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Full Length Research Paper

The distribution of Rare Earth Elements (REE) in surficial lake sediments before and after tailings dam failure (FYR Macedonia)

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The concentration and distribution of rare earth elements (REEs) in the surficial lake sediments of Lake Kalimanci were studied in an attempt to establish the reasons for their enrichment. Results indicate that REE are tightly related to the catchment geology. Possible anthropogenic effects were evaluated by employing an enrichment factor, which revealed that the surficial sediments from Lake Kalimanci have a natural origin with a minor enrichment of the defined REE. Sequential extraction analysis revealed that REE in the surficial sediments of Lake Kalimanci are predominantly bounded to the exchangeable fraction and therefore highly bio available for living organisms.

Keywords: REE, Surficial lake sediment, Enrichment factor, Sequential extraction procedure

INTRODUCTION

Over recent decades rare earth elements (REE) are increasingly being used in many everyday devices (e.g., alloys, batteries, cell phones, magnets, computer memory and much more). Fifteen chemical elements (lanthanides) that occur together in the periodic table are well-known REE. Those that range from La to Sm are known as light rare earth elements (LREE) and those from Gd to Lu are heavy rare earth elements (HREE). These metals have similar properties (chemical and physical) and are for this reason often found together and with other elements, in different geological deposits and they have a similar behaviour in the environment (Henderson, 1984; Tyler, 2004; Hu et al., 2006). Comparison among REE is facilitated by normalising the analyses to a reference standard such as chondrite and average shales (Taylor and McLennan, 1995).

REE are as abundant in the Earth's crust as Cu, Pb and Zn, and are more abundant than Sn, Co, Ag and Hg in Earth's crust (Wang et al., 1998). REE are associated with varieties of igneous rocks, gold and copper deposits and they are also found in a wide variety of REE-rich accessory minerals, such as: apatite, titanite, monazite, etc. (Clark, 1984; Mason and Moore, 1982). REE are widely used as tracers for a range of geological processes because of their similar electronic configurations, which give rise to predictable differences in chemical behaviour along the series (Lipin and McKay, 1998). There is a number of comprehensive studies about the geochemistry of REE in sediments, (Ross et

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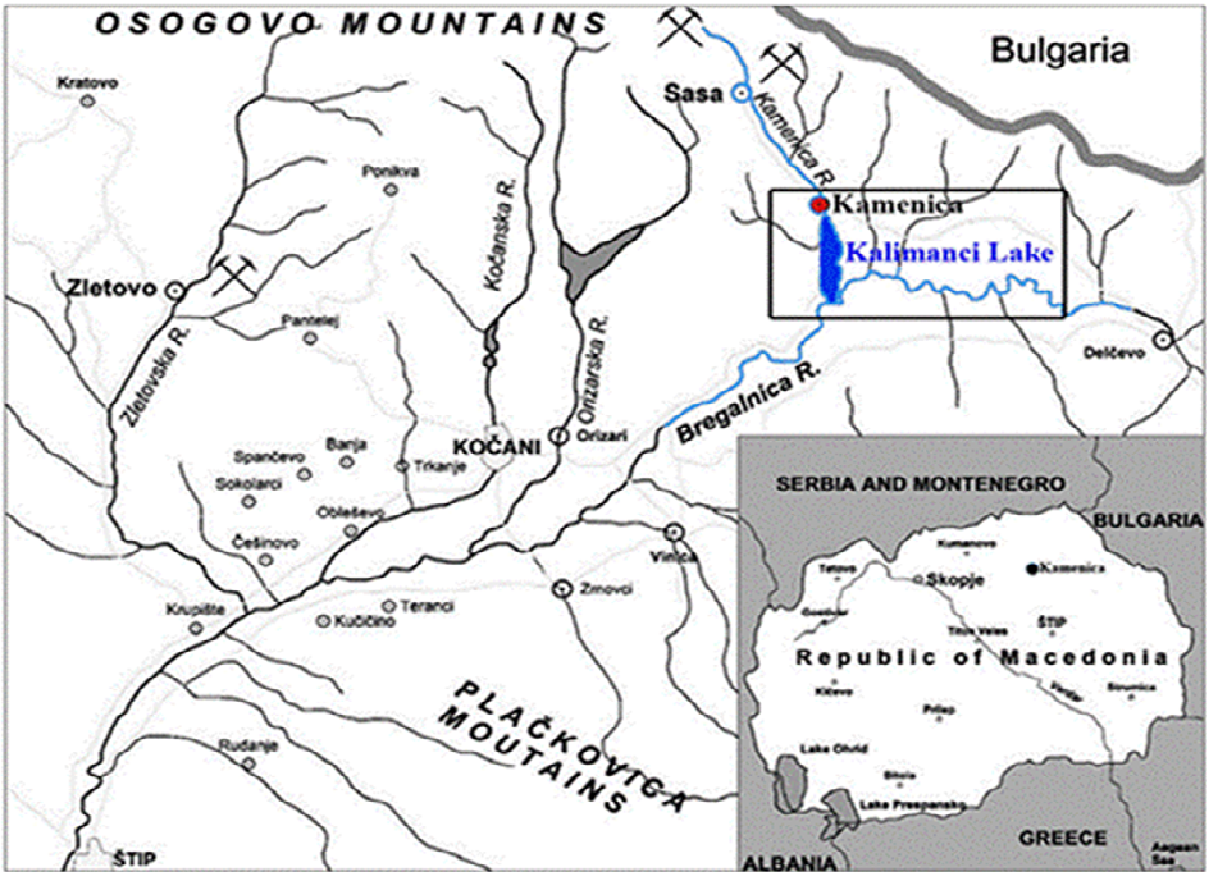

Figure 1. Map of study area.

al., 1995; Leleyter et al., 1999; Rengarajan and Sarin, 2004; Singh and Rajamani, 2001). However, in this part of Europe there is no baseline data regarding this study area, thus such studies are important in evaluating the REE pollution status of at least one part of these active mining areas.

Fractionation and mobility of the REE is highly dependent on the weathering and distribution of the minerals that contain the REE. The REE can be also retained through precipitation of aluminium-phosphate-sulphate minerals (Walter et al., 1995). Fe-Mn weathering products (Walter et al., 1995) and clay minerals are known as good traps for the REE. In addition to the weathering of geological deposits, the key factor for REE mobility is pH. The solubility of the REE tends to increase with decreasing pH (Nesbitt, 1979; Goldstein and Jacobsen, 1988).

A sequential extraction method is often used for determining the mode of occurrence of trace elements in lake sediments (Ebrahimpour and Mushrifah, 2008; Lopez et al., 2010; Villalobos-Castañeda et al., 2010; Singh et al., 2008), but there is a lack of studies of REE distribution in surficial lake sediments, especially in the widespread eastern area of the Republic of Macedonia. There are to date only few published studies concerning the behaviour and speciation of REE in this area (Serafimovski et al., 2006; Rogan Šmuc et al., 2012).

The objectives of this present study were to estimate the REE content in surficial sediments from Lake Kalimanci, both before and after the Sasa tailings dam failure and also to assess their mobility by employing a sequential extraction procedure. In order to estimate the contribution of REE to the Lake Kalimanci sediments from sources other than a natural origin, we also calculate an enrichment factor (EF). This allows us to examine whether there is any connection between Lake Kalimanci and the nearby Kočani paddy field (Rogan Šmuc, 2012).

MATERIALS AND METHODS

Environmental setting

Lake Kalimanci lies next to small town of Makedonska Kamenica (eastern Macedonia), about 5 km from the Sasa-Toranica ore district (Figure 1). The lake covers an area of 4.23 km^2 and contains approximately 127 million

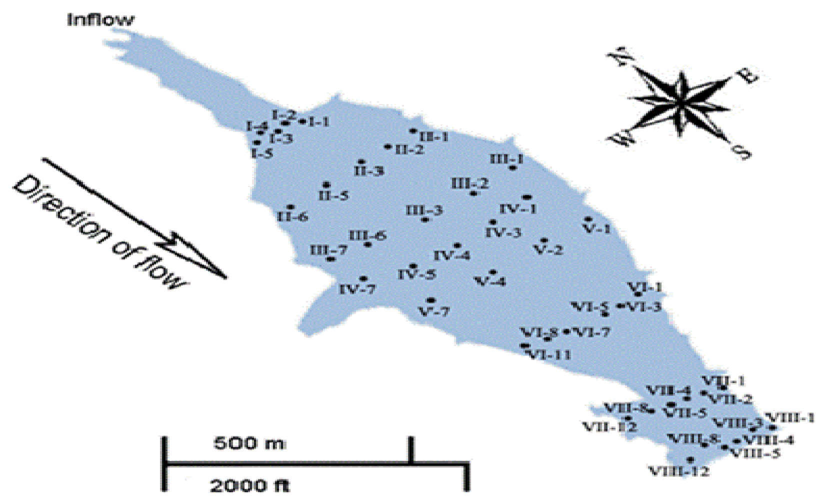

Figure 2. Distribution of sampling stations across Lake Kalimanci.

m^3 of water. The basic purpose of Lake Kalimanci is the storage of water, which is used to irrigate around 30,000 hectares of mainly rice fields in the Kočani Valley and Ovce Pole. As a result, the lake is characterised by large changes in water level, with dry season levels occasionally decreasing to only a few centimetres depth in inner (deeper) areas. Such changes mean that surficial lake sediments are often exposed to oxic conditions. In winter and spring the maximum depth of the lake can reach 80 m, with the exception of the northern margin of the lake where the River Kamenica enters. This area is very shallow and swampy and as a consequence, contains the largest amount of Sasa tailings dam material. Lake Kalimanci also has two inflowing tributaries which feed the lake and drain the southern Osogovo Mountains. The first of these tributaries is the River Bregalnica which, together with its tributaries, drains igneous metamorphic and sedimentary rocks of Precambrian to Holocene age, as well as mine waste and tailings from both abandoned and active Pb-Zn mines, and polymetallic mineralised material from the Serbo-Macedonian Massif (Osogovo Mountains). The second tributary is the River Kamenica which drains mine waste including: tailings, mill sewage and mine effluent derived from the Sasa Pb-Zn polymetallic ore deposit. The River Kamenica then flows directly into the artificial Lake Kalimanci.

Lake sediments are composed of a complex mixture of mineral fragments resulting from the weathering of rocks in the surrounding area, as also found in the drainage basin of the Kamenica River, whose organic and inorganic components are deposited in Lake Kalimanci. Thus, each component shows characteristic concentrations of REE. Therefore, REE distribution is a useful tool for characterising the origin and sedimentation processes of the lake sediments. According to XRD analysis, the Lake Kalimanci mineral assemblage contains mainly: quartz, plagioclase, K-feldspars, muscovite, illite, clinochlor, hornblende, gypsum, calcite, dolomite, smithsonite, pyrite, marcasite, goethite, diaspore, and in few samples, there was also found sphalerite and galena.

The Sasa Pb-Zn deposit lies within the Sasa-Toranica mining district in the Osogovo Mountains of eastern Macedonia. The geology of the Toranica-Sasa ore field comprises various rocks of both metamorphic and igneous origin, with the latter of Tertiary age. The most economically valuable mineralisation is closely related to that of quartz-graphite schists, with the ore consisting mainly of: galena, sphalerite, chalcopyrite and pyrite. Further studies have revealed more details of the complexity of the deposit's mineralogy, including the presence of: galena, sphalerite, chalcopyrite, pyrite, pyrrhotite, magnetite, martite, bornite, enargite, tetrahedrite, marcasite, barite, native gold, cubanite and native bismuth (Serafimovski and Aleksandrov 1995; Stojanov et al., 1995; Serafimovski et al., 2006).

In 2003 a major environmental disaster took place in eastern Macedonia when part of the Sasa Mine tailings dam collapsed and caused an intensive flow of tailings dam material through the Kamenica valley. Between 70,000 and 100,000 m^3 of tailings dam material was discharged into Lake Kalimanci, causing significant ecological damage (Rogan Šmuc, et al., 2009).

Sampling methods

17 surficial sediment samples from Lake Kalimanci were taken before the accident in August 2001. The sampling collection was resumed in September 2007, three years after the accident happened and 31 samples were taken. The chosen sampling locations were formed into 8 profiles (Figure 2) through Lake Kalimanci and were

mostly related to the area around the River Kamenica tributary on the northern site of the lake, which is directly connected to the Sasa mine area. The sediment pH ranged between 5.3 and 7.5 and the redox potential ranged between -325 mV and +180 mV.

The samples were collected with plastic corers (10 cm long tube with a 7 cm internal diameter). They were than packed into plastic bags and stored in the laboratory at 4 °C. The collected lake sediment samples were dried at 50 °C for 48 hours, sieved through a 0.315 mm polyethylene sieve to remove plant debris and homogenised by a mechanical agate grinder to a fine powder for subsequent analysis.

Sediment samples were analysed for major, minor, trace and REE concentrations at a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd – Ontario, Canada) using a variety of different analytical methods. After extraction of sub-samples, 0.5g of each sample were leached with 2-2-2-HCl-HNO_3-H_2O at 95 °C and analysed by ICP Mass Spectroscopy. According to official laboratory reports, the accuracy and precision of the surface sediment analyses were assessed via the use of an international reference material such as USGS standard MAG-1 (sediment). The analytical precision and accuracy were both better than ± 6%, as indicated by the results of duplicate measurement of 3 lake samples and of the MAG-1 standard.

Sequential extraction procedure

Selected lake sediment samples (I-4, II-3, III-3, V-7, VI-11, VII-11, VIII-8) were also analysed for chemical partitioning of REE by employing a sequential extraction method devised by a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd – Ontario, Canada). Within this procedure the sequential extraction scheme included a water-soluble fraction (F 1), an exchangeable + carbonate fraction (F 2), an oxidizable-organic fraction (F 3), an Fe–Mn oxide bound-reducible fraction (F 4) and a residual + reducible fraction (F 5). Reagents used per one gram of sample are F1 - 20 mL distilled water, F2 - 20 mL ammonium acetate, F3 - 20 ml 0.1 M sodium pyrophosphate ($Na_3P_2O_7$), F4 - 20 ml 0.1 M hydroxylamine hydrochloride (60 °C), F5 - 20 ml 0.25 M hydroxylamine.

For drawing the graphs we have had to replace the values below the limit of detection. According to Verbovšek (2011) the values under the detection limit should be replaced with LOD/√2. This was considered the best, as the average error is only 0.2% for this method of replacement.

RESULTS AND DISCUSSION

REE in surficial lake sediments

The measured concentrations of REE from the sampling from 2001 and 2007 in surficial sediments from Lake Kalimanci are presented in Table 1, together with basic descriptive statistics and concentrations of REE in upper continental crust, adopted by Taylor and McLenan (1985), Wedepohl (1995) and the average concentrations from the nearby Osogovo Mountains (Serafimovski et al., 2006). All statistical analyses were performed using the original statistical software program Statistica 8.

The ΣREE concentrations in surficial lake sediments varied between 127.33 and 333.40 for samples from 2001 and between 150.15 and 282.91 for 2007, after the Sasa tailings dam failure. Descriptive statistics showed that the sum of REE, LREE and the ratio between LREE and HREE are slightly higher in 2001. The sum of HREE is higher in year 2007.

Comparing the mean values of ΣREE, ΣLREE, ΣHREE and LREE/HREE ratio for 2001-2007 with those from Table 1 we can conclude that the highest values of ΣREE were calculated for the nearby Osogovo mountains (211.29), the sum of LREE was also the highest in same location (192.9), whilst the sum of HREE was highest in the surficial sediments from lake Kalimanci in 2007. High content of REE in the Lake Kalimanci surficial sediments are mostly due to precipitation of sulphate minerals and sulphosalts in the study area and the high content of clay minerals.

LREE accounted for 87.09% (2001) and 86.54% (2007) of the total REE in the investigated surficial lake sediments. This correlates well with the percentage of LREE in the upper continental crust (Taylor and McLenan, 1985; Wedepohl, 1995) and also agrees with the conclusions of Tyler (2004), that LREEs are usually more abundant than HREE in the Earth's crust. The salic minerals (feldspars, quartz) preferentially concentrate LREE, which also explains the high percentage of LREE in surficial sediments from Lake Kalimanci. The elevated contents of HREE in surficial lake sediments in both sampling years (2001, 2007) could be explained by the contribution of the mafic and ultramafic rocks in the nearby area, which contain HREE rich minerals: potassium feldspars, amphiboles and pyroxenes (Serafimovski and Aleksandrov, 1995; Laveuf and Cornu 2009).

The average ratio LREE/HREE is 6.80 for 2001 and 6.44 for 2007. The LREE/HREE ratios in both sampling years are much the same through all eight sampling profiles in Lake Kalimanci, which verify that the source material of REE or their fractionation has not changed throughout the lake. This coincides with mineral compositions within the lake and the measured pH values; none of these factors have drastically changed. Mao et al., (2011) suggested that the LREE/HREE ratio

Table 1. Comparison of REE contents in surficial sediments of Lake Kalimanci between sampling years 2001 and 2007.

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Locations	Year	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	ΣREE	ΣLREE	ΣHREE	LREE/HREE
I-2	2001	31,80	65,40	7,15	26,70	5,40	1,26	4,53	0,75	4,35	0,90	2,72	0,42	2,74	0,42	154,54	136,45	18,09	7,54
II-2	2001	32,80	64,70	7,72	29,10	5,60	1,28	5,43	0,77	4,54	0,92	2,77	0,41	2,82	0,43	159,29	139,92	19,37	7,22
II-5	2001	39,00	77,90	8,98	34,60	7,10	1,56	6,39	1,09	5,93	1,23	3,80	0,54	3,78	0,55	192,45	167,58	24,87	6,74
III-2	2001	29,60	58,50	6,79	26,10	5,00	1,23	4,67	0,76	4,53	0,95	2,85	0,44	3,02	0,42	144,86	125,99	18,87	6,68
III-7	2001	52,50	102,90	12,05	45,10	9,20	1,96	8,64	1,46	7,99	1,60	4,80	0,72	4,83	0,70	254,45	221,75	32,7	6,78
IV-1	2001	44,10	86,70	10,11	36,30	7,70	1,52	6,75	1,18	6,38	1,29	3,86	0,59	3,71	0,55	210,74	184,91	25,83	7,16
IV-3	2001	26,10	51,90	6,17	21,90	4,70	1,10	4,00	0,70	3,89	0,82	2,52	0,38	2,77	0,38	127,33	110,77	16,56	6,69
IV-5	2001	44,10	87,50	10,33	38,40	7,90	1,78	7,66	1,29	7,08	1,45	4,30	0,66	4,51	0,65	217,61	188,23	29,38	6,41
V-2	2001	44,30	88,80	10,29	39,40	8,30	1,80	6,98	1,17	6,78	1,43	4,33	0,63	4,18	0,58	218,97	191,09	27,88	6,85
V-7	2001	54,65	107,65	12,38	47,55	9,90	1,93	8,75	1,43	8,23	1,68	5,03	0,75	5,09	0,76	265,755	232,13	33,625	6,90
VI-1	2001	55,80	109,70	12,63	51,10	10,20	2,07	9,56	1,59	9,28	1,86	5,36	0,81	5,48	0,82	276,26	239,43	36,83	6,50
VI-3	2001	32,00	63,30	7,11	28,90	5,70	1,15	4,91	0,77	4,75	0,98	2,95	0,44	3,42	0,50	156,88	137,01	19,87	6,90
VI-8	2001	49,80	96,30	11,15	44,00	9,20	1,73	9,12	1,47	8,33	1,81	5,22	0,80	5,39	0,85	245,17	210,45	34,72	6,06
VII-2	2001	33,30	66,80	7,44	29,40	6,00	1,29	5,44	0,88	4,83	0,98	2,91	0,46	3,16	0,43	163,32	142,94	20,38	7,01
VII-5	2001	61,40	120,60	14,18	56,20	11,50	2,29	11,00	1,81	10,07	2,04	5,91	0,86	6,05	0,88	304,79	263,88	40,91	6,45
VIII-3	2001	31,80	66,70	7,28	28,80	5,70	1,19	5,51	0,86	4,74	1,00	3,11	0,49	3,10	0,49	160,77	140,28	20,49	6,85
VIII-5	2001	65,70	135,50	15,56	61,10	13,10	2,35	11,40	1,86	10,43	2,16	6,40	0,98	5,97	0,89	333,4	290,96	42,44	6,86
Mean	2001	42,87	85,34	9,84	37,92	7,78	1,62	7,10	1,17	6,60	1,36	4,05	0,61	4,12	0,61	210,98	183,75	27,22	6,80
Median	2001	44,10	86,70	10,11	36,30	7,70	1,56	6,75	1,17	6,38	1,29	3,86	0,59	3,78	0,55	210,74	184,91	25,83	6,85
Min	2001	26,10	51,90	6,17	21,90	4,70	1,10	4,00	0,70	3,89	0,82	2,52	0,38	2,74	0,38	127,33	110,77	16,56	6,06
Max	2001	65,70	135,50	15,56	61,10	13,10	2,35	11,40	1,86	10,43	2,16	6,40	0,98	6,05	0,89	333,40	290,96	42,44	7,54
Std. Dev.	2001	12,11	23,97	2,83	11,40	2,46	0,41	2,30	0,39	2,14	0,44	1,23	0,18	1,16	0,18	60,98	52,68	8,39	0,34
I-1	2007	33,10	68,50	8,62	33,10	6,56	1,44	6,50	1,00	5,68	1,14	3,31	0,53	3,35	0,49	173,32	149,88	23,44	6,39
I-2	2007	34,30	70,10	9,10	35,30	6,88	1,50	6,72	1,06	5,95	1,23	3,46	0,57	3,48	0,53	180,18	155,68	24,5	6,35
I-3	2007	33,70	68,30	8,73	33,10	6,51	1,45	6,44	1,06	5,93	1,24	3,60	0,61	3,73	0,53	174,93	150,34	24,59	6,11
I-4	2007	36,70	74,00	9,57	37,30	7,46	1,70	7,27	1,13	6,21	1,29	3,58	0,58	3,49	0,52	190,8	165,03	25,77	6,40
I-5	2007	33,20	66,30	8,61	33,10	6,38	1,38	5,99	0,97	5,25	1,04	3,17	0,51	3,02	0,45	169,37	147,59	21,78	6,78
II-1	2007	41,00	86,00	11,31	44,40	8,72	2,01	9,14	1,44	8,20	1,68	4,80	0,72	4,38	0,67	224,47	191,43	33,04	5,79
II-3	2007	41,00	80,60	10,92	42,00	8,15	1,92	8,12	1,31	7,14	1,42	4,18	0,64	3,83	0,57	211,8	182,67	29,13	6,27
II-5	2007	38,80	73,90	9,92	37,60	7,36	1,68	7,33	1,18	6,61	1,33	3,73	0,60	3,59	0,54	194,17	167,58	26,59	6,30
II-6	2007	37,60	76,20	9,83	37,50	7,26	1,66	7,19	1,13	6,46	1,26	3,72	0,59	3,61	0,54	194,55	168,39	26,16	6,44
III-1	2007	42,10	84,30	10,97	42,00	8,54	1,83	8,46	1,38	7,73	1,55	4,45	0,69	4,29	0,64	218,93	187,91	31,02	6,06
III-2	2007	40,40	80,50	10,38	40,20	7,90	1,70	7,68	1,21	6,96	1,42	3,85	0,61	3,73	0,57	207,11	179,38	27,73	6,47
III-3	2007	37,80	76,20	9,94	39,20	7,57	1,71	7,28	1,18	6,36	1,31	3,77	0,59	3,64	0,54	197,09	170,71	26,38	6,47
III-6	2007	38,00	76,80	10,39	38,50	7,44	1,70	8,25	1,16	6,88	1,44	4,02	0,64	3,71	0,61	199,54	171,13	28,41	6,02
IV-1	2007	39,90	80,60	10,42	41,50	8,06	1,68	7,60	1,22	6,73	1,35	3,83	0,63	3,77	0,57	207,86	180,48	27,38	6,59
IV-4	2007	36,40	73,90	9,45	37,10	7,08	1,57	6,84	1,09	6,15	1,25	3,71	0,57	3,48	0,52	189,11	163,93	25,18	6,51
IV-7	2007	43,50	88,70	11,44	44,90	8,82	1,90	8,64	1,40	7,76	1,56	4,74	0,71	4,33	0,66	229,06	197,36	31,7	6,23
V-1	2007	42,40	85,30	11,15	42,90	8,39	1,82	8,10	1,36	7,51	1,49	4,40	0,68	4,29	0,65	220,44	190,14	30,3	6,28
V-4	2007	30,60	63,50	7,85	30,60	5,78	1,31	5,55	0,87	4,90	0,96	2,84	0,45	2,78	0,42	158,41	138,33	20,08	6,89

Table 1. Continue

V-7	2007	40,30	80,70	10,58	43,10	8,07	1,76	7,82	1,26	6,87	1,40	3,98	0,62	3,86	0,57	210,89	182,75	28,14	6,49
VI-1	2007	44,90	92,70	11,79	46,50	8,96	1,78	9,00	1,44	8,14	1,66	4,95	0,75	4,90	0,72	238,19	204,85	33,34	6,14
VI-5	2007	38,40	79,90	10,09	39,80	7,73	1,71	7,35	1,21	6,51	1,31	3,84	0,61	3,75	0,55	202,76	175,92	26,84	6,55
VI-7	2007	31,10	61,80	7,90	32,30	5,90	1,34	5,82	0,93	5,03	1,04	2,98	0,45	2,92	0,44	159,95	139	20,95	6,63
VI-11	2007	43,40	88,20	11,48	46,20	8,69	1,81	8,65	1,40	7,76	1,62	4,63	0,70	4,40	0,63	229,57	197,97	31,6	6,26
VII-1	2007	46,70	95,70	12,43	49,70	9,52	1,99	9,26	1,48	8,04	1,64	4,75	0,70	4,39	0,64	246,94	214,05	32,89	6,51
VII-4	2007	44,00	89,60	11,59	47,10	8,87	1,90	8,68	1,36	7,63	1,53	4,30	0,66	4,20	0,62	232,04	201,16	30,88	6,51
VII-8	2007	28,60	59,70	7,39	29,60	5,41	1,20	5,16	0,83	4,66	0,98	2,88	0,45	2,86	0,43	150,15	130,7	19,45	6,72
VII-12	2007	44,60	90,80	11,82	48,00	9,02	1,85	8,82	1,42	7,41	1,53	4,46	0,69	4,17	0,64	235,23	204,24	30,99	6,59
VIII-1	2007	42,70	86,50	10,99	44,50	8,37	1,77	7,82	1,27	6,91	1,37	3,97	0,61	3,90	0,56	221,24	193,06	28,18	6,85
VIII-4	2007	35,70	72,50	9,19	38,10	6,83	1,60	6,65	1,07	5,81	1,19	3,50	0,52	3,42	0,50	186,58	162,32	24,26	6,69
VIII-8	2007	42,10	86,30	11,06	45,20	8,46	1,77	8,18	1,29	7,30	1,42	4,18	0,62	3,90	0,59	222,37	193,12	29,25	6,60
VIII-12	2007	54,30	109,20	14,34	58,10	10,81	2,03	10,52	1,67	8,82	1,75	5,15	0,78	4,73	0,71	282,91	246,75	36,16	6,82
Mean	2007	39,27	79,59	10,30	40,60	7,79	1,69	7,64	1,22	6,75	1,37	3,96	0,62	3,80	0,57	205,16	177,54	27,62	6,44
Median	2007	39,90	80,50	10,39	40,20	7,90	1,71	7,68	1,21	6,87	1,37	3,85	0,61	3,75	0,57	207,11	179,38	27,73	6,47
Min	2007	28,60	59,70	7,39	29,60	5,41	1,20	5,16	0,83	4,66	0,96	2,84	0,45	2,78	0,42	150,15	130,70	19,45	5,79
Max	2007	54,30	109,20	14,34	58,10	10,81	2,03	10,52	1,67	8,82	1,75	5,15	0,78	4,90	0,72	282,91	246,75	36,16	6,89
Std. Dev.	2007	5,37	10,88	1,49	6,27	1,19	0,21	1,21	0,19	1,04	0,21	0,61	0,08	0,53	0,08	29,07	25,10	4,11	0,26

and Eu anomaly can be used to trace weathering intensity. In the present study lower LREE/HREE ratios and a significant Eu anomaly are detected in the lake sediments and also in the vulcanites from Osogovo Mountains, which provides powerful evidence to support the hypothesis that REE in the lake sediments originate mainly from nearby rocks and are not result of mining activity.

Sediments from Lake Kalimanci predominantly originate from the acidic and intermediate igneous and metamorphic rocks: granites, diabases, different schists,

gabbros and cipolini marbles (Serafimovski and Aleksandrov, 1995). The main sediment input into Lake Kalimanci is the River Kamenica, which flows through the Osogovo Mountains and discharges into lake. It is well-known that chemical weathering affects the chemical composition of rocks in the order: plagioclase feldspars > Kfeldspar > quartz. The weathering residues of all feldspars are different clay minerals. However, the chemistry of bed rocks often does not reflect the exact source before weathering, because a lot of minerals (e.g., feldspars) become progressively depleted, thus new sediments become less representative of the source rock (Nesbitt et al., 1996). That is why the abundance and patterns of REE are reasonably well preserved during weathering, as they are far less mobile during sedimentary processes.

The widespread area around Lake Kalimanci is a very old mining area, where the Pb-Zn Sasa-Toranica and Pb-Zn Zletovo Kratovo mines are located. The Sasa Mine is directly connected with Lake Kalimanci through the Kamenica River, which also connects to the Sasa tailings dam. To investigate the REE associations with major oxides in the surficial lake sediments Pearson R correlation analyses were applied to all samples studied. The correlation matrices show highly positive correlations between elements from the LREE group and also between elements from the HREE group in both sampling years (2001, 2007). Thus, we can conclude that LREE and HREE have similar inputs and common geochemical characteristics in the Lake Kalimanci surficial sediments. The Pearson correlation matrices (Table 2) revealed interesting connections among REE and major oxides, especially the connection between REE, silica and carbonates. In both sampling years (2001, 2007) there was a negative correlation between SiO2 and the REE. In 2001, the measured mean value of SiO2 was 60.23%, which had a strong negative correlation with all REE, whilst the average percentage of carbonates (MgO, CaO) was measured at 1.51% and 1.92%. For 2007, the average content of SiO2 was 50.21% and for carbonates (MgO, CaO) 2.23% and 5.35%. Because of the Sasa tailings dam failure in 2003, a Pearson correlation analysis was made for tailings dam material (with unpublished data) to find out how the failure affected the Lake Kalimanci surficial sediments. Samples from the Sasa tailings dam material were analysed for their total element concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd) using different analytical methods and on average contain, in 2004: 46.87% SiO2, 2.37% MgO and 12.82% CaO and in 2010: 35.11% SiO2, 1.97% MgO and 12.59% CaO (unpublished data). From these results we can conclude that the Sasa tailings dam failure in 2003 did

Table 2. Pearson correlation matrix for REEs and major oxides in surficial lake sediments.

2001	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SiO_2	1,00	**-0,91**	**-0,98**	**-0,93**	-0,23	**0,94**	**-0,81**	-0,25	**-0,93**	**-0,69**	**-0,89**	**-0,87**	**-0,86**	**-0,87**	**-0,87**	**-0,87**	**-0,92**	**-0,86**	**-0,88**	**-0,87**	**-0,87**	**-0,89**	**-0,85**	**-0,86**	**-0,83**
Al_2O_3	**-0,91**	1,00	**0,84**	**0,74**	-0,12	**-0,88**	**0,85**	0,47	**0,77**	0,40	**0,91**	**0,93**	**0,92**	**0,93**	**0,92**	**0,92**	**0,93**	**0,90**	**0,90**	**0,91**	**0,91**	**0,92**	**0,90**	**0,90**	**0,88**
Fe_2O_3	**-0,98**	**0,84**	1,00	**0,95**	0,32	**-0,95**	**0,73**	0,24	**0,94**	**0,76**	**0,84**	**0,81**	**0,81**	**0,82**	**0,83**	**0,82**	**0,87**	**0,83**	**0,84**	**0,84**	**0,84**	**0,85**	**0,82**	**0,83**	**0,81**
MgO	**-0,93**	**0,74**	**0,95**	1,00	0,45	**-0,87**	**0,68**	0,09	**0,93**	**0,80**	**0,73**	**0,71**	**0,71**	**0,72**	**0,73**	**0,73**	**0,80**	**0,72**	**0,74**	**0,74**	**0,75**	**0,76**	**0,72**	**0,74**	**0,70**
CaO	-0,23	-0,12	0,32	0,45	1,00	**-0,15**	0,17	-0,15	0,22	**0,59**	-0,06	-0,24	-0,23	-0,22	-0,21	-0,20	-0,12	-0,23	-0,20	-0,21	-0,20	-0,18	-0,23	-0,21	-0,24
Na_2O	**0,94**	**-0,88**	**-0,95**	**-0,87**	-0,15	1,00	**-0,68**	-0,39	**-0,91**	**-0,64**	**-0,79**	**-0,86**	**-0,87**	**-0,87**	**-0,88**	**-0,88**	**-0,92**	**-0,86**	**-0,87**	**-0,87**	**-0,86**	**-0,88**	**-0,85**	**-0,85**	**-0,81**
K2O	**-0,81**	**0,85**	**0,73**	**0,68**	0,17	**-0,68**	1,00	0,40	**0,58**	0,36	**0,77**	**0,64**	**0,62**	**0,64**	**0,61**	**0,61**	**0,68**	**0,59**	**0,60**	**0,61**	**0,61**	**0,62**	**0,58**	**0,60**	**0,57**
TiO_2	-0,25	0,47	0,24	0,09	-0,15	-0,39	0,40	1,00	0,02	-0,15	0,24	0,28	0,30	0,27	0,27	0,28	0,24	0,24	0,22	0,23	0,23	0,26	0,25	0,25	0,25
P_2O_5	**-0,93**	**0,77**	**0,94**	**0,93**	0,22	**-0,91**	**0,58**	0,02	1,00	**0,77**	**0,79**	**0,83**	**0,83**	**0,84**	**0,86**	**0,85**	**0,90**	**0,86**	**0,87**	**0,87**	**0,87**	**0,87**	**0,85**	**0,87**	**0,83**
MnO	**-0,69**	0,40	**0,76**	**0,80**	**0,59**	**-0,64**	0,36	-0,15	**0,77**	1,00	0,45	0,45	0,45	0,46	0,47	0,46	**0,54**	**0,49**	**0,52**	**0,49**	**0,49**	**0,49**	0,45	**0,49**	0,45
Cr_2O_3	**-0,89**	**0,91**	**0,84**	**0,73**	-0,06	**-0,79**	**0,77**	0,24	**0,79**	0,45	1,00	**0,91**	**0,90**	**0,90**	**0,90**	**0,90**	**0,90**	**0,90**	**0,90**	**0,90**	**0,91**	**0,91**	**0,90**	**0,90**	**0,90**
La	**-0,87**	**0,93**	**0,81**	**0,71**	-0,24	**-0,86**	**0,64**	0,28	**0,83**	0,45	**0,91**	1,00	**1,00**	**1,00**	**0,99**	**0,99**	**0,98**	**0,99**	**0,99**	**0,99**	**0,98**	**0,99**	**0,98**	**0,97**	**0,96**
Ce	**-0,86**	**0,92**	**0,81**	**0,71**	-0,23	**-0,87**	**0,62**	0,30	**0,83**	0,45	**0,90**	**1,00**	1,00	**1,00**	**0,99**	**1,00**	**0,98**	**0,98**	**0,98**	**0,98**	**0,98**	**0,98**	**0,98**	**0,96**	**0,95**
Pr	**-0,87**	**0,93**	**0,82**	**0,72**	-0,22	**-0,87**	**0,64**	0,27	**0,84**	0,46	**0,90**	**1,00**	**1,00**	1,00	**0,99**	**0,99**	**0,98**	**0,99**	**0,99**	**0,99**	**0,98**	**0,98**	**0,98**	**0,96**	**0,95**
Nd	**-0,87**	**0,92**	**0,83**	**0,73**	-0,21	**-0,88**	**0,61**	0,27	**0,86**	0,47	**0,90**	**0,99**	**0,99**	**0,99**	1,00	**1,00**	**0,98**	**0,99**	**0,99**	**0,99**	**0,99**	**0,99**	**0,98**	**0,97**	**0,96**
Sm	**-0,87**	**0,92**	**0,82**	**0,73**	-0,20	**-0,88**	**0,61**	0,28	**0,85**	0,46	**0,90**	**0,99**	**1,00**	**0,99**	**1,00**	1,00	**0,98**	**0,99**	**0,98**	**0,99**	**0,98**	**0,99**	**0,98**	**0,97**	**0,95**
Eu	**-0,92**	**0,93**	**0,87**	**0,80**	-0,12	**-0,92**	**0,68**	0,24	**0,90**	**0,54**	**0,90**	**0,98**	**0,98**	**0,98**	**0,98**	**0,98**	1,00	**0,97**	**0,98**	**0,98**	**0,97**	**0,97**	**0,96**	**0,95**	**0,93**
Gd	**-0,86**	**0,90**	**0,83**	**0,72**	-0,23	**-0,86**	**0,59**	0,24	**0,86**	**0,49**	**0,90**	**0,99**	**0,98**	**0,99**	**0,99**	**0,99**	**0,97**	1,00	**0,99**	**0,99**	**0,99**	**0,99**	**0,99**	**0,98**	**0,98**
Tb	**-0,88**	**0,90**	**0,84**	**0,74**	-0,20	**-0,87**	**0,60**	0,22	**0,87**	**0,52**	**0,90**	**0,99**	**0,98**	**0,99**	**0,99**	**0,98**	**0,98**	**0,99**	1,00	**1,00**	**0,99**	**0,99**	**0,99**	**0,98**	**0,97**
Dy	**-0,87**	**0,91**	**0,84**	**0,74**	-0,21	**-0,87**	**0,61**	0,23	**0,87**	**0,49**	**0,90**	**0,99**	**0,98**	**0,99**	**0,99**	**0,99**	**0,98**	**0,99**	**1,00**	1,00	**1,00**	**1,00**	**0,99**	**0,99**	**0,98**
Ho	**-0,87**	**0,91**	**0,84**	**0,75**	-0,20	**-0,86**	**0,61**	0,23	**0,87**	**0,49**	**0,91**	**0,98**	**0,98**	**0,98**	**0,99**	**0,98**	**0,97**	**0,99**	**0,99**	**1,00**	1,00	**1,00**	**1,00**	**0,99**	**0,99**
Er	**-0,89**	**0,92**	**0,85**	**0,76**	-0,18	**-0,88**	**0,62**	0,26	**0,87**	**0,49**	**0,91**	**0,99**	**0,98**	**0,98**	**0,99**	**0,99**	**0,97**	**0,99**	**0,99**	**1,00**	**1,00**	1,00	**1,00**	**0,99**	**0,98**
Tm	**-0,85**	**0,90**	**0,82**	**0,72**	-0,23	**-0,85**	**0,58**	0,25	**0,85**	0,45	**0,90**	**0,98**	**0,98**	**0,98**	**0,98**	**0,98**	**0,96**	**0,99**	**0,99**	**0,99**	**1,00**	**1,00**	1,00	**0,98**	**0,98**
Yb	**-0,86**	**0,90**	**0,83**	**0,74**	-0,21	**-0,85**	**0,60**	0,25	**0,87**	**0,49**	**0,90**	**0,97**	**0,96**	**0,96**	**0,97**	**0,97**	**0,95**	**0,98**	**0,98**	**0,99**	**0,99**	**0,99**	**0,98**	1,00	**0,99**
Lu	**-0,83**	**0,88**	**0,81**	**0,70**	-0,24	**-0,81**	**0,57**	0,25	**0,83**	0,45	**0,90**	**0,96**	**0,95**	**0,95**	**0,96**	**0,95**	**0,93**	**0,98**	**0,97**	**0,98**	**0,99**	**0,98**	**0,98**	**0,99**	1,00

2007	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SiO_2	1,00	-0,28	**-0,41**	**-0,85**	**-0,71**	**0,86**	-0,17	**0,49**	**-0,88**	**-0,50**	**-0,80**	**-0,50**	**-0,44**	**-0,50**	**-0,52**	**-0,48**	**-0,58**	**-0,51**	**-0,47**	**-0,45**	**-0,46**	**-0,40**	-0,34	-0,32	**-0,37**
Al_2O_3	-0,28	1,00	**-0,44**	-0,03	**-0,45**	0,02	**0,92**	**0,45**	-0,06	**-0,40**	**0,45**	**0,85**	**0,87**	**0,86**	**0,83**	**0,87**	**0,82**	**0,85**	**0,85**	**0,86**	**0,83**	**0,83**	**0,85**	**0,83**	**0,84**
Fe_2O_3	**-0,41**	**-0,44**	1,00	**0,49**	**0,68**	**-0,74**	**-0,57**	**-0,52**	**0,56**	**0,89**	**0,46**	-0,26	-0,26	-0,28	-0,18	-0,28	-0,22	-0,30	-0,29	-0,33	-0,33	-0,34	**-0,47**	**-0,39**	**-0,38**
MgO	**-0,85**	-0,03	**0,49**	1,00	**0,81**	**-0,77**	0,01	**-0,59**	**0,90**	**0,64**	**0,57**	0,10	0,02	0,10	0,10	0,09	0,28	0,12	0,10	0,10	0,09	0,03	-0,01	-0,04	0,01
CaO	**-0,71**	**-0,45**	**0,68**	**0,81**	1,00	**-0,79**	**-0,47**	**-0,77**	**0,82**	**0,73**	**0,41**	-0,17	-0,24	-0,18	-0,15	-0,21	-0,11	-0,18	-0,21	-0,24	-0,21	-0,27	-0,33	-0,35	-0,30
Na_2O	**0,86**	0,02	**-0,74**	**-0,77**	**-0,79**	1,00	0,19	**0,71**	**-0,89**	**-0,78**	**-0,82**	-0,27	-0,22	-0,24	-0,32	-0,23	-0,29	-0,21	-0,20	-0,14	-0,14	-0,11	0,01	-0,02	-0,03
K2O	-0,17	**0,92**	**-0,57**	0,01	**-0,47**	0,19	1,00	**0,46**	-0,10	**-0,46**	0,21	**0,65**	**0,65**	**0,67**	**0,61**	**0,69**	**0,72**	**0,69**	**0,68**	**0,71**	**0,69**	**0,67**	**0,73**	**0,67**	**0,70**
TiO_2	**0,49**	**0,45**	**-0,52**	**-0,59**	**-0,77**	**0,71**	**0,46**	1,00	**-0,71**	**-0,66**	-0,32	0,21	0,27	0,22	0,17	0,24	0,15	0,24	0,27	0,33	0,33	**0,36**	**0,42**	**0,47**	**0,45**
P_2O_5	**-0,88**	-0,06	**0,56**	**0,90**	**0,82**	**-0,89**	-0,10	**-0,71**	1,00	**0,70**	**0,68**	0,18	0,12	0,17	0,20	0,16	0,30	0,16	0,15	0,12	0,13	0,08	0,00	0,00	0,02
MnO	**-0,50**	**-0,40**	**0,89**	**0,64**	**0,73**	**-0,78**	**-0,46**	**-0,66**	**0,70**	1,00	**0,49**	-0,26	-0,28	-0,28	-0,19	-0,27	-0,19	-0,29	-0,28	-0,31	-0,32	-0,35	**-0,45**	**-0,40**	**-0,38**
Cr_2O_3	**-0,80**	**0,45**	**0,46**	**0,57**	**0,41**	**-0,82**	0,21	-0,32	**0,68**	**0,49**	1,00	**0,61**	**0,59**	**0,59**	**0,66**	**0,58**	**0,56**	**0,55**	**0,55**	**0,50**	**0,48**	**0,47**	**0,36**	**0,41**	**0,41**
La	**-0,50**	**0,85**	-0,26	0,10	-0,17	-0,27	**0,65**	0,21	0,18	-0,26	**0,61**	1,00	**0,99**	**0,99**	**0,99**	**0,99**	**0,92**	**0,96**	**0,97**	**0,95**	**0,93**	**0,93**	**0,91**	**0,91**	**0,90**
Ce	**-0,44**	**0,87**	-0,26	0,02	-0,24	-0,22	**0,65**	0,27	0,12	-0,28	**0,59**	**0,99**	1,00	**0,99**	**0,99**	**0,99**	**0,91**	**0,97**	**0,97**	**0,95**	**0,93**	**0,94**	**0,92**	**0,93**	**0,92**
Pr	**-0,50**	**0,86**	-0,28	0,10	-0,18	-0,24	**0,67**	0,22	0,17	-0,28	**0,59**	**0,99**	**0,99**	1,00	**0,99**	**0,99**	**0,93**	**0,98**	**0,98**	**0,97**	**0,95**	**0,95**	**0,93**	**0,92**	**0,92**
Nd	**-0,52**	**0,83**	-0,18	0,10	-0,15	-0,32	**0,61**	0,17	0,20	-0,19	**0,66**	**0,99**	**0,99**	**0,99**	1,00	**0,98**	**0,91**	**0,96**	**0,96**	**0,93**	**0,91**	**0,92**	**0,88**	**0,89**	**0,88**
Sm	**-0,48**	**0,87**	-0,28	0,09	-0,21	-0,23	**0,69**	0,24	0,16	-0,27	**0,58**	**0,99**	**0,99**	**0,99**	**0,98**	1,00	**0,94**	**0,98**	**0,99**	**0,97**	**0,95**	**0,95**	**0,93**	**0,93**	**0,92**
Eu	**-0,58**	**0,82**	-0,22	0,28	-0,11	-0,29	**0,72**	0,15	0,30	-0,19	**0,56**	**0,92**	**0,91**	**0,93**	**0,91**	**0,94**	1,00	**0,95**	**0,95**	**0,95**	**0,93**	**0,92**	**0,90**	**0,88**	**0,89**
Gd	**-0,51**	**0,85**	-0,30	0,12	-0,18	-0,21	**0,69**	0,24	0,16	-0,29	**0,55**	**0,96**	**0,97**	**0,98**	**0,96**	**0,98**	**0,95**	1,00	**0,98**	**0,98**	**0,98**	**0,97**	**0,96**	**0,94**	**0,96**
Tb	**-0,47**	**0,85**	-0,29	0,10	-0,21	-0,20	**0,68**	0,27	0,15	-0,28	**0,55**	**0,97**	**0,97**	**0,98**	**0,96**	**0,99**	**0,95**	**0,98**	1,00	**0,98**	**0,97**	**0,98**	**0,96**	**0,96**	**0,95**
Dy	**-0,45**	**0,86**	-0,33	0,10	-0,24	-0,14	**0,71**	0,33	0,12	-0,31	**0,50**	**0,95**	**0,95**	**0,97**	**0,93**	**0,97**	**0,95**	**0,98**	**0,98**	1,00	**0,99**	**0,99**	**0,97**	**0,97**	**0,97**
Ho	**-0,46**	**0,83**	-0,33	0,09	-0,21	-0,14	**0,69**	0,33	0,13	-0,32	**0,48**	**0,93**	**0,93**	**0,95**	**0,91**	**0,95**	**0,93**	**0,98**	**0,97**	**0,99**	1,00	**0,99**	**0,98**	**0,97**	**0,98**
Er	**-0,40**	**0,83**	-0,34	0,03	-0,27	-0,11	**0,67**	**0,36**	0,08	-0,35	**0,47**	**0,93**	**0,94**	**0,95**	**0,92**	**0,95**	**0,92**	**0,97**	**0,98**	**0,99**	**0,99**	1,00	**0,98**	**0,98**	**0,98**
Tm	-0,34	**0,85**	**-0,47**	-0,01	-0,33	0,01	**0,73**	**0,42**	0,00	**-0,45**	**0,36**	**0,91**	**0,92**	**0,93**	**0,88**	**0,93**	**0,90**	**0,96**	**0,96**	**0,97**	**0,98**	**0,98**	1,00	**0,98**	**0,98**
Yb	-0,32	**0,83**	**-0,39**	-0,04	-0,35	-0,02	**0,67**	**0,47**	0,00	**-0,40**	**0,41**	**0,91**	**0,93**	**0,92**	**0,89**	**0,93**	**0,88**	**0,94**	**0,96**	**0,97**	**0,97**	**0,98**	**0,98**	1,00	**0,98**
Lu	**-0,37**	**0,84**	**-0,38**	0,01	-0,30	-0,03	**0,70**	**0,45**	0,02	**-0,38**	**0,41**	**0,90**	**0,92**	**0,92**	**0,88**	**0,92**	**0,89**	**0,96**	**0,95**	**0,97**	**0,98**	**0,98**	**0,98**	**0,98**	1,00

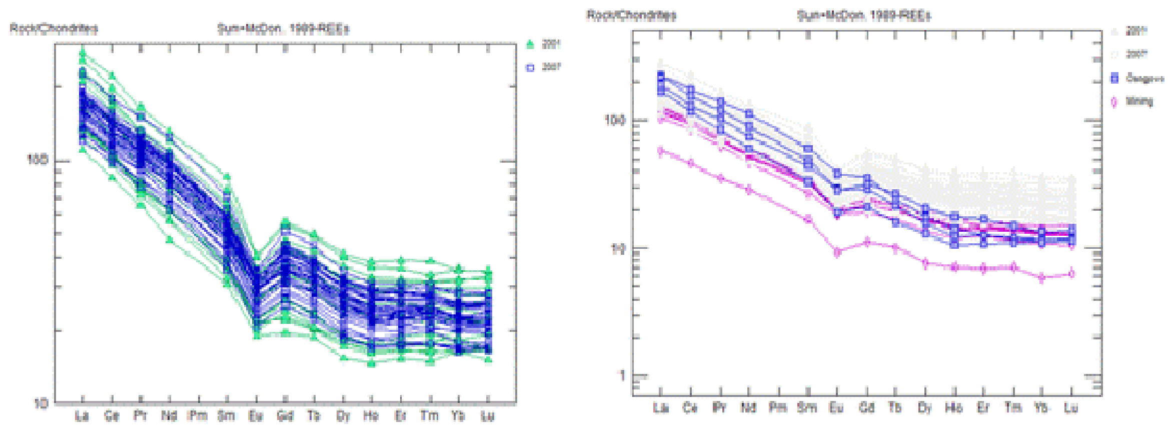

Figure 3. Chondrite – normalised REE diagrams for surficial sediments from Lake Kalimanci. (**Osogovo**=granitic rocks: dacites, trahidacites from the Osogovo Mountains (Serafimovski et al., 2005) **Mining**= Sasa tailings dam material (unpublished data).

not affect the REE concentrations in the Lake Kalimanci surficial sediments. Therefore, it is obvious that the REE content in the surficial sediments of Lake Kalimanci are the result of chemical and physical weathering of nearby igneous and metamorphic rocks. The different concentrations of silica and carbonates are presumably connected with different places of Pb-Zn ore excavation. According to Vrhovnik et al., (2010) the most important Pb and Zn ore bodies are usually found in quartz-muscovite-graphitic schists and also in greenschists, cippoline marbles and dacites. Thus, when the percentage of carbonates is high (2001) the excavation processes must have been occurring in carbonate rocks and when the percentage of carbonates decreases and the percentage of silica rises, the excavation must have been in quartz rich schists. To recover the new ore body, large amounts of gangue material must be grinded what contribute to speed of weathering processes. While we were dealing with the Pb-Zn mining area we also checked the correlations among REE, Pb and Zn. The results revealed that there are no correlations between those elements, therefore the Pb-Zn ore deposit does not affect the amount of REE in the Lake Kalimanci surficial sediments, but that their concentrations are connected with non-metallic minerals of nearby rock formations.

The inter-element correlation matrix between the REE and other major elements shows different correlations for both sampling years. In 2001, there was a strong positive correlation between Fe and all REE, and a positive correlation between Mn and Eu, Gd, Tb, Dy, Ho, Er and Yb, but Mn had no correlation with LREE. Surficial sediment samples from 2007 revealed a bad correlation with REE; there was a negative correlation between Fe, Mn and Tm, Yb and Lu. However, K and Al had strong positive correlations with all REE in both sampling years. This is possibly attributed to the accommodation of REE within K and Al-bearing minerals and thus, the REE are not strongly bound by Fe-Mn oxides. Chemical weathering of ferromagnesian and feldspar minerals yield clay minerals rich with K and Al. A strong positive correlation among REE and K and Al suggests that clay minerals can accommodate REE released from the weathered primary minerals.

Unfortunately, the study of REE in the Kamenica River has not yet finished; consequently we can only predict that the REE are delivered to Lake Kalimanci through the Kamnica River from the nearby Osogovo Mountains.

The chondrite-normalised patterns of REE in the surficial sediments of Lake Kalimanci are given in Figure 3. Data normalisation was done with REE concentrations adopted by Sun and McDonough (1989). Chondrite normalised patterns of the surficial sediments from Lake Kalimanci, selected granitic rocks from the Osogovo Mountains and those from the Sasa tailings dam material do not differ appreciably from each other and are similar to that of the REE concentrations adopted by Sun and McDonough (1989). The pattern is characterised by LREE enrichment, negative Eu anomaly and fairly flat HREE pattern.

Europium anomalies

Significant Eu anomalies occur mainly in crustal rocks as a result of intracrustal fractionation separating granitic melts from residues containing feldspars, which is the major host of Eu^{2+} in rocks (Gao and Wedepohl, 1995). Eu^{2+} is compatible in plagioclase and K-feldspar, relative to Eu^{3+}, which is incompatible. Also, Hanson (1980) and Saunders (1984) report that intermediate and felsic volcanic rocks possess substantial negative Eu anomalies, owing to crystal fractionation of feldspars in the melt, whereas mafic rocks typically have smaller or even lack negative Eu anomalies. Gao and Wedepohl (1995) reported that granitic melts are the major source

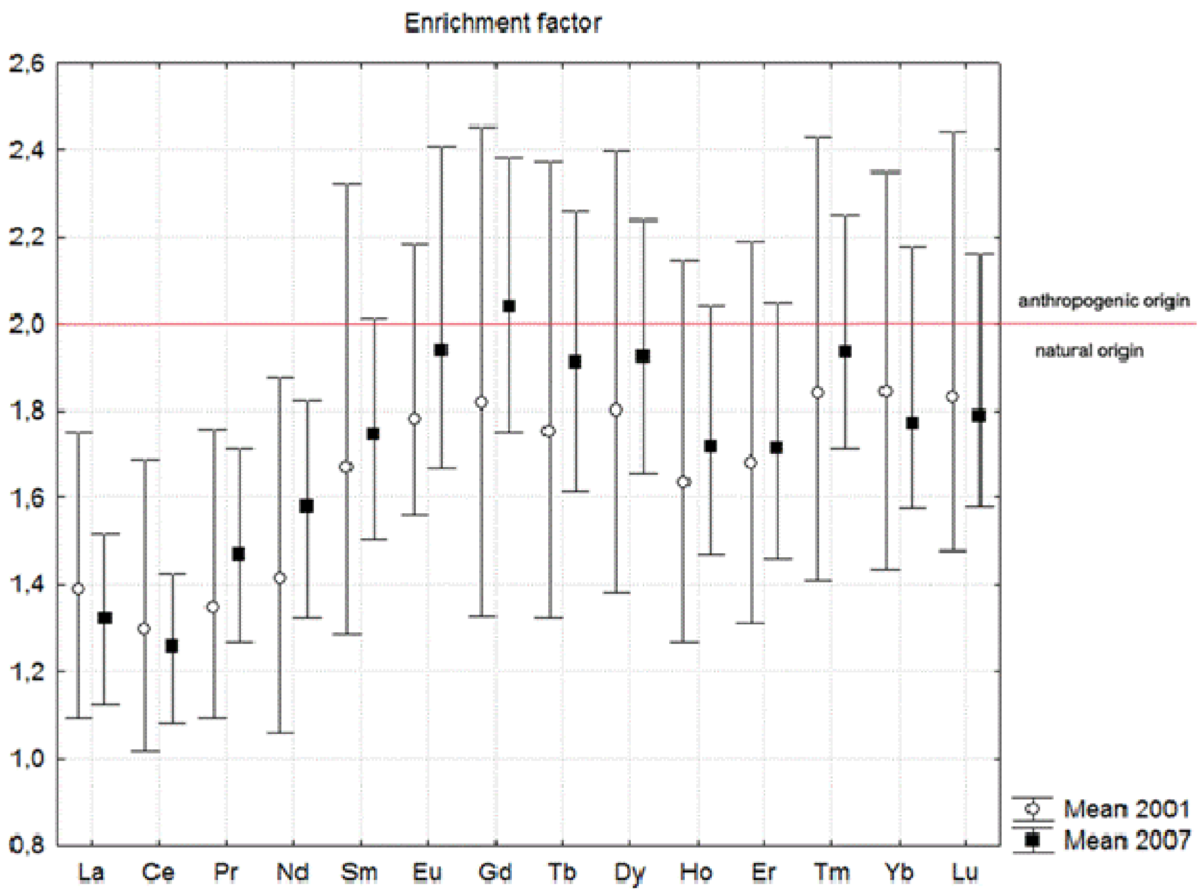

Figure 4. Mean, minium and maximum values of calculated EF for surficial sediments for both sampling years 2001 and 2007.

of negative Eu anomalies, mostly because of their equilibrium with plagioclase-rich residuum. The negative Eu anomaly in the surficial sediments from Lake Kalimanci and from the Osogovo Mountains vulcanites can be related to the original source rocks, which must have been Eu depleted by fractionation of plagioclase feldspars during their igneous and metamorphic history, in addition to the fractionation processes in the Lake Kalimanci basin. Roelandts and Deblond, (1992) reported that REE are generally valuable indicators of petrogenetic processes and that therefore, the Eu anomalies can also characterise massive sulphide deposits in this study.

Enrichment factor

In order to estimate the contribution of REE to lake sediments from other than natural origins, enrichment factors (EF) with respect to the composition of Post-Archean average Australian shale (PAAS), adopted by Taylor and McLennan (1985) were calculated, with the following equation:

EF= (M/Al) sample/ (M/Al) crust

where: (M/Al)sample denotes the measured REE, divided by the aluminium ratio of the sample and (M/Al) crust denotes the corresponding REE to aluminium ratio in PAAS. Values of EF below 2 can be considered to be of natural origin and values above 2 are suggestive of anthropogenic sources (Grousset et al., 1995).

Calculated mean values of EF for all the studied REE from the Lake Kalimanci surficial sediments in both sampling years (2001 – 2007) are listed as follows: La 1.49–1.32, Ce 1.30–1.26, Pr 1.35–1.47, Nd 1.42–1.58, Sm 1.67–1.75, Eu 1.78–1.94, Gd 1.82–2.04, Tb 1.75–1.91, Dy 1.80–1.93, Ho 1.63–1.72, Er 1.68–1.71, Tm 1.84–1.93, Yb 1.84–1.77 and Lu 1.83–1.79. In both sampling years, before (2001) and after the Sasa tailings dam failure (2007), the mean values of EF ≤ 2 (Figure 4), except Gd, suggesting that they are mainly of natural origin. Gd has a slightly higher mean value (2.18) of EF in 2007 after the Sasa tailings dam failure, but most likely this also has a natural origin, whilst there were no minerals detected related with Gd (e.g., monazite, bastnäsite). According to Birth's (2003) interpretation of EF has surficial sediments from Lake Kalimanci minor enrichment.

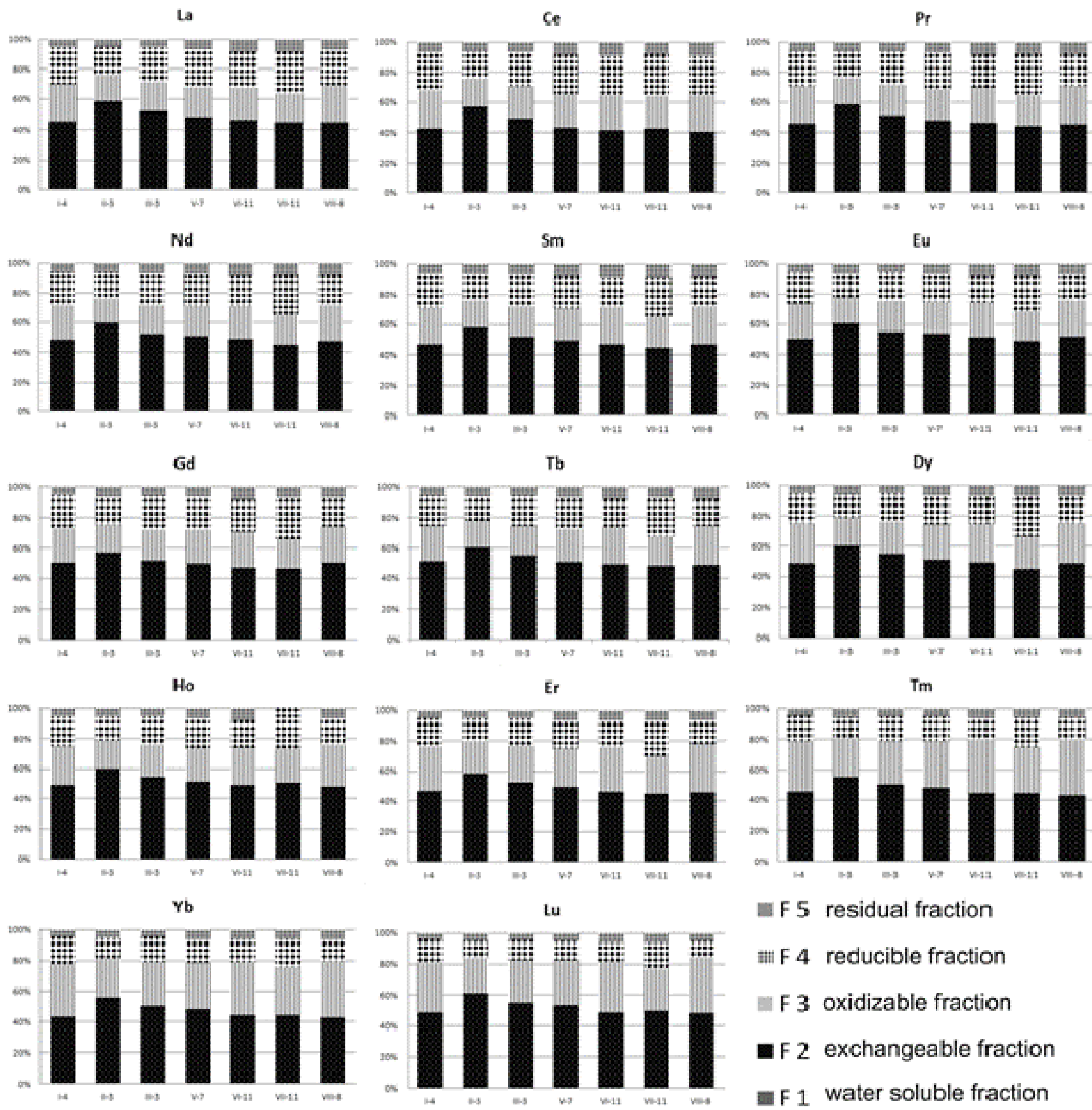

Figure 5. The results of the sequential extraction procedure.

REEs mobility and bioavailability

Sequential extraction experiments were completed for seven samples of Lake Kalimanci surficial sediments from 2007. Within this procedure the sequential extraction scheme included a water-soluble fraction (F 1), an exchangeable + carbonate fraction (F 2), an oxidisable-organic fraction (F 3), an Fe–Mn oxide bound-reducible fraction (F 4) and a residual + reducible fraction (F 5). The sums of the contents of all five leaching stages are presented with the total contents in Figure 5.

Water-soluble fraction (F1) elements are relatively labile and thus, may be more readily leachable and potentially bioavailable in the environment (Hsu and Lo 2001). Van Herck and Vandercasteele (2001) have reported that this fraction consists of elements that are easily soluble, highly mobile and potentially bioavailable and thus, the leaching of REE from this fraction is a major environmental concern (Filgueiras et al., 2002). The Exchangeable fraction (F2) includes elements that are adsorbed onto the solid surface by relatively weak electrostatic interactive forces and which can then be released through ion-exchange processes, as well as elements that are precipitated with carbonates (Filgueiras et al., 2002). REE in this fraction are the most readily available for biota and thereby very labile. This is also the fraction most labile bound to the sediment and, therefore, the most dangerous for the environment. The Oxidisable fraction (F3) corresponds to elements that occur as oxidizable minerals and also to organically-bound elements. Elements bound to this fraction can be released under oxidising conditions (Filgueiras et al., 2002; Fuentes et al., 2004). The Reducible fraction (F4) usually consists of oxides of Mn and Fe that are extracted together and which act as a cement, being present as nodules between particles or coating them. Elements are strongly bound to these oxides, but are thermodynamically unstable in anoxic conditions (Filgueiras et al., 2002; Fuentes et al., 2004). The Reducible + residual fraction (F5) corresponds to elements linked to amorphous Fe hydroxides (reducible part) that are expected to be released to the environment under reducing conditions. REE in this fraction can only be mobilised as a result of weathering and therefore have only very long-term effects (Filgueiras et al., 2002; Kazi et al., 2002). The elements that correspond primarily to this fraction are those that are associated with minerals in which they form part of the crystalline structure and which, as a result, are unlikely to be released from sediments. Thus, elements in the residual phase are considered to be stable and inert if there are no extreme conditions.

In all the surficial sediment samples from Lake Kalimanci REE were predominantly associated with the exchangeable fraction (F2) (Figure 5). The second most important was the oxidisable fraction (F3), closely followed by the reducible fraction (F4). In all the studied samples REE were less bound to the reducible + residual fraction (F5) and water soluble fraction (F1). The percentages of REE determined in the present study were in following order: exchangeable fraction (F2) > oxidisable fraction (F3) > reducible fraction (F4) > reducible + residual fraction (F5) > water soluble fraction (F1).

Residual forms are stable under natural conditions, are water soluble and exchangeable fractions are very easily activated or unstable under natural conditions. A five-step sequential extraction procedure showed that the majority of REE are bound to the exchangeable fraction (F2). Thus, the unstable fractions of REE have a potential impact on the environment, because REE in those fractions are not fixed in the lattices of minerals (Hu et al., 2006). Cao et al., (2001) report that mobility of REE depends mainly on pH value, whilst the redox potential does not affect the REE mobility, except for Ce. Separation of REE in the exchangeable fraction decreased with a decline of pH or redox potential (Cao et al., 2001).

The sequential extraction procedure was also applied in the nearby Kočani paddy fields (Rogan Šmuc et al., 2012). Rogan Šmuc et al., (2012) reported that low percentages of REE are bound to the exchangeable fraction in paddy soils from the Kočani field. Meanwhile, the REE in the surficial sediments from Lake Kalimanci are strongly bound to the exchangeable fraction. Also, the trace elements Cd, Pb, Zn, Ni, Co and Cu were found to be highly mobile in the exchangeable fraction (F2), whilst Mo and As were the most exchangeable and highly mobile in the oxidizable fraction (F3) in the surficial sediment samples from Lake Kalimanci (Vrhovnik et al., In press). Even though the mineral assemblage in both locations (Lake Kalimanci and Kočani Valley) is much the same, the adjacent areas are predominantly acidic with intermediate igneous rocks and pH during sampling ranged between 5.2–7.2 in both locations. Therefore, there must be another factor that affects the REE bioavailability in the Lake Kalimanci surficial sediments. To clarify this, further investigations are needed in Lake Kalimanci, the River Kamenica and in adjacent areas.

Summary

The REE concentrations and mobility in the surficial sediments were studied to establish their occurrence and their enrichment in Lake Kalimanci. Results indicate that REE from Lake Kalimanci are strongly related to the catchment geology of the acidic and intermediate igneous rock lithologies from the Osogovo Mountains. Surficial sediments from Lake Kalimanci appear to preserve the REE patterns of their source area (Osogovo Mountains), indicating that REE in surficial sediments are the result of geological weathering. Surficial sediments are characterised by high ΣREE enrichment, with averages in 2001of 210.98 and in 2007 of 205.16. Small differences are most likely due to different ore excavation locations in the Osogovo Mountains, where the background rocks can be rich with Si or Ca, Mg minerals, which influence the REE contents in the surficial lake sediments. The chondrite normalised patterns reveal a negative Eu anomaly, LREE enrichment and a fairly flat HREE pattern. The results of EF reveal that the surficial sediments from Lake Kalimanci have minor enrichment and natural origins, therefore REE contents in the surficial sediments are not the result of Pb-Zn mining activity nearby. Results of a sequential extraction procedure show that high percentages of REE were bound to the exchangeable fraction and a low percentage of REE was extracted in the residual fraction. Whilst REE bound to the exchangeable fraction are highly bioavailable, there exists a potential danger for uptake by edible plants that can seriously affect human health. The possible anthropogenic effects will be evaluated in the following study. In addition to the anthropogenic effects some questions still remain unanswered and therefore further investigations are needed.

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