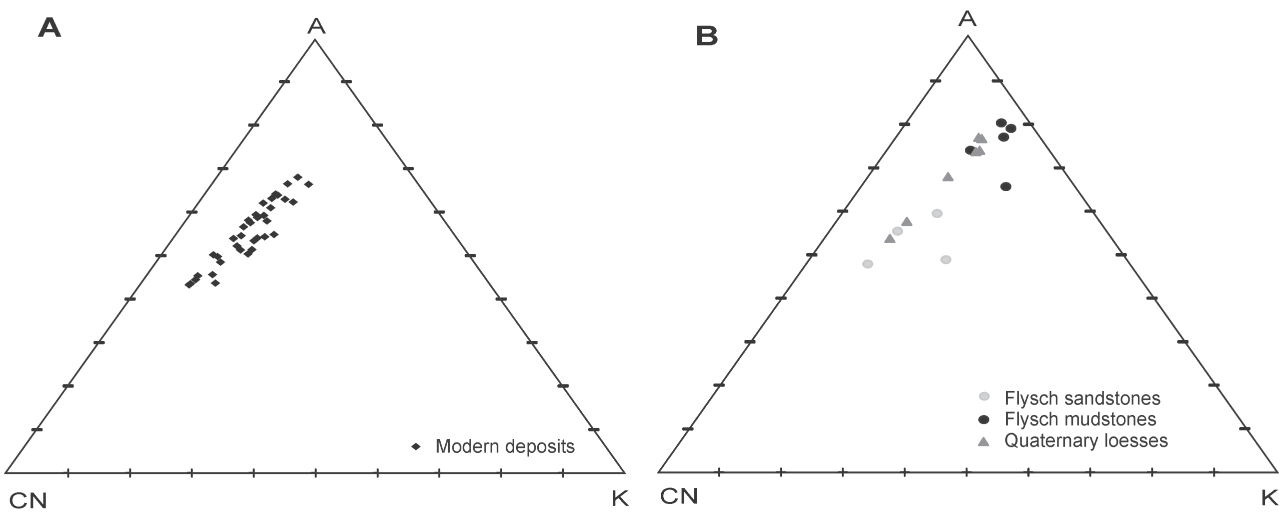

Fig. 11. Ternary plot CN–A–K for: **A** — studied sediment and **B** — source rocks.

Table 5: The chemical composition of potential source rocks: **A** — major elements (results in %), **B** — heavy metals (results in ppm).

A

Rocks	No. of analyses	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
VFS	22	80.7	0.3	4.4	1.4	0.7	0.04	0.7	2.1	0.6	0.9	0.06
UFS	2	83.1	0.21	4.0	0.7	0.13	0.09	0.2	2.0	0.3	1.8	0.02
RFS	17	82.0	0.3	6.9	0.8	1.4	0.04	0.7	1.9	1.0	1.8	0.04
LFS	9	85.6	0.22	6.7	0.6	0.3	0.02	0.2	0.3	0.8	2.4	0.02
VFM	47	51.4	0.62	12.3	3.5	0.9	0.08	1.7	10.4	0.4	2.6	0.08
UFM	19	56.8	0.86	16.8	5.1	1.0	0.12	2.7	1.9	0.9	3.1	0.12
RFM	23	56.6	0.97	19.8	4.1	1.7	0.03	2.3	0.6	0.8	4.5	0.09
LFM	4	55.9	1.01	21.9	3.9	1.0	0.03	1.7	0.5	0.4	4.9	0.07
BFM	26	55.4	0.87	19.2	7.3	1.0	0.08	2.1	0.5	0.5	3.7	0.1
QL	6	70.4	0.79	11.3	3.5	0.4	0.07	1.1	2.2	0.9	2.2	0.23

B

Rocks	No. of analyses	As	Be	Cr	Cu	Mo	Ni	Pb	Zn	V	Co
VFS	22	<5	1	65	9	1	19	6	20	34	5
UFS	2	<5	1	34	5	1	16.5	10.5	8	13.5	5
RFS	17	<5	1	28	7	1	12	12	28	26	5
LFS	9	<5	2	20	8	<1	9	18	16	15	<5
VFM	47	<5	2.1	107	42	<1	56	16	85	112	13
UFM	19	5	2	266	57	<1	161	22	124	158	26
RFM	23	5	4	138	52	1	55	30	109	153	16
LFM	4	5	4	116	51	1	30	30	82	155	11
BFM	26	<5	4	139	68	<1	86	31	124	141	23
QL	6	7.8	1.6	68.0	17.2	<7	35.5	10.2	56.7	57	11.3

Interpretations and discussion

A combination of grain size, petrography and geochemistry enable an evaluation of source rocks and the factors controlling sediment composition. The data on modern fluvial deposits revealed that their mineralogy and chemistry changed with grain size. It is due to (1) multiple sources contributing to grains with mineralogically and texturally distinct characteristics, (2) physical weathering of non-stable grains, and (3) sorting of compositionally distinct grains during transport (Johnsson 1993). All these factors can be observed in this study.

The prevalence of sand/silt and varied gravel role reflect a wider spectra of transportation with a dominance of the suspended load (Owens et al. 2005). A low presence of clay mainly favours transport as discrete particles (Dropo & Ongley 1994).

Although the longitudinal transport of material dominates within the fluvial basin, the role of confluences and additional/transverse sources of material (bank erosion, adjacent slopes or ravines) to the main axial drainage are locally important. The granules and pebbles formed by rock debris mostly originated from the flysch rocks of the Rača Unit or older fluvial and proluvial gravels. The anthropogenic and organic materials in the gravel fraction are linked to human activities. Seasonal differences in their relative content can be due to the following: i) the annual cycle of the harvest season and plant production with its peak in the summer months and/or, ii) a different mode of erosion and provenance reflecting seasonal variability in fluvial discharge. The higher downstream content of the coarse anthropogenic material is associated with the position within densely populated urban areas (the towns of Zlín and Otrokovice). Human activities are directly (anthropogenic material) or indirectly (organic material) responsible for its delivery.

The seasonal variability in fluvial discharge plays an important role. Limited precipitation during the summer months with torrential storms supports the erosion of coarser detritus from adjacent slopes to the river course particularly upstream and also accentuates the role of local sources. More regular and higher fluvial discharge during the late autumn, winter and spring favours a wider/variegated provenance and a downstream redeposition of the material within the fluvial course. The progressive reduction of grain size, even subtle, and increasingly better sorting of sediment within a reasonably short transport distance (>70 km) could indicate the role of either the weathering processes in the catchment area (Sensarma et al. 2008) or the recycling/select redistribution of the material.

The studied deposits are relatively immature. The linear and almost horizontal arrangement of the data in Fig. 7E and the low K_2O/Al_2O_3 ratios indicate a recycling of the source quartz-rich sedimentary rocks (Cox & Lowe 1995; Passchier 2004), a similar source and a relatively low content of phyllosilicates as well as the important role of quartz.

With no extra input of detritus, the sediment recycling results in a negative correlation between SiO_2 and TiO_2 (Gu et al. 2002) and its product will contain more quartz (i.e. SiO_2), less feldspar and clays (lower content of TiO_2, Al_2O_3 and MgO) (Cox & Lowe 1995; Corcoran 2005). Although the role of recycling in the studied deposits can be documented in general, SiO_2 and TiO_2 do not show a consistent negative correlation. It points to a situation when simple alongstream recycling is "complicated" by an additional transverse input of the "fresh" material into the fluvial course. The relative preferential removal of finer-grained material in the upstream part of the basin with its enrichment downstream also influenced the composition.

The different relation of grain size with SiO_2 vs. K_2O, Na_2O, MgO, Al_2O_3, Fe_2O_3, and TiO_2 reflects variations in the mineral composition (quartz vs. feldspar, plagioclases, clay minerals) in different grain size fractions. The low concentration of alkali elements and their negative correlation to SiO_2 reflects the relatively low presence of feldspar and plagioclases, and the dominance of quartz. Areal variations in the

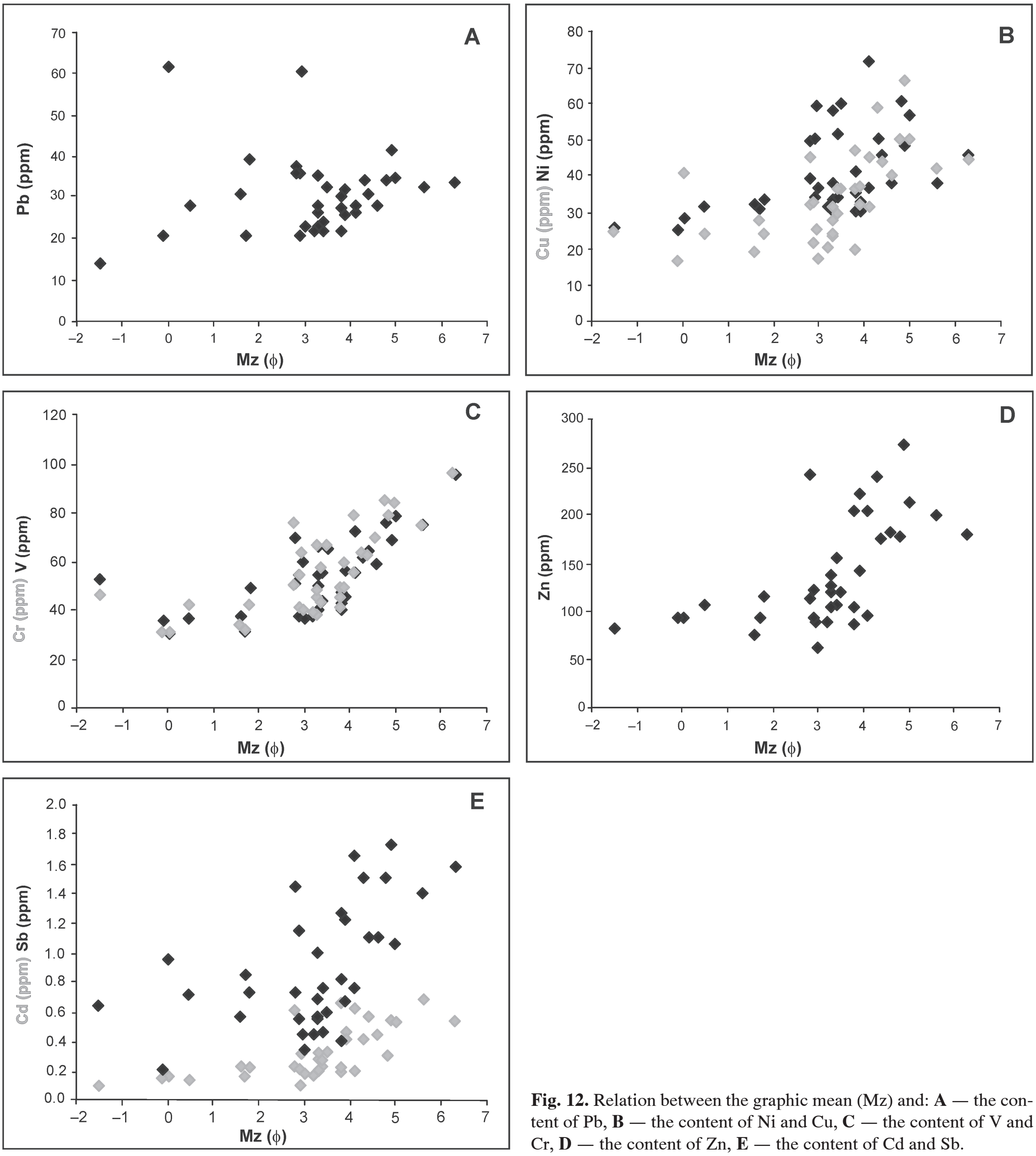

Fig. 12. Relation between the graphic mean (Mz) and: **A** — the content of Pb, **B** — the content of Ni and Cu, **C** — the content of V and Cr, **D** — the content of Zn, **E** — the content of Cd and Sb.

content of major elements are not consistent with element relative mobility during weathering and reveals a relation between chemical composition and lithologies (similarly as Passchier & Whitehead 2006). The increase in the abundance of heavy metals and iron with decreasing grain size reflects the higher concentration of certain minerals (pyroxene, chromite, chlorite) in finer grain size fractions and, possibly, a sorption of heavy metals on an organic substance.

The similarity of CIA values with possible source rocks and tight clustering near the feldspar join in the triangular plot A–CN–K (Fig. 11A,B) indicates mainly physical weathering and the low role of chemical weathering. The elongated distribution of the studied samples in the A–CN–K diagram reflects the varied role of the weathering trend/clay minerals and can be associated with grain size variations (Corcoran 2005). The CIA values are typical of recycled sediments (Young & Nesbitt 1998) and its variations reflect differences in the proportions of feldspar versus aluminous clay minerals. The effect of chemical weathering depended on (1) intensity (controlled primarily by the climate and vegetation) and (2) available time

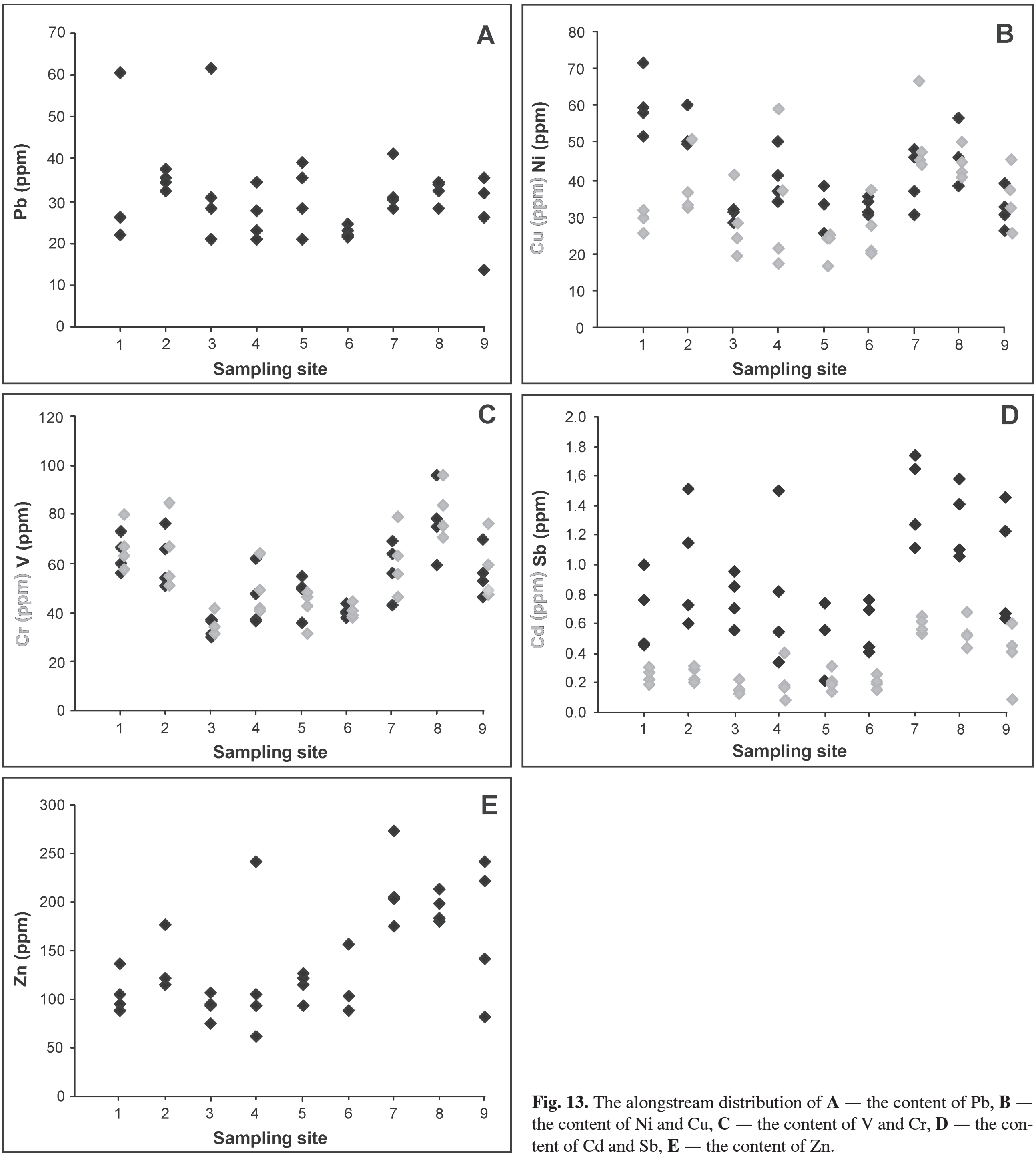

Fig. 13. The alongstream distribution of **A** — the content of Pb, **B** — the content of Ni and Cu, **C** — the content of V and Cr, **D** — the content of Cd and Sb, **E** — the content of Zn.

for weathering. The second effect including a complex set of factors, the physiography of which is particularly important (Johnsson 1993; Le Pera et al. 2001). A typical fractionation (Cox & Lowe 1995) was not achieved because the mud fraction of the studied sediments does not consist mainly of the clay minerals formed by the chemical alteration of the source rocks. Erosion on the relatively steep slopes tends to (1) quickly isolate detritus from the weathered rocks and (2) rapid and short transport leads to minimal sediment maturation and alteration. Among the muds, quartz is enriched by more unstable phases, particularly by the breakdown of lithic fragments and granular disintegration (Johnsson & Meade 1990). The relief suggests mechanical erosion with rapid sediment transport and short temporary storage. Chemical weathering during transport appears to be negligible; it was suppressed by mechanical disintegration which is considered the main mechanism responsible for sand compositional variation during fluvial transport (Ibbeken & Schleyer 1991). Chemical alteration and mechanical breakdown of the source rocks, followed by hydraulic sorting of particles during transport, often leads

Table 6: Characteristics of sites — sediment heavy mineral content (results in ppm).

Site code	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Hg (ppm)	Ni (ppm)	Pb (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
	Median (Minimum–Maximum)										
SS 1	6.21 (4.80–7.48)	0.25 (0.19–0.31)	17.60 (12.70–24.70)	67.10 (57.70–79.80)	29.73 (25.53–31.90)	0.05 (0.04–0.07)	60.03 (51.90–71.30)	33.76 (26.10–60.40)	0.67 (0.45–1.00)	63.86 (56.00–72.90)	106.54 (88.54–137.0)
SS 2	6.33 (5.20–6.90)	0.26 (0.20–0.32)	15.99 (11.90–19.60)	64.58 (51.20–85.00)	38.35 (32.50–50.90)	0.05 (0.04–0.08)	55.16 (49.60–60.40)	35.10 (34.30 – 37.80)	1.00 (0.60–1.51)	64.78 (51.10–76.20)	133.40 (121.0–177.0)
SS 3	4.30 (4.00–4.62)	0.17 (0.13–0.26)	9.30 (7.80–11.54)	35.07 (31.50–42.30)	28.24 (19.51–41.10)	0.05 (0.04–0.07)	30.73 (28.40–32.17)	35.29 (20.70–61.50)	0.77 (0.56–1.00)	33.89 (30.10–37.36)	92.09 (122.08–177.0)
SS 4	4.32 (3.819–4.40)	0.26 (0.10–0.40)	11.18 (9.80–12.20)	48.92 (40.56–64.20)	33.82 (17.31–59.10)	0.09 (0.02–0.09)	40.47 (33.40–50.40)	26.44 (20.80–34.40)	0.80 (0.34–1.50)	45.93 (36.55–62.10)	125.35 (74.52–106.0)
SS 5	4.89 (4.00–5.30)	0.22 (0.10–0.32)	11.06 (6.40 – 14.99)	42.24 (31.70–48.35)	22.50 (16.80–24.60)	0.05 (0.04–0.07)	32.52 (25.20–38.14)	30.92 (20.90–37.20)	0.52 (0.20–0.70)	47.72 (35.80–54.91)	114.05 (62.0–241.0)
SS 6	3.75 (3.34–4.04)	0.21 (0.16–0.30)	10.11 (7.80–12.66)	40.79 (38.40–44.20)	26.46 (20.04–37.20)	0.11 (0.05–0.23)	32.85 (30.60–35.31)	22.73 (21.66–24.30)	0.58 (0.41–0.80)	40.36 (37.50–43.80)	109.11 (93.5–126.79)
SS 7	4.49 (3.40–4.93)	0.60 (0.54–0.70)	12.29 (7.60–16.70)	61.00 (46.10–79.20)	51.09 (41.12–66.90)	0.37 (0.26–0.45)	40.28 (30.50–48.10)	32.57 (28.10–41.30)	1.44 (1.11–1.73)	58.14 (43.30–69.40)	214.37 (175.66–274.0)
SS 8	6.97 (5.45–9.60)	0.55 (0.44–0.70)	14.12 (10.60–18.56)	81.54 (70.50–96.20)	44.61 (40.50–50.54)	0.31 (0.19–0.47)	44.68 (38.00–36.48)	32.22 (28.20–34.68)	1.29 (1.06–1.60)	77.15 (59.50–95.80)	193.87 (180.0–213.38)
SS 9	4.88 (3.30–7.00)	0.49 (0.10–0.61)	11.02 (9.10–12.27)	58.11 (47.20–76.20)	35.05 (25.20–45.40)	0.28 (0.09–0.46)	31.94 (30.20–39.10)	26.87 (13.80–35.60)	1.00 (0.64–1.50)	56.04 (46.07–69.50)	171.79 (81.3–242.0)

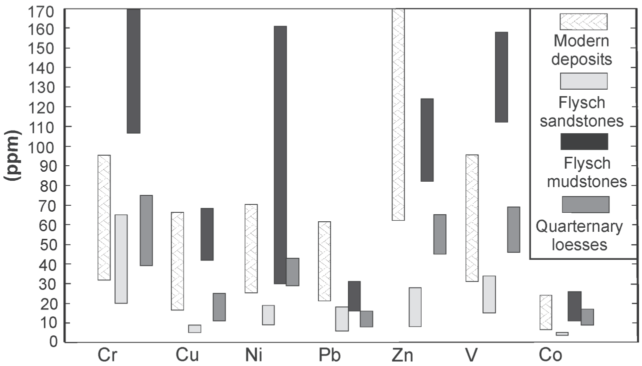

Fig. 14. The content of selected heavy metals in both studied modern deposits and source rocks.

to preferential enrichment of specific minerals in certain grain-size fractions. Therefore, sediment composition tends to be a function of grain size (Whitmore et al. 2004). A number of authors have indicated that sediment grain size affects both modal composition and geochemistry (Roser & Korsch 1986; Cox & Lowe 1996; Whitmore et al. 2004).

The elongated line for the studied samples (Figs. 8a, 9) indicates a mixing of sand with mud during deposition (see Young & Nesbitt 1998) and is consistent with the composition of flysch rocks (particularly sandstones) and Quaternary loesses. The reduction of Al content in comparison with possible source rocks can be a result of preferential removal of Al in the form of fine clay particles. The position of flysch mudstones does not completely fit with the linear array, being enriched both in Ti and mainly Al. The trends in Figs. 8a, 9 and 11a,b point to a non-uniform source. More coarse-grained (sandy) samples show a lower content of both Ti and Al. Increased Al content in muds could be due to a separation of fine-grained clay minerals from quartz and feldspar during transportation. The behaviour of Ti could be explained by either fine-grained Ti-rich minerals (Fe and Ti oxides or hydroxides), by incorporation of Ti to clays, or by the partially different provenance of the varied grain size fractions (Young & Nesbitt 1998; Passchier & Whitehead 2006). Sandy grains predominantly originate from flysch sandstones. The sandstones of the Vsetín Member are typical with a lower content of Al and alkali elements and a high SiO_2 content. Loesses have a high content of quartz (45–50 %), plagioclases form about 11–14 % and mica minerals predominate in the clay fraction (Adamová 1990a,b). The provenance from Quaternary loesses in the middle part of the area under study suits well with their predominant occurrence in this area (see Fig. 2) and the local source of material.

The alongstream variations in the heavy metal content reflect differences in the sediment provenance, but are also influenced by anthropogenic sources. In the upstream part of the area (typically SS 1 and 2) a provenance from flysch sandstones predominates. The highly enhanced metal concentrations in the deposits with respect to the source rocks are ascribed to anthropogenic sources or, partially, originate from flysch mudstones. The highest concentrations of metals were in contrast recognized in the downstream area (particularly

SS 7 and 8), where the provenance from flysch mudstones predominates. These mudstones are characterized by a high concentration of metals. The concentrations of metals in the modern sediments in these areas are usually lower than in the source rocks, except for Pb and Zn. The lowest concentrations of heavy metals were usually observed in the middle part of the study area (SS 3, 4 and 6) which is typical for an important source from the Quaternary loesses.

An enhanced abundance of ferromagnesian elements (Fe, Mg, Mn, Cr, Ni, V, and Cr/Ni ratio) in sedimentary rocks is usually interpreted as an indication of the provenance from mafic and ultramafic igneous rocks (Bock et al. 2008). In this study, the reason for the increased content of these metals is ascribed to flysch mudstone source and anthropogenic pollution. The contents of Cr, Co, Cu, Ni, and V are affected only locally or seasonally; their concentrations are usually similar in modern sediments and source rocks.

The contents of Pb and Zn are highly enhanced in comparison with the natural background in the entire study area. The anthropogenic source of Cr, Cd, Ni, Cu, As, Zn was demonstrated in soils by comparing the studied area with soils formed on similar parental rocks in adjacent areas (Adamová 1989). This situation reveals a complicated distribution of metals in the adjacent modern depositional environments in addition to different processes in their formation and provenance. The rapid increase in heavy metal content is associated with the urban area in the surroundings of the towns of Zlín and Otrokovice. The rubber/shoe manufacturing industry and traffic seem to be the main sources of pollutants.

The flysch deposits underwent the "separation" of sandstone and mudstone components during the weathering and transportation processes. The sorting of grains with a distinct grain size and composition led to the enrichment of the material with the provenance from sandstone in the upstream area whereas the material sourced from mudstones was enriched in the downstream area. Several recycling/redeposition events gradually influenced the reduction in the grain size. In addition, the grain size of sediments was controlled by the grain size of the source rocks and by local sources, as the proportion of sand-prone quartzes (SiO_2) was reduced downstream.

Conclusions

The studied modern fluvial deposits from the Dřevnice River Basin (eastern Moravia, Czech Republic) are relatively immature; they are composed of predominantly lithic arenites, apart from a few which are sublithic arenites and wacke. The deposits are poorly sorted and can be predominantly classified as sands, silty sands, or sandy silts. Both the gravel and clay contents are relatively low.

Alongstream and seasonal variations in (1) grain size, (2) gravel petrography, (3) clay mineralogy, and (4) geochemistry (major elements, heavy metals) of modern sediments were recognized. Differences in sediment fabric and composition can be associated with a different mode of erosion, reflecting a seasonal variability in fluvial discharge, and a different provenance in various parts of the basin. More regular and higher fluvial discharges during the late autumn, winter and spring favour a larger/varied provenance and an alongstream sediment redistribution. In contrast, the limited precipitation during the summer months supports the local erosion and local provenance. The provenance study revealed the source of the fluvial deposits from recycled older sedimentary rocks, more precisely from flysch sandstones, flysch mudstones and Quaternary loesses. The sediments with the source in flysch mudstones predominate far downstream, whereas the deposits with the source in flysch sandstones predominate mainly upstream. The ones with the provenance from loesses are typical of the middle part of the studied area.

The contents of Pb and Zn are highly enhanced in comparison with the natural background in the study area. The rapid increase in heavy metal content is associated with the urban area in the surroundings of the towns of Zlín and Otrokovice. The anthropogenic sources of Pb and Zn are connected with the rubber/shoe manufacturing industry and traffic. The contents of other heavy metals, namely Cr, Co, Cu, Ni and V, are usually lower than in source rocks. Enhanced concentrations of these metals were recognized only locally or seasonally.

Discrimination of potential sediment sources and identification of natural and anthropogenic input can be proved only by a complex diagnostic approach, because of the natural spatial variability of source rocks in the fluvial system, the complexity of sediment transport and delivery processes. The presented case study shows principles based on which it is possible to interpret results of sedimentary studies in similar geological situations.

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