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ORIGINAL ARTICLE

Assessment of potential sediment contamination using screening methods (XRF, TGA/MS) taking into account principles of green chemistry, Eastern Slovakia

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Abstract Mining and milling of metal ores coupled with industries have bequeathed many countries the legacy of wide distribution of metal contaminants in sediments. The aim of this study was to assess potential sediment contamination via useful screening methods (XRF, CHNS, TGA/MS). The sediments were collected from the water reservoir Krompachy Eastern Slovakia in April 2015. Within the frame of evaluation it was found that the concentrations of the study elements (Cu, Zn, As, Pb, Cr, Ni, Cd) exceeded some of the MPC, TV and IV values. Sample **c** was the most polluted by metals, which evident according to it's the highest CHNS proportion as well as the highest clay and silt proportion. In the samples studied the best correlation was confirmed between weight losses in the temperature range (400–620 °C) and the following metal concentrations: Cu ($r = 0.89$), Zn ($r = 0.88$), As ($r = 0.93$), Hg ($r = 0.83$), Pb ($r = 0.87$). The greatest proportions of m/z 44, m/z 18 were detected at temperatures (400–620 °C) associated with decomposition of minerals such as siderite, barite, and exothermic loss of more refractory aromatic C took also place.

Keywords Bottom sediment · Heavy metals · Pollution · Thermal analysis coupled with mass spectrometry

Introduction

Environmental pollution by potentially toxic substances is a worldwide problem with regard to human health. The Eastern Slovakia region is polluted due to various anthropogenic activities including industrial activities, mining, metallurgy, transport network, household waste and sludge coming from urban areas as well as fertilizers, pesticides, insecticides, which are dispersed in soil, water, and air. These results have a negative impact on fauna, flora, and human health. Therefore, it is important to assess the extent to which the individual components of the environment in Eastern Slovakia are contaminated. For the assessment of potential environmental contamination, it is important to combine data obtained by various screening methods. For a quick and easy screening of environmental samples for contamination, it is possible to use screening methods such as elemental analysis—X-ray fluorescence spectrometry (XRF), thermal analysis (TG/DTG, DTA) coupled with mass spectrometry (MS), which are one of the fast methods taking into account the principles of green chemistry. It is well known that thermal analysis is primarily used in the field of material sciences, but also has a long history in geosciences. Thermal analysis is widely used in the study of minerals, for their identification, qualitative analysis, isomorphism transitions, existence of certain molecules, or ions, etc. Sulphate and silicate minerals may contain free, crystalline, and constitutional water. These kinds of specimens, can undergo dehydration, decomposition, polymorphic transformation, recrystallization, melting and valence-state change of variable-valence elements during heating (Hatakeyama and Liu 1998). The combination of thermal analysis with mass spectrometry offers several advantages in thermal gas emission determination such as real-time analysis, qualitative and quantitative analysis

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(Arenillas et al. 1999). Thermal analysis is also widely utilized in environmental studies, in which it was used as a first screening method to evaluate the potential contamination of sediments (Rodríguez-Barroso et al. 2010) or to study thermal degradation and kinetic study of chosen types of biomass in order to evaluate their usefulness as a supplementary fuel in the iron ore sintering process (Findorák et al. 2016). The other screening method X-ray fluorescence spectrometry is a general analytical method. It can use it to analyze major and trace elements in rocks, minerals, and sediment. This method is favorite from other because it is non-destructive. Alexakis (2011), Sharma et al. (2016), Zhu et al. (2016), deals with diagnosis of sediment quality and assessment of heavy metal contamination by other geological methods, which are useful and interesting in sediment geochemistry. The spatial distribution of chemical elements in stream sediments and evaluation of geogenic and anthropogenic factors controlling the distribution of elements in sediments was studied by methodology such as geomorphological analysis, chemical analysis, factor analysis, and comparison of element contents with other data sets (Papadopoulou-Vrynioti et al. 2013). For the above reasons, the aim of this study is the use of screening methods to obtain information about potential contamination, physico-chemical properties of sediments from the Krompachy area of Eastern Slovakia, which are contaminated by former mining activity. The sediments were collected from a reservoir in the town of the Krompachy, the central part of the historical region Spiš, which is situated near the plant Kovohuty a.s. The plant represents one of the most important sources of emissions that significantly contribute to air pollution in this region. Sediments as well as the River Hornád are contaminated by these emissions. In this region the effect of distance from a heavy metal pollution source on the soil nematode community was investigated at four sampling sites along a 4 km transect, starting at the Kovohuty a.s. Krompachy (pollution source) by Šalamún et al. (2012).

Materials and methods

Localization of the sediments studied

Four areas at the water reservoir Krompachy near the Kovohuty plant were studied (Fig. 1). This reservoir is filled with water from the Hornád river. The river may promote the contaminant migration from villages Rudňany and Slovinky (Eastern Slovakia) into the reservoir. These villages represent classic examples of mining villages in the Spiš region. In the past there was intensive mining activity in these villages. The sludge bed Rudňany was formed by the silting-up of the tailings from the processing of complex siderite-sulphidic and barite-sulphidic ores (Jakabský et al. 2010). It is well known that this area poses an environmental risk; therefore many authors (Findoráková et al. 2014; Hančuľák et al. 2006; Jakabský et al. 2010; Lalinská et al. 2011; Petrák et al. 2013) have studied this area from different perspectives. The ore area Slovinky is a part of the biggest deposit of modern ores in the Spiš region. The greatest accumulation of Cu ores (in quartz–siderite–sulfidic veins) was in the Slovinky–Gelnica ore deposit. Wall rocks of the Slovinky deposit are mostly quartz–sericites, black phyllites, metarhyolites, and metatuffs of the Early Palaeozoic Gelnica Group, metabasalts, metatuffs, and sericite–chloritic phyllites of the Rakovec Group, conglomerates and breccias of the Permian Krompachy Group, and shales, sandstones, and limestones of the Mesozoic Stratená Group (Hiller et al. 2016). Also the contamination of sediments from reservoir comes from anthropogenic pollution from industrial waste (Kovohuty plant).

Sampling

Sediments were collected in April 2015 from four sites at the water reservoir Krompachy. Four replicates from each site were collected by "Multisampler" from depth 50 cm and mixed together. In these samples the pH was measured at the sampling location with a hand-held pH/mV meter (VARIO pH SET). Then the representative samples marked **a**, **b**, **c**, **d** were dried at 25 °C, quartered and wet sieved for chemical, mineralogical, and thermal studies.

Methods

X-ray powder diffraction (XRPD)

X-ray powder diffraction was used for the analysis of the sample before and after the thermo-analytical treatment. The XRPD data was collected over an angular range $10° < 2\Theta < 60°$ in 0.03° steps using a Bruker D8 Advance diffractometer, working with Cu K_α radiation and equipped with a secondary graphite monochromator. Diffraction patterns were processed with the Diffrac^{plus} Basic analysis program with a PDF-2 Database.

Thermal analysis coupled with mass spectrometry and XRF instrumentation

A TG–DTA of the sediments was conducted using a Netzsch STA 449 F3 Jupiter simultaneous thermal analyser. The sample (amount 100 mg) was placed in an Al_2O_3 crucible. The experiment was carried out at the following experimental conditions: 10 °C/min, heating rate from 40

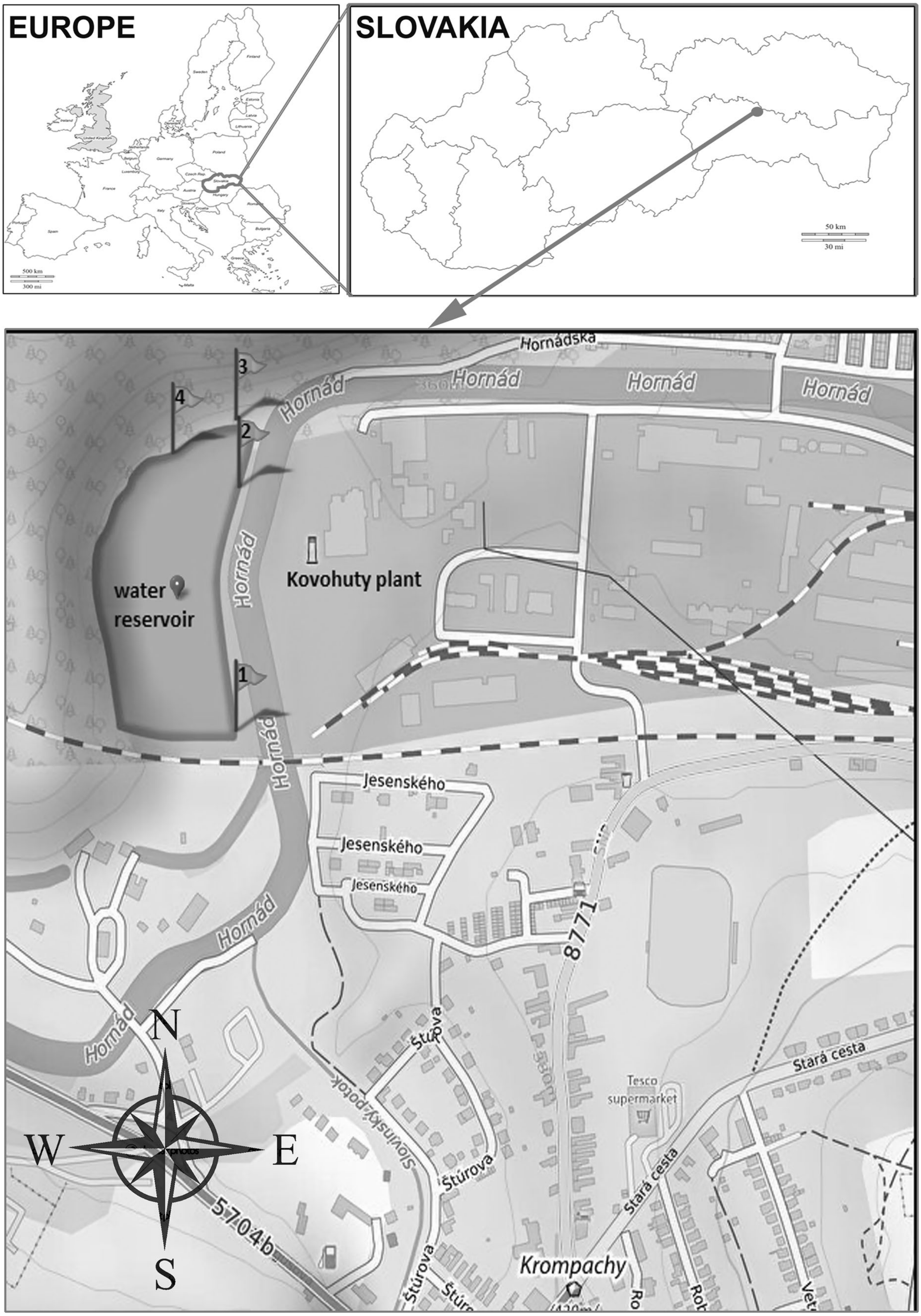

Fig. 1 Location map showing study area

to 1000 °C at steady airflow. TG–DTA-MS evolved gas analysis was carried out by simultaneously coupling the TG–DTA system through an adapter head in the STA 449F3 Jupiter gas outlet via a heated capillary up to 300 °C to a Netzsch Aëlos QMS 403D quadrupole mass spectrometry system (range 1–300 amu). The concentrations of heavy metals in the sediment were determined using a SPECTRO XEPOS X-ray fluorescence spectrometer model XEPO3 [range of elements: Na(11)–U(92), scattering targets: Mo, Co, Al_2O_3, Pd, HOPG-crystal, X-ray lamp (type VF50): Pd with Be window, resolution: 145 keV on line $K\alpha$ Mn]. The sample for XRF analysis was dried and sieved to below 100 μm, then 5 g of sample were homogenized with 1 g of Clariant micro powder C (CEREOX BM-0002-1) and then pressed under 15 t to a pellet with a 32 mm diameter.

CHNS analysis was performed by an elementary analyzer Vario MACRO cube (Elementar Analysensysteme GmbH, Germany) using a thermal conductivity detector. A combustion tube was set up at 1150 °C and the reduction tube at 850 °C. Sulfanilamide ($C = 41.81\%$, $N = 16.26\%$, $H = 4.65\%$, $S = 18.62\%$) was used as the CHNS standard.

Results

Granulometric analysis, CHNS analysis

Granulometric analysis was performed on a set of these samples. Firstly, the samples were wet sieved to separate the coarser particles (>63 μm), then a decantation process was carried out (gravity settling in deionized water) to characterize the finer fraction. The analysis indicated that the clay fraction (<2 μm) ranges between 20.5 and 31.7 wt%, the silt fraction (2–63 μm) between 58.3 and 64.7 wt%, and that the sand fraction (>63 μm) is subordinate (<10.9 wt%) (Table 1; Fig. 2). Thus it is evident that clay and silt fractions prevail, over a subordinate sand fraction. For sediment research the fine-grained fractions are very important due to their large specific surfaces, which have the largest share of the toxic elements sorbed. The pH of the sediments ranges from 7.25 to 7.71 indicating their alkaline nature. Organic matter within the sediment plays an important role in the accumulation and release of several metals into the river system. The organic matter in the sediments studied was in the range 9.23–12.07%. From Table 1 it is evident that the highest values of CHNS are in sample **c**, which has the largest proportion of clay and silt.

Elemental analysis

The current concentration of seven heavy metals (Cu, Zn, As, Pb, Cr, Ni, Cd) in total sediment was analyzed using X-ray fluorescence spectrometry. The quality of the sediment was established with reference to methodical instructions 549/1998-2 for assessing risks from pollution of sediments streams and water reservoirs. The values obtained were compared with the test values (TV), the maximum permissible concentrations (MPC) and the intervention values (IV), which are listed in Table 2. During evaluation it was found that the concentrations of the study elements exceeded some of the MPC, TV, and IV values. According to other national guideline such as for example national guideline values of marine sediment quality of China (GB 18668-2002) (Li et al. 2012) or maximum allowable concentrations (MAC) in Lithuanian sediments (Raulinaitis et al. 2012) it is evident that our samples are high contaminated with Ni, Cu, Pb. From Table 2 it is evident that sample **c** is the most contaminated. This contamination correlates with the highest concentration of CHNS and also the highest percentage of clay and silt. The present data was compared with metal concentration in other sediments; soils reported for similar mining areas in Krompachy Eastern Slovakia, during the last decade. The highest concentrations of Cu, As, Pb, Zn (1271, 170, 380, 1333 mg/kg, respectively) have been found in the grassland Krompachy by Angelovičová et al. (2015). Also a strong Cu, Pb, Zn, Hg contamination (1287, 102, 832, 99 mg/kg, respectively) was confirmed by Angelovičová and Fazekašová (2014) in one soil sample collected in April 2012 from grasslands in the cadastre of Rudňany village. According to our results and the results of many other researchers, this study area in Eastern Slovakia near the mining areas is evidently heavily polluted by heavy metals. Also many studies have demonstrated that the presence of organic matter has increased the adsorption of trace metals onto clay surfaces (Schmitt et al. 2002).

Table 1 Grain size distribution (wt%), elemental CHNS analysis (wt%) and water pH in contact with each sediment

Sediment samples	Clay	Silt	Sand	C	H	N	S	pH
a	26.3	59.2	6.5	4.61	0.82	0.33	0.39	7.50
b	20.5	58.3	10.9	6.06	1.22	0.55	0.63	7.71
c	31.7	62.3	4.9	7.65	0.68	0.33	0.32	7.25
d	24.9	64.7	3.6	4.54	0.87	0.38	0.39	7.42

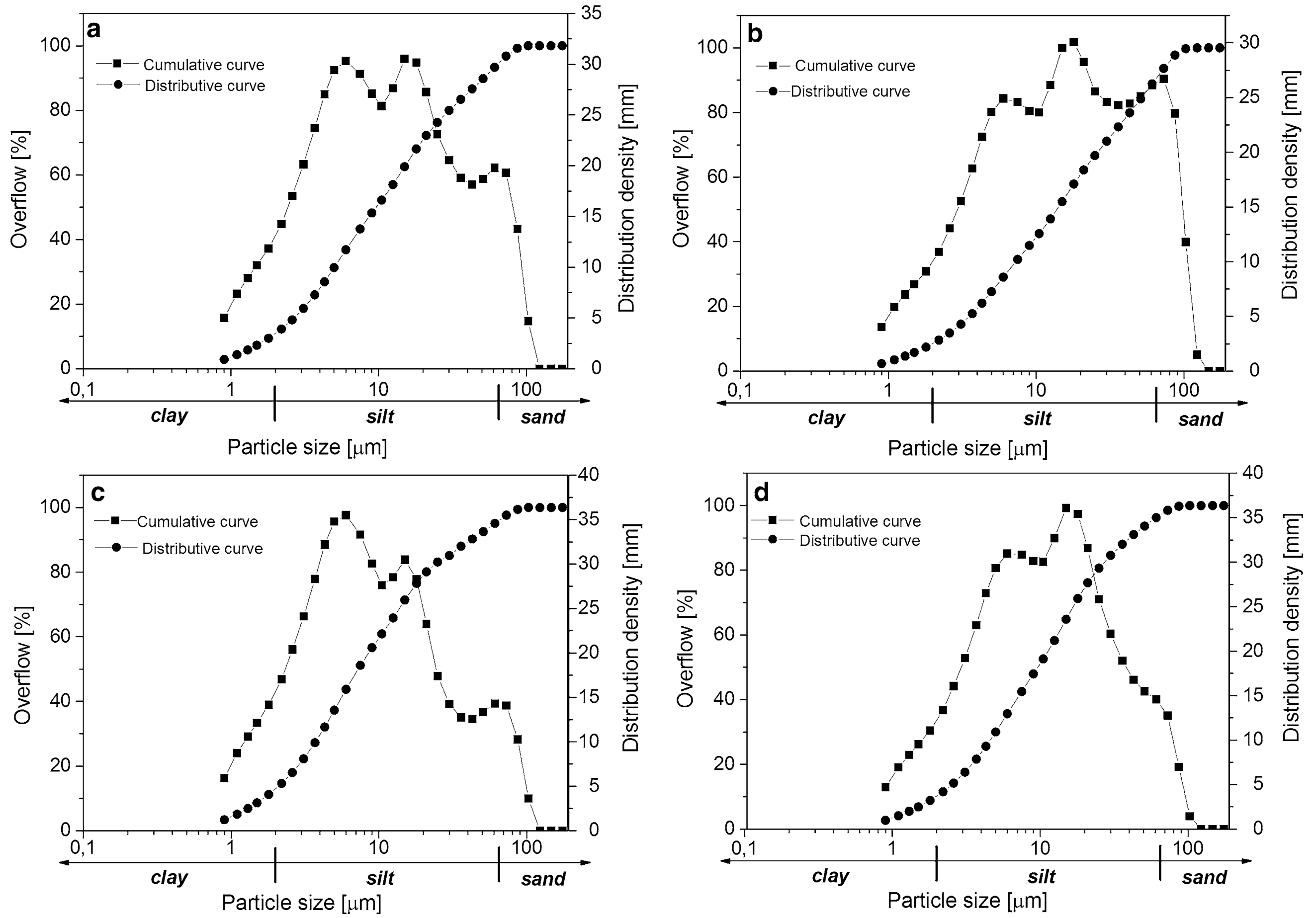

Fig. 2 Results of granulometric analysis of sediments **a**, **b**, **c**, **d**

Table 2 The concentrations of heavy metals (mg/kg) in the total sample

Sediment samples	Ni	Cu	Zn	As	Hg	Pb
Concentration (mg/kg)						
a	68.9	331.6	379.3	52.8	35.4	85.7
b	64.1	359.0	345.2	44.9	55.6	77.2
c	78.9	509.4	644.7	80.3	99.9	141.1
d	71.3	386.1	429.9	61.9	55.4	94.8
Norm used for comparison (mg/kg)						
TV	35	36	140	29	0.3	85
MPC	44	73	620	55	10	530
IV	210	190	720	55	10	530

TV testing value, *MPC* maximum permissible concentration, *IV* intervention value

Thermal anlysis (TG/DTG, DTA) coupled with mass spectrometry (MS) and X-ray diffraction analysis

The evaluation of contaminated sediments by thermal analysis is problematic due to their heterogeneity. The use of (20 mg) standard sample amounts does not lead to reliable results. For this reason we used about 100 mg sample amounts. In this study we used thermal analysis coupled with MS because they are useful methods for predicting and identifying evolved components during thermal decomposition. To best characterize thermal decomposition of the samples studied X-ray diffraction analysis was used to identify mineralogical species before and after thermal analysis. This phase analysis of sediments **a**, **b**, **c**, **d** confirmed the presence of minerals, such as barite (ICDD 00-024-1035), siderite (ICDD 01-083-1764), quartz (ICDD 01-078-1252), illite (ICDD 00-058-2016), muscovite (00-046-1409), vermiculite (00-016-0613) and virgilite (01-073-2336). Quartz was the main mineral and the others were present in smaller amounts. Amorphous phases could not be identified by X-ray diffraction. After thermal decomposition only quartz, virgilite, and hematite were found. Thermal decomposition of all sediments was very similar, with weight differences only at concrete thermal intervals (Table 3). The weight and enthalpy changes as a function of temperature are shown in Fig. 3.

The first weight loss corresponding to an endothermic reaction occurs below 100 °C or nearly 100 °C in all

Table 3 Weight losses (W_i/%) at TG curve corresponding to the main peaks shown in the DTG and sum corresponding to total weight loss

Sediment samples	W_1/% (50–210 °C)	W_2/% (210–400 °C)	W_3/% (400–620 °C)	W_4/% (620–750 °C)	W_5/% (750–900 °C)	SUM/% W_1–W_5
a	1.9	3.26	3.62	0.85	2.39	12.02
b	2.06	3.45	3.63	1.51	2.36	13.01
c	2.5	3.63	4.23	1.52	2.39	14.27
d	2.86	4.05	4.05	1.13	1.55	13.64

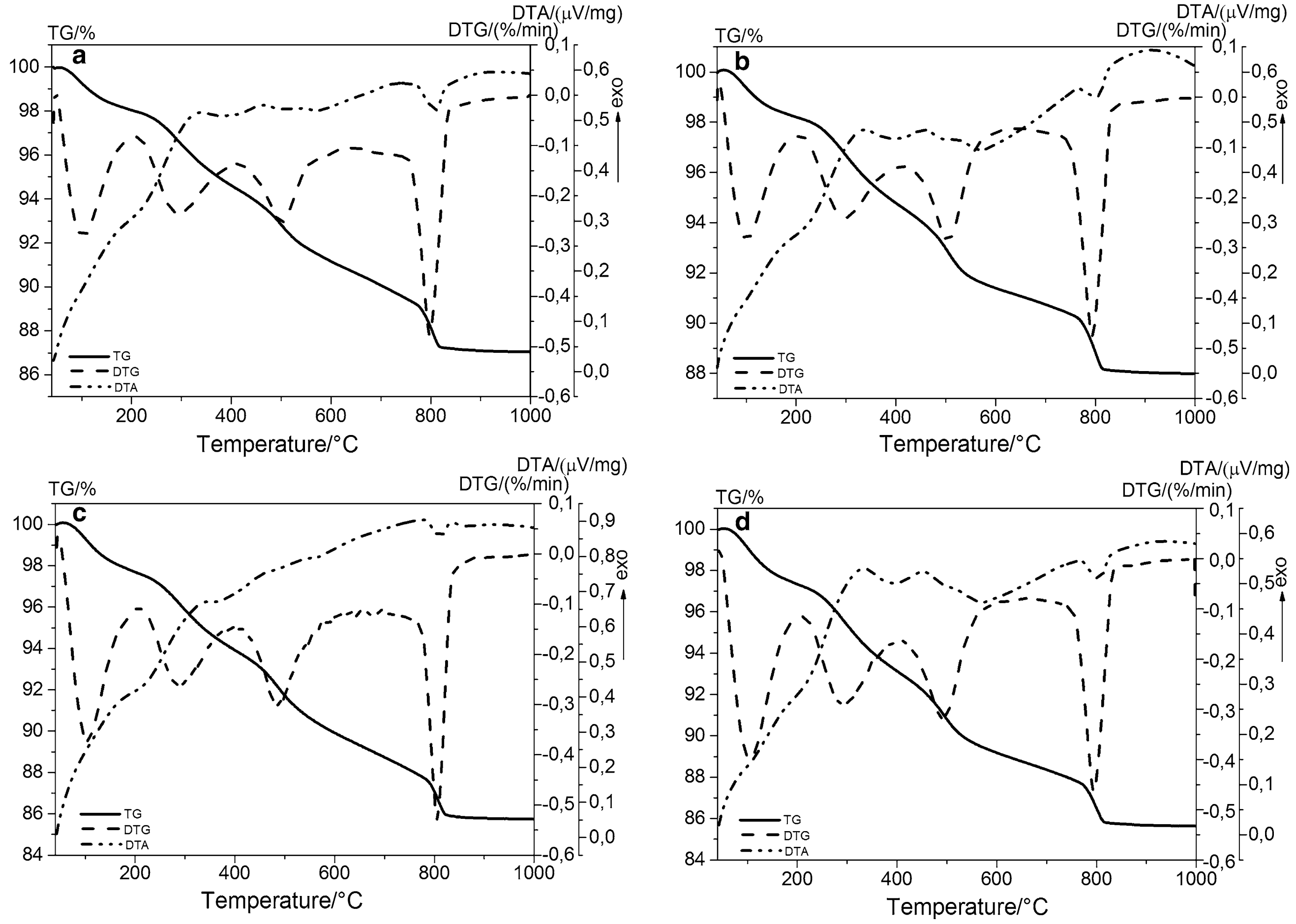

Fig. 3 TG/DTG and DTA curves for sediments **a**, **b**, **c**, **d** at heating rate 10 °C/min in an air atmosphere

samples studied. This can be attributed to dehydration of the sediment. In the temperature range 210–400 °C dehydroxylation of clay minerals occurred and exothermic decomposition of labile aliphatic and carboxylic groups began. The third and fourth steps in the temperature ranges, 400–620 and 620–750 °C respectively, correspond to the decomposition of minerals such as siderite and barite which was confirmed by the XRPD analysis. In the third step exothermic loss of more refractory aromatic C takes place too. In the fourth step the CO_2, CH_4 or N_2O could be released. Differences in the intensity of endothermic or exothermic peaks between the samples studied can be attributed to different amounts of absorbed water, CO_2 and CH_4, respectively. On the basis of the XRPD results obtained after heating the sample to 900 °C—the formation of iron oxide was confirmed and quartz remained.

Mass spectrometry was used to monitor gas emissions which are identified by their molecular masses giving the following *m/z* signals: 16, 17, 18, 44, which were identified for all sediments in the air atmosphere. The results are shown in Fig. 4. The value *m/z* 18 is associated with the emission of H_2O in the dehydration process in all study samples. The maximum amounts of evolved H_2O (*m/z* 18) were at 300–320 °C. Traces of H_2O were detected in all the

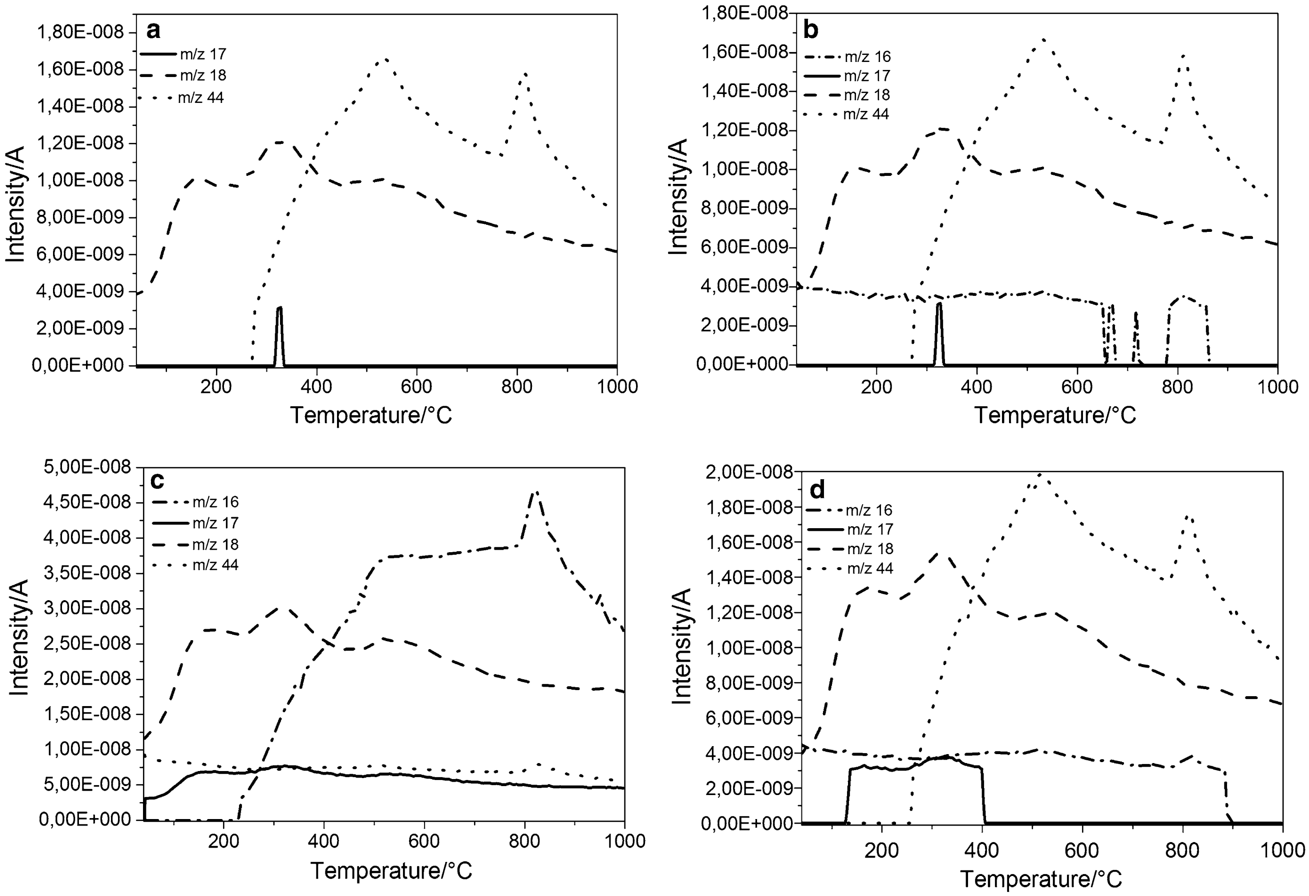

Fig. 4 Thermograms of ion current *m/z* 16, 17, 18, 44 for all samples studied **a**, **b**, **c**, **d**

samples at 100–120 and 300–350 °C. Dehydroxylation of clay minerals was confirmed in the range 150–400 °C (*m/z* 17). The value of *m/z* 16 is associated with the emission of CH_4, CO_2 and N_2O emissions are associated with *m/z* 44 in the temperature range 400–900 °C. Release of these compounds was observed at the third and fourth step of decomposition in the air atmosphere. The maximum amount of the gas CO_2 evolved from the combustion was at 510–540 °C followed by a shoulder at 820–840 °C.

Correlation between XRF and thermal screening methods

The correlation between weight losses (%) shown in Table 3 and heavy metal concentrations (Table 2) were calculated using the Pearson matrix correlation. The results obtained show a better correlation between weight losses in the temperature range (400–620 °C) and metal concentrations. The correlation coefficient for each study element and weight losses are: Cu ($r = 0.89$), Zn ($r = 0.88$), As ($r = 0.93$), Hg ($r = 0.83$), Pb ($r = 0.87$). In this temperature range refractory aromatic C is also found in then thermal study. The highest weight loss percentages in the range assume organic pollution and therefore high metal concentrations, which is also evident from Tables 1 and 2.

Conclusions

In this study pollution has been shown to take place as well as correlations between screening methods used. The best correlation was found between the weight losses in the temperature range (400–620 °C) and the following metal concentrations: Cu ($r = 0.89$), Zn ($r = 0.88$), As ($r = 0.93$), Hg ($r = 0.83$), Pb ($r = 0.87$). Within the frame of evaluation it was found that the concentrations of the study elements (Cu, Zn, As, Pb, Cr, Ni, Cd) far exceeded some of the MPC, TV and IV values. In relation with international limits sediments are high contaminated with Ni, Cu, Pb. All of sediments studied differ in their chemical and physical properties. In the sample **c** the highest metal pollution and also the highest concentration of CHNS elements and the highest percentage of clay and silt proportion were found. It is evident that organic matter, CHNS and clay, silt fraction play an important role in the accumulation and release of metals in the sediments. The minerals barite, siderite, quartz, illite, muscovite, vermiculite, virgilite were found in the samples studied. Thermal analysis coupled with MS was used to distinguish between the different evolved components in samples. The results of a simultaneous MS investigation are dominated by the evolution of CO_2, H_2O, CH_4 during thermal analysis.

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