Occurrence and Distribution of Technology-critical Elements (TCE) in Recent Freshwater and Marine Pristine Lake Sediments in Croatia: a Case Study

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Original Research

Keywords: technology-critical elements, sediments, freshwater and marine lakes, Croatia

DOI: https://doi.org/10.21203/rs.3.rs-163798/v1

Abstract

The appearance and vertical distribution of technology-critical elements (TCE) such as Li, Nb, Sc, Ga, Y, La, Sb, Ge, Te, and W were investigated in sediment cores taken in pristine freshwater and marine lakes located within protected areas of Croatia (Plitvice Lakes, Visovac Lake, and Mir Lake). These lake systems are isolated from the direct impact of human activities, and accordingly, the geochemical research in such environments may help to assess temporal trends in historical deposition of anthropogenic TCE. The analytical method of choice in determining the concentration of TCEs was High resolution inductively coupled plasma - mass spectrometry (HR ICP-MS). The results obtained have shown that the measured TCE spanned with wide ranges of concentrations, as a result of the different input of terrigenous material into the investigated lake systems which is further diluted by the formation of authigenic and biogenic carbonates. Evaluation of the anthropogenic impact on TCE levels showed low enrichment of Sb and Te in the upper sediment layers of the Mir Lake and the Plitvice Lakes. Despite that, concentrations of investigated TCE were low, compared to results described in the literature, indicating that the investigated remote lakes can be considered uncontaminated with these elements.

Introduction

The development of new technologies in communication, computing, and the production of clean energy lead to the emergence of new potentially harmful trace metals in natural systems (Fillela and Rodriguez-Murillo 2017). For some of these metals imbalance between metal supply and demand has inspired the concept of metal criticality and these elements which are produced as byproducts, and do not have effective substitutes for their use in specialized applications, were defined as the most critical (Greadel et al. 2015). As demand for many of these technology-critical elements (TCE) started only recently, our knowledge concerning their distribution, behavior, and the impact of their use on the environment (particularly for Nb, Ta, Ga, In, Ge, and Te) was not systematically scrutinized (Cobelo-Garcia et al. 2015; Fillela and Rodriguez-Murillo 2017). In addition, for many of these elements, suitable analytical methods for their measurements are still limited, due to previous lack of interest for their development, and low levels of TCE concentration in environmental samples (Yang et al. 2013; Fillela and Rodushkin 2018; Rodushkin et al. 2018).

Metal inputs in pristine areas are derived mainly from natural sources and depend primarily on the local geology and weathering processes (Jin et al. 2006; Augustsson et al. 2010). Previous investigations have shown that such aquatic systems are characterized by relatively low concentrations of contaminants (Mikac et al. 2011; Roberts et al. 2019). As such, they are highly vulnerable to additional anthropogenic inputs and represent ideal systems to study influence of different sources of metals on their deposition and impact on the environment. It is well known that undisturbed cores of the lake sediments represent natural archives for identification of sources of contaminants and reconstruction of the past environmental changes in long-term and recent anthropogenic and atmospheric inputs (Grahn et al. 2006; Mikac et al. 2011; Sondi et al. 2017; Roberts et al. 2019; Wiklund et al. 2020).

Croatia has many pristine freshwaters and marine lake water systems of which National Park Plitvice in Central Croatia, National park Krka in the coastal region, Nature Park Telašćica on the island Dugi Otok on the eastern Adriatic, should be especially emphasized. In these systems distribution and contamination with trace metals have been studied (Cukrov et al. 2008, 2013; Mikac et al. 2011, Dautović et al. 2014; Mlakar et al. 2015), however, except some data on REE (Fiket et al. 2018), occurrence and distribution of TCE have not been studied in these systems.

In this work vertical distribution of Li, Nb, Sc, Ga, Y, La, Sb, Ge, Te, and W concentrations was investigated on undisturbed sediment cores retrieved from three freshwater lakes from the National Park Plitvice, one from freshwater lake Visovac located in the he National Park Krka and one from enclosed marine lake from the Nature Park Telašćica. Sediments from the Plitvice Lakes (Horvatinčić et al. 2008, 2014, 2017) and the Lake Visovac (Mikac et al. 2017) were previously dated, enabling estimation of the historical trends of anthropogenic impacts of TCE for these lakes. In order to determine elements Te, Ga, Ge and Nb, which we previously did not measure, we have validated the method for their determination by HR ICP-MS technique, with enough high sensitivity to detect low levels of TCE expected in the carbonate-rich sediments of these environments. The main aim of this study was to determine the sources, distribution, and historical record of TCE deposition, and to determine to what extent their geochemical cycles depend on anthropogenic contribution in the recent past.

Material And Methods

Study areas

The Plitvice Lakes are situated in the Dinaric karst of the central part of Croatia and consist of a cascade water system of 16 lakes of different sizes, interconnected by channels and waterfalls (Fig. 1). Since 1979 they have been included in the UNESCO World Natural and Cultural Heritage List. The Plitvice Lakes drainage area is characterized by several geological units, mainly, Cretaceous limestones and Triassic dolomites. The lakes receive water from two main karstic springs, Bijela Rijeka and Crna Rijeka, which are situated in the upper part of the drainage area. These two streams merge and form the Matica River that flows into the Lake Prošće and represents the main source of water for the Plitvice Lake system. The lakes are characterized by the intense formation of biogenic calcite, forming tufa barriers (Horvatinčić et al. 2008) and lake sediments with high content of carbonates, particularly calcite (Table 1). The most significant sections of this setting, considering the size and water depth, are the two largest lakes, the Lake Prošće and the Lake Kozjak (Table 1). The Lake Prošće is situated in the upper area, away from the major roads and tourist routes, while the Lake Kozjak is exposed to more intensive tourist activities. The Plitvice National Park is receiving over 1 million visitors per year.

Table 1
Basic characteristics of investigated lakes and sampled sediment cores.

Name of National (Nature) Park	**Data about sediment cores**				
Name of lake and sediment core	**Sampling depth (m)**	**Core length (cm)**	**Sed. rate (cm/year)** **Time period (year)**	**Carbonate (%)**	**Aluminum (%)**
Plitvice					
Lake Prošće (area: 0.68 km^2, max depth: 40 m)					
P4	5	40	0.7 (2011 – 1955)[1]	24–40[1]	2.2–5.2
P1	39	44	0.3 (2011 – 1868)[1]	60–70[1]	1.5–2.5
Lake Kozjak (area: 0.82 km^2, max depth: 46 m)					
K2	22	46	0.2 (2011 – 1791)[2]	90–95[2]	0.3–0.7
Lake Kaludjerovac (area: 0.02 km^2, max depth: 14 m)					
Kal	14	30	0.3 (2011 – 1921)[1]	95–98[1]	0.1–0.2
Krka					
Lake Visovac (area: 7.9 km^2, max depth: 24 m)					
V1	16	40	0.9 (2012 – 1969)[3]	46–60[3]	3.2–4.8
V3	24	44	0.45 (2012 – 1916)[3]	50–75[3]	2.2–6.7
V5	6	44	-	34–70[3]	2.5–7.9
V6	5	40	-	47–57[3]	3.3–5.3
Telašćica					
Lake Mir (area: 0.23 km^2, max depth: 6 m)					
Mir	6	90	-	35–53[4]	0.4–2.1

[1] Horvatinčić et al. 2017; [2] Horvatinčić et al. 2014; [3] Mikac et al. 2017; [4] Sondi et al. in preparation.

The Lake Visovac is a part of the Krka River water system draining carbonate terrains (Fig. 1). The geological settings of the entire catchment area consist of limestones and dolomites of Cretaceous and Palaeogene age (Cukrov et al. 2013). This system is characterized by numerous tufa barriers forming alternate lotic and lentic environments and lakes of different sizes. The area included in this study is the river section between waterfalls Roški Slap and Skradinski Buk, which includes the Visovac Lake. The Visovac Lake is situated in the lower course of the Krka River and belongs to the National Park Krka (Table 1). In the south, the Visovac Lake is fed from the left bank by the Čikola River, the largest tributary of the Krka River.

The main anthropogenic source of pollutants to the Krka River is metal and electroplating facilities located in the town of Knin, situated 30 km upstream of the Visovac Lake, and agricultural activities in the area (Cukrov et al. 2013; Filipović et al. 2018).

The Lake Mir is a small a shallow marine lake situated in the south-eastern part of the Dugi Otok Island in the protected area of the Nature Park Talaščica (the central part of the eastern Adriatic coast) (Fig. 1, Table 1). The lake was formed after the last Ice Age when the karst depression was filled by sea water. It is separated from the open sea by the 90-m thick karst bedrock barrier, through which occasional circulation of seawater is allowed. This environment is built of carbonate rocks and exhibits typical karstic morphological features, while the surrounding soils mainly consist of Terra Rossa soil (Fiket et al. 2018). The karstic background, with occasional occurrences of Terra Rossa, characterizes this system as a carbonate-rich environment (Table 1).

Sediment cores collection

In all lake systems undisturbed sediment cores (30 to 90 cm long, Table 1) were collected using the Uwitec gravity corer.

In the Plitvice Lakes sediments cores were retrieved in 2011 in three lakes (Fig. 1, Table 1): the Prošće Lake (cores P4 in front of the inflow of the Matica stream and P1 in the deepest part of the lake), the Kozjak Lake (core K2 in the central part of the lake) and in the small Lake Kaluđerovac (core Kal in the deepest part of the lake). Estimated sedimentation rates in these lakes were published earlier (Horvatinčić et al. 2008, 2014, 2017) and presented in Table 1.

In the Visovac Lake four sediment cores were sampled in 2012 (Fig. 1, Table 1): core V1 was taken downstream of the Roški Slap waterfalls at the beginning of the lake, core V3 in deepest, central part of the lake, core V5 upstream of the Skradinski Buk waterfalls, at the end of the lake, and core V6 was taken in the southern part at the inflow of the Čikola River. Average sedimentation rates of two sediment cores (V1 and V3) were estimated earlier by using the vertical distribution of ^{137}Cs activities (Mikac et al. 2017) and are given in Table 1.

In the lake Mir, one long core was sampled in 2014 in the central, deepest part of the lake at a depth of 6 m (Fig. 1, Table 1). Unfortunately, this sediment core was not dated, and there is also lack of the literature data on the sedimentation rate in lake Mir, which is still unknown.

Sediment core analyses

Sediment cores were subdivided into 2 cm segments, dried on room temperature and ground to a fine powder. Subsamples (0.05–0.1 g) were subjected to the total digestion using a closed microwave system (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure (I: 5 ml HNO_3 + 1 ml HCl + 1 ml HF and II: 6 ml 40 g L^{-1} H_3BO_3). After digestion samples were diluted (2-fold for Te and 10-fold for other elements), acidified with 2% (v/v) HNO_3 and indium (In, 1 µg L^{-1}) was added as an internal standard. The multielement analysis was performed using a High Resolution Inductively Coupled Plasma - Mass Spectrometer (HR ICP-MS) Element 2 (Thermo, Bremen, Germany). Following isotopes on the chosen instrument resolutions (LR-low resolution, MR-medium resolution, HR-high resolution) were used for detection: LR – ^{7}Li, ^{125}Te, ^{126}Te, ^{128}Te, ^{93}Nb, MR – ^{45}Sc, ^{69}Ga, ^{71}Ga, ^{72}Ge, ^{74}Ge, ^{89}Y, ^{93}Nb, ^{121}Sb, ^{125}Te, ^{126}Te, ^{128}Te, ^{139}La, ^{186}W and HR – ^{72}Ge. External calibration method was used for quantification, with diluted multi-element standard solutions (in the range of 0.1–10 µg L^{-1}) prepared from the multi-element standard or combining single reference standard solutions (Analytika, Prague, Czech Republic), while indium (1 µg L^{-1}) was used as an internal standard. Analytical quality control was performed by simultaneous analysis of procedural blanks and several geological certified reference materials: soil NCS DC 773902 (GBW 07410), marine sediment NCSDC 77302(GBW 07410), and stream sediment NCS DC 73309 (GBW 07311), which are certified for most of the measured elements. Recoveries of the method for elements Li, Sc, Sb, Y, and La were described earlier (Fiket et al. 2017) and varied between 86 and 105 %. Recoveries for different isotopes of elements Ga, Ge, Nb, Te, and W are presented in Table 2. Limits of detections (LOD) of the method, calculated as three times the standard deviation of ten consecutive measurements of the procedural blank, are presented for all elements in Table 3, and varied from 0.002 to 0.1 mg kg^{-1}, depending on the element.

Table 2
Recoveries of measured isotopes of Te, Ge, Nb, and W in different geological certified reference materials.

Isotope/ Resolution	**CRM soil NCS DC 773902 (GBW 7410)**			**CRM stream sediment NCS DC 73309 (GBW 07311)**			**CRM marine sediment NCS DC 77302 (GBW 07410)**		
	certified (mg kg^{-1})	**measured (mg kg^{-1})**	**recovery (%)**	**certified (mg kg^{-1})**	**measured (mg kg^{-1})**	**recovery (%)**	**certified (mg kg^{-1})**	**measured (mg kg^{-1})**	**recovery (%)**
^{125}Te (LR)	0.035	0.120	350	0.38	0.554	145	-	0.06	-
^{125}Te (MR)	0.035	0.069	200	0.38	0.473	124	-	-	-
^{126}Te (LR)	0.035	0.044	125	0.38	0.450	118	-	0.05	-
^{126}Te (MR)	0.035	0.041	117	0.38	0.438	115	-	-	-
^{128}Te (LR)	0.035	0.045	130	0.38	0.454	118	-	-	-
^{128}Te (MR)	0.035	0.036	104	0.38	0.425	112	-	-	-
^{72}Ge (MR)	1.6	5.1	310	1.81	5.12	280	-	7.5	-
^{74}Ge (MR)	1.6	1.5	94	1.81	1.75	97	-	1.5	-
^{72}Ge (HR)	1.6	1.6	98	1.81	1.6	88	-	-	-
^{93}Nb (LR)	17.1	15.7	92	25	22	88	19.1	16.5	86
^{93}Nb (MR)	17.1	15.5	91	25	22	88	19.1	16.0	84
^{69}Ga (MR)	18.8	17.6	94	18.5	15.9	86	16.1	15.2	94
^{71}Ga (MR)	18.8	17.8	94	18.5	15.6	84	16.1	15.2	94
^{184}W (MR)	5	5.5	110	126	125	99	2.1	2.4	114

Table 3
Detection limits of the method for measured TCE and ranges of their concentrations in sediment cores.

Element	Concentration (mg kg^{-1})									
	LOD	Plitvice (4 cores) P1,P4, K2, Kal			Visovac (4 cores) V1, V3, V5, V6			Mir (1 core)		
		Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Li	0.1	0.8–41	13.5	12.5	26–147	64	60	5.2–23.7	14.8	15.8
Nb	0.1	0.19-13.0	3.8	3.2	3.9–17.4	9.7	9.5	1.2–5.2	3.2	3.3
Sc	0.1	0.6–9.7	3.3	2.7	3.6–15.4	8.4	8.2	0.67–3.82	2.17	2.18
Ga	0.1	0.19–11.9	3.7	3.6	5.1–19.8	11.0	10.7	1.0-4.7	2.83	2.99
Y	0.03	0.42–41.7	13.4	15.4	7.6–30.8	17	15.4	1.7–7.3	4.6	4.8
La	0.03	0.44–42.3	10.9	9.8	10.2–42.3	23.6	22.5	2.8–11.5	7.5	7.8
Sb	0.01	0.02–1.33	0.47	0.49	0.43–1.81	0.94	0.90	0.08–0.45	0.26	0.25
Ge	0.01	0.01–1.04	0.37	0.33	0.4–1.5	0.90	0.82	0.07–0.39	0.25	0.26
W	0.01	0.07–1.67	0.52	0.42	0.7–2.6	1.4	1.3	0.04–0.53	0.28	0.32
Te	0.002	0.004–0.068	0.022	0.020	0.021–0.101	0.051	0.048	0.009–0.050	0.030	0.030

Calculating the enrichment factors (EF)

Enrichment factors for investigated TCE in the lake sediment were calculated as:

$$Me\ EF = (Me_i/Al_i)/(Me_{bk}/Al_{bk})$$

where: Me_i and Al_i are metal or aluminum concentration (mg kg^{-1}) of sediment interval (i) and Me_{bk} and Al_{bk} are mean metal or aluminum concentration in the bottom sediment layers, which correspond to sediments deposited in the 19th or the beginning of the 20th century.

Result And Discussion

Validation of the method for Nb, Ga, Ge, W, and Te determination in sediment

From ten TCE measured in this work, validation of the analytical method was earlier published for Li, Sc, Sb, Y, and La, which are more commonly measured in geological samples (Fiket et al. 2017). Here we present the results of analysis of Ga, Ge, Nb, Te and W in several different geological CRMs (soil, stream sediment and marine sediment), of which two are certified for all these elements and one for three of them (Table 2). For most of these elements, several isotopes and different instrumental resolutions are tested to define the best combination regarding accuracy and sensitivity. Namely, many of the isotopes of these elements are suffering from serious spectral interferences during ICP-MS measurement (Filella and Rodushkin 2018) and these authors provided a concise guide for the choice of isotopes and resolutions when using HR-ICPMS, and presented results of their measurements in CRM of river water. Following their recommendations, we made a choice of isotopes and resolution for analysis of Ga, Ge, Te, and Nb in geological CRMs (Table 2), while for W the most abundant isotope ^{184}W, which should be free of major interferences, was used (Morisson et al. 2016). For Te analysis, in addition to ^{125}Te and ^{126}Te recommended by Fillela and Roduskhin (2018) and Yung et al (2013), we also tested isotope ^{128}Te, which was recently used for the analysis of Te in freshwater sediments from various lakes in Canada (Wiklund et al. 2018). Recoveries for these elements in three different CRMs (Table 2) showed that for Ga both isotopes ^{69}Ga and ^{71}Ga can be used on MR, for Ge either ^{74}Ge on MR or ^{72}Ge on HR, while ^{93}Nb can be measured both on LR and MR. The most demanding element is Te, because of its very low concentration in geological samples and isobaric interferences of Ba on the most abundant isotope ^{130}Te. Yang et al. (2013) recommended analysis of ^{126}Te in geological samples, as they found that ^{125}Te suffer more from the interference of AgO^+. Our results of CRMs analysis (Table 2) confirmed that ^{125}Te is suffering from interferences (AgO^+ and $^{85}Rb^{40}Ar^+$) on both LR and MR, especially in CRM for soil, where Te level is low (0.035 mg kg^{-1}). Isotope ^{128}Te, which may suffer from the interference of $^{88}Sr^{40}Ar$ (Filella and Rodushkin 2018), gave too high recovery on LR for soil CRM, but could be used on MR for both CRMs. Analysis of different Te isotopes in our sediments confirmed that isotope ^{125}Te gives higher concentrations (up to two times) than isotope ^{126}Te. Isotope ^{128}Te was suffering from the interferences on LR in the Plitvice sediments (giving 2–4 times higher concentrations than with ^{126}Te) and on both LR and MR in sediments of the Lake Mir (giving 7 times higher concentrations than with ^{126}Te), due to much higher level of Sr (2000–6000 mg kg^{-1}) in sediments from the Lake Mir than in the Plitvice Lakes (60–80 mg kg^{-1}). According to these results, we have chosen isotope ^{126}Te on LR (which gives better LOD and RSD than ^{126}Te on MR) for the determination of Te in our sediment samples. Detection limits for the determination of all analyzed TCE are given in Table 3. They were sufficiently low for the determination of low levels of these elements in the carbonate-rich sediments.

Distribution of TCE in the lake sediments

Concentrations (ranges, mean and median values) of measured TCE in sediments of the investigated lake systems are presented in Table 3 and vertical profiles of their concentration in sediment cores are displayed in Figs. 2, 3 and 4. Overall ranges of concentrations, which included all samples, are presented in Table 4, together with some literature data for the same elements in the marine and freshwater sediments. For comparison, we have used data for the coastal sediments (as we did not find data for marine lake sediments) from Japan (Otha et al. 2010) and the USA (Dolor et al. 2009), and freshwater lakes from Finland (Augustsson et al. 2010), China (Jin et al. 2006), Canada (Wiklund et al. 2018, 2020) and Macedonia (Vrhovnik et al. 2013). As we could not find more data for freshwater lake sediment for Ge, we used data on the long sediment core from the Baltic sea, which includes both older freshwater and more recent marine sediment (Ingri et al. 2014). Most of these areas are remote and not exposed to direct anthropogenic influence.

Table 4
Comparison of some literature data for TCE in marine and freshwater sediments with results from this work.

Element	Literature data, ranges and mean values (mg kg^{-1})				This work (mg kg^{-1})
	Coastal sediment	Freshwater lake 1 (Baltic for Ge)	Freshwater lake 2	FOREGS (median)	All investigated lakes (ranges and median)
Li	5.2–68 (27)[1]	15–32 (23)[3]	26–49 (35)[4]	20.8 (Sed)	0.8–147 (18.4)
Nb	0.7–2.8 (4.7)[1]	2.1–4.3 (3.0)[3]	12–16 (13)[4]	13 (Sed)	0.19–17.4 (4.0)
Sc	1.6–67 (11)[1]	4.7–8.3 (6.8)[3]	9–13 (11)[4]	8.2 (Soil)	0.6–15.4 (3.2)
Ga	2.2–20.9 (12.3)[1]	5.4–10 (7.6)[3]	13–19 (16)[4]	12 (Sed)	0.19–19.8 (4.0)
Y	2.5–34 (14)[1]	12–27 (17)[3]	17–26 (22)[4]	25.7 (Sed)	0.42–41.7 (9.2)
La	2.9–31 (11)[1]	33–98 (50)[3]	36–45 (40)[4]	32.5 (Sed)	0.44–42.3 (10.6)
Sb	0.4–1.49 (1.2)[2] (10)*	0.6–3.6 (1.7)[5]	0.06–1.2 (0.68)[6]	0.62 (Sed)	0.02–1.81 (0.45)
Ge	1.6–2.3 (2.0)[2] (4.2)*	1.3–1.7[7]	0.27–1.25 (0.65)[6]	1 (Soil)	0.01–1.5 (0.37)
W	1.11–1.89 (1.4)[2] (3.7)*	1.9–2.4 (2.2)[4]	0.05–0.43 (0.12)[6]	1.24 (Sed)	0.07–2.6 (0.42)
Te	0.04–0.17 (0.1)[2] (75)*	< 0.02–0.07[8] (10)*	< 0.02–0.420 (0.16)[6]	0.03 (Soil)	0.004-0.10 (0.031)

* – range includes locations more distant from pollution, in parentheses with *is maximum at polluted locations

[1] Otha et al. 2010; [2] Dolor et al. 2009; [3] Augustnsson et al. 2010; [4] Jin et al. 2006; [5] Vrhovnik et al. 2013; [6] Wiklund et al. 2020; [7] Ingri et al. 2014; [8] Wiklund et al. 2018.

The ranges of concentrations for all TCE, when considering all samples from this study, are very wide, much wider than in the cited literature. The minimal concentrations of TCE are much lower (up to 10 times) than the minimum values in the literature. Median values for our sediments were also lower than the average (or median) values from the literature, which was used for comparison. They were also 2–3 times lower than FOREGS data for median values in the stream sediments in Europe (or soil for those elements for which data for sediments are not available), except for Y, Sb and Te, for which our median values were similar to those in FOREGS Atlas. Large ranges of TCE concentrations are a consequence of a great difference in sediments composition of the investigated lakes, from the almost entirely carbonate sediments in the Lake Kaluđerovac (Plitvice Lakes) to the clayey-rich material from the Visovac Lake (Table 1). For all TCE median and mean values are the highest in the Visovac Lake sediment (Table 3), comparing to the sediment from the Plitvice Lakes and the Lake Mir, which showed comparable average concentrations. The only exception is Y, which median concentration in Plitvice and Visovac sediments are similar.

Plitvice Lakes

Figure 2 displays vertical distribution of TCE concentrations in sediments of the Plitvice Lakes. For all TCEs concentrations decreased in order: P4 > P1 > K2 > Kal, in accordance with an increase of carbonate content and decrease of aluminum content in these sediment cores (Table 1). In sediments of the Lake Prošće (core P4) concentrations of all TCE were 20–40 times (depending on the element) higher than in sediments of the Lake Kaluđerovac. Variations in vertical profiles were similar to variations in Al profiles (Fig. S1) and were especially pronounced in the core P4. Core P4 is located close to the main tributary Matica which represents the most important sources of water and terrigenous material for the Plitvice Lakes system. Previous investigations have shown that surrounding source rocks (dolomites with small amounts of quartz and aluminosilicates) and soils are the main source of materials in sediments at locations P4, while the share of these minerals is low in sediments at location P1, where a significant amount of calcite was determined (Horvatinčić et al. 2017). Calcite was also the dominant mineral phase in the sediments where terrigenous input is small (the Lake Kozjak), or negligible (the Lake Kaluđerovac) (Horvatinčić et al. 2014, 2107). The morphological features of the calcite showed the structures typical for inorganically precipitated carbonates (Sondi et al. 2011), indicating that calcite in lakes is formed by active authigenic precipitation in water rather than by the erosion of surrounding carbonate rocks. Significant variations in the vertical profile of the core P4 relate to variations in the input of terrigenous material which depends on the flowrate of the tributaries. For example, the maximum at the 20–25 cm layers was a consequence of an extremely rainy period in spring 1981 (Horvatinčić et al. 2017).

The relationship between Al and metals can be used to distinguish between enrichment of geogenic and anthropogenic origin, as Al is of terrigenous origin and its concentration in lake sediments are not generally affected by anthropogenic influence (Roberts et al. 2019). Correlations of TCE with Al in all sediment cores are presented in Fig. 5. These correlations showed that sediments of the Lake Prošće have different geochemical composition than sediments from other Plitvice Lakes (Kozjak, Kaluđerovac), as well as the other investigated lakes, with proportionally lower content of Li, and much higher content of Y and partly La, in both P4 and P1 cores. This may be connected with weathering of surroundings soils or unique geological background of this lake, which was previously shown to be the main source of other trace elements, including some ecotoxic metals (Cd, Zn, Ni and Tl) to the Plitvice Lakes system (Dautović et al. 2014). However, numerous travertine barriers between the lakes, as well as efficient removal of the dissolved elements in the lentic parts of the system, mainly by co-precipitation with authigenic calcite and Mn oxides (Dautović et al. 2014), prevent the transport of elements to the lower lakes. For other TCE significant deviations from the general correlation with Al (Fig. 5) are not visible. In all four sediment cores elements Li, Nb, Sc, Ga, Y, and La were highly positively correlated with Al with correlation coefficient (r) being higher than 0.95, while this correlation was weaker for Sb, Ge, W and Te, with r ranging from 0.01–0.6 in cores P1, K2 and Kal, and 0.7–0.8 in the core P4. Weaker correlations between Al and elements Sb, Ge, W and Te may suggest a partly anthropogenic origin of these elements in the Plitvice Lakes sediments.

Lake Visovac

On Fig. 3 are shown vertical profiles of TCE concentrations in sediments of the Visovac Lake. For all TCE concentrations were similar in cores V1, V3, and V6 and the highest in the core V5. Variations in vertical profiles were similar to variations in Al profiles (Fig. S1) and were greatest in the core V5, where a pronounced maximum is visible in the central part of the core. Generally, concentrations of both Al and TCE are increasing with the sediment depth, indicating a continuous decrease of input of terrigenous material to the lake from the past to the present. Decreasing input of terrigenous material in the last decades, demonstrated also in other parts of the Krka River, was ascribed to advanced afforestation and changes in agricultural practices in the surrounding area (Cukrov et al. 2013). Vertical profiles of ^{137}Cs, which was used for dating of V1, V3, and V5 sediment cores, indicated that V5 core was disturbed, and that the pronounced maximum in the central part should be a consequence of a massive input of surrounding soil to the lake in the past at this location (Mikac et al. 2017), so dating of this core was not possible. Higher concentrations of Al and all TCE in these layers are due to their higher concentrations in surrounding soils than in the lake sediment, where dilution by authigenic and biogenic carbonates decreases the metals content. The multi-element analysis of the same sediment cores (Mikac et al. 2017) showed partly different geochemical composition of material transported to the Visovac Lake by the rivers Krka (location V1) and Čikola (location V6), with the presence of dolomites in the drainage area of the Krka River. However, this difference was not visible in the relationship of measured TCEs with Al in cores V1 and V6 (Fig. 5). However, the concentrations of Nb and La were below TCE-Al line in the core V3, in the central part of the lake (Fig. 5), where the share of the fine authigenic calcite particles prevails, comparing to more coarse sediment, with lower share of carbonates, at the entrances to the lake (cores V1 and V6) (Mikac et al. 2017). This may indicate that dilution effect caused by carbonates has a greater influence on Nb and La compared to Al, which is more abundant in the finer fraction. In all four sediment cores very good positive correlations between Al and all TCE were obtained ($r > 0.9$), with little bit weaker correlations ($r = 0.6–0.9$) for Sb in the cores V1 and V3 and Te ($r = 0.4$) in the core V1.

Lake Mir

Figure 4 shows vertical profiles of TCE concentration in sediment core from the lake Mir. All measured TCE showed significant variations within the long sediment core, with RSD from 35 to 45 %. Variations of TCE along the core followed variations in the vertical profile of Al in the same core (Fig. S1). Previous investigations (Mlakar et al. 2015; Fiket et al. 2018) of metals distribution in the surface sediments of the lake Mir showed that the composition of the lake sediments is primarily influenced by natural processes: geological background dominated by carbonates and red soils, particle size distribution reflecting the bathymetry of the basin, and overall biological production (Mlakar et al. 2015). Comparison of REY (REE + Y) patterns in surrounding soils and lake sediment confirmed that the red soils were the main source of REY and other trace elements to the lake sediment (Fiket et al. 2018). The more recent investigation, showed that an additional important process is taking place in the lake Mir, the intensive authigenic precipitation of aragonite (I. Sondi, in the preparation according to the personal communication). Therefore, variations in the vertical profiles of TCE should be a consequence of the irregular input of terrigenous material into the lake (which is dependent on the amount of rainfall), in combination with seasonal authigenic precipitation of aragonite. Correlations with Al (Fig. 5) showed that Li, Nb, Sc, Ga, Y and La were highly positively correlated with Al ($r > 0.95$), correlation with Al was weaker for W ($r = 0.55$), Ge ($r = 0.68$) and Te ($r = 0.55$) and was not present for Sb ($r = 0.09$).

Evaluation of anthropogenic impact

Correlations of TCE with Al indicated that concentrations of some elements (Sb, W, Ge, Te) could be influenced by anthropogenic contribution. In order to evaluate the extent of possible anthropogenic impact, we calculated enrichment factors for TCE in the sediment cores for which background concentrations could be estimated, e.g., for which bottom sediment was deposited in the late 19th or early 20th century, before the major anthropogenic influence has started. Thus, enrichment factors were calculated for sediment cores P1, K2, and Kal from the Plitvice Lakes and core V3 from the Visovac Lake, in which the oldest sediments were deposited during that period (Table 1). EFs were not evaluated for two dated sediment cores, V1 and P4, in which, due to relatively high sedimentation rate, the bottom of the cores corresponded to the sediment deposited after 1950 (Table 1). However, we calculated EFs also for sediment core from the Lake Mir, in spite of the fact that it was not dated. Namely, as there is no direct input of material into the lake by streams, except occasional transport of surrounding soil with big rains, sedimentation rate should be low and not higher than 0.5 cm/year, making 90 cm long core at least 180 years old. Birch (2017) has defined the following EF thresholds: 1.0-1.5, 1.5-3.0, 3.0–5.0 and 5.0–10.0 to represent evidence of pristine conditions, minimal, moderate, and considerable enrichment, respectively. We used this scale to evaluate the degree of pollution in our sediment cores. In Table 5 are presented calculated EFs for all measures TCE in cores P1, K2, Kal, V3, and Mir. For elements Li, Nb, Sc, Ga, Y and La they ranged from 0.8 to 1.3 and confirmed that anthropogenic enrichment of these elements is not present in any of the investigated lakes. However, for other elements, maximal EFs were higher and EFs varied in the ranges 0.6–3.5 for Sb, 0.7–2.5 for Ge, 0.4-2.0 for W and 0.7-2.0 for Te, indicating the minimal or moderate anthropogenic influence on these TCE levels. Temporal trends of anthropogenic impact can be evaluated from EFs profiles of TCEs in the sediment cores (Fig. 6), where also EF profiles for Pb (from the same sediment cores, results will be published elsewhere) are presented for comparison.

Table 5
Ranges of enrichment factors (EF) in sediment cores (P1, K2, Kal, V3 and Mir) in which background concentrations could be determined.

Element	Range of EFs in sediment cores				
	Plitvice Lakes			Lake Visovac	Lake Mir
	P1	K2	Kal	V3	MIR
Li	0.8-1.0	1.0-1.1	0.9−1.2	0.9-1.0	0.9−1.2
Nb	0.9−1.1	1.0-1.1	1.0-1.2	1.0-1.3	0.9−1.3
Sc	0.9−1.1	0.9−1.2	0.9-1.0	1.0−1.0	0.9−1.3
Ga	1.0-1.1	1.0−1.0	0.8−1.1	1.0−1.0	0.9−1.3
Y	1.0-1.3	0.8−1.1	0.9−1.2	1.0-1.2	0.9−1.2
La	1.0-1.1	0.9−1.1	0.9−1.2	1.0-1.2	0.9−1.3
Sb	0.9−**1.9**	0.7−**2.5**	0.9-**2.0**	0.8−1.5	0.6−**3.5**
Ge	0.8−1.5	0.7−1.4	0.8−1.5	0.9−1.2	0.7-**2.0**
W	0.9−1.5	0.7−1.4	0.8−1.4	0.9−1.3	0.4-**2.0**
Te	0.8−**1.9**	0.8−**1.6**	0.8−1.3	0.8−1.2	0.7-**2.0**

The most pronounced anthropogenic impact was found for Sb, for which EFs indicated, according to the scale of Birch (2017), minimal enrichment (EF = 1.5-3.0) in all 3 cores from the Plitvice Lakes (P1, K2, and Kal) and moderate enrichment (EF = 3.0−5.0) in the sediment core from the Mir Lake. The increase of anthropogenic impact on Sb level in the Plitvice Lakes started more intensively after the Second world war and reached maximum about 1990, after which it started to decrease. Vertical profiles of EFs for Sb followed closely profiles of EFs for Pb (Fig. 6), but EFs for Sb were much lower than those for Pb. Similar pollution trends of Pb and Sb were shown previously for the sediment of the lake Kozjak (Mikac et al. 2011) and were interpreted as a consequence of the use of leaded gasoline which started more intensively after 1950, peaked in the period 1980−1990 and was phased out after 2000, resulting in the emission of alkyl-lead compounds into the atmosphere and significant contamination of surface waters by lead and organolead compounds in Croatia (Mikac and Branica 1994a; Mikac and Branica 1994b). Smelting of lead sulfide ores, which are rarely monomineralic, also releases other elements, and lead pollution in atmospheric particles is regularly accompanied by other trace elements like Zn, Cu, Sb, Bi, Ag, Tl (Krachler et al. 2008). Due to its many commercial uses, especially those in automotive brakes, Sb was found to be one of the most enriched elements in the urban environment and one of the most heavily influenced by anthropogenic activity (Fillela et al. 2002; Sen et al. 2012; Fillela and He 2020; Wiklund et al. 2020). The highest enrichment for Sb was found in sediments of the Lake Mir, where an increase of EFs starts at a depth of about 30 cm, continues to the dept of 10–15 cm and then decreases toward the surface, closely following the profile for Pb (Fig. 6). To define when these pollutions started, sedimentation rate in the lake should be determined. The close relationship between Pb and Sb suggests that the sources of pollution for these elements are the same, and possibly related to the road traffic. However, more detailed interpretation of the anthropogenic impact on the Lake Mir needs further research, since this lake is located on the island separated from the urban areas. In spite of the evident anthropogenic enrichment of Sb, it should be emphasized that maximal Sb concentrations are low in comparison with existing sediment quality criteria for this element (Maccready et al. 2006) which define 2 mg kg^{-1} for Sb as a limit under which adverse effects are rarely expected.

The next element which showed maximal EFs between 1.5-2.0 (minimal anthropogenic impact) in both Plitvice and Mir sediments was Te (Table 5, Fig. 6), with the maximal EFs recorded in similar layers (around 1990) as for Sb and Pb (Fig. 6). In a recent study of atmospheric tellurium contamination of numerous lakes in Canada (Wiklud et al. 2018) it was shown that the main sources of anthropogenic Te were metal (copper) smelters and coal mining/combustion facilities and that long-range atmospheric transport (more than 1000 km) and deposition of Te to remote lakes were significant. Taking into account this knowledge, we may presume that, in addition to coal combustion, the mining and smelting of copper in the town of Bor in Eastern Serbia (500 km from the Plitvice Lakes), which is possibly the most important mining and metallurgical center in southeast Europe (Dimitrijević et al. 2009; Urošević et al. 2018), could be a distant source of Te. Mining of the copper ores in Bor started in 1903, but smelting began only in 1935, and environmental protection measures were introduced first in 2015 (Urošević et al. 2018). As Te is rarely measured, there are no data on Te levels in this area, but severe pollution of air with S and As (Dimitrijević et al. 2009) and soil with Cu and Pb (Dimitrijević et al. 2015) was found.

Elements Ge and W did not show anthropogenic enrichment in the Plitvice Lakes (Table 5, Fig. 6), but demonstrated EFs between 1.5 and 2 in the upper 10 cm of the sediment of the lake Mir, similarly as for Te. As it was discussed previously, to interpret these results and define possible contamination sources of these elements further geochemical study of this lake is needed.

Any of TCE which is prone to anthropogenic influence (Sb, Ge, Te, W) did not show elevated EFs in sediments of the Lake Visovac (Table 5, Fig. 6). In sediments of this lake low anthropogenic input of Pb, Cr, and Cu by the Čikola River was demonstrated, as well as significant enrichment in deeper sediment layers with Cd and Zn in the past (Mikac et al. 2017), brought to the Visovac Lake by the Krka River from the zinc electroplating facilities located upstream in the area of the town of Knin (Cukrov et al. 2008; Filipović Marijić et al. 2018). Obviously, these contamination sources did not result in enrichment with elements Sb, Ge, Te and W.

Although for some TCE anthropogenic influence is demonstrated, it is very low and concentrations of all these elements are much lower than in similar studies from the literature, proving that the investigated lakes can be considered uncontaminated with these elements. This is in accordance with previous studies which showed that the investigated lakes are unpolluted regarding other trace elements like Cd, Pb, Cu, and Zn (Mikac et al. 2011; Cukrov et al. 2008; Mlakar et al. 2015).

Conclusions

Concentrations of measured TCE (Li, Nb, Sc, Ga, Y, La, Sb, Ge, Te, W) spanned with wide ranges of concentrations, from very low in almost entirely carbonate-rich sediments to about 100 times higher concentrations in sediments rich with clay mineral phases. Correlations of TCE with Al indicated that levels of all TCE were principally defined by the input of terrigenous material into the researched lake system, which is in all investigated lake systems further diluted by authigenic and biogenic carbonates. Evaluation of the anthropogenic impact on TCE levels in sediment cores for which background concentrations could be estimated (where bottom sediments were deposited in the late 19th or early 20th century) showed minimal or moderate anthropogenic enrichment of some TCE. Sb and Te were slightly enriched in the upper layers of the sediment core from the Mir Lake and after 1950 in dated sediment cores from the Plitvice Lakes, suggesting long-range anthropogenic sourced atmospheric deposition of these TCE. Concentrations of all TCE were much lower than in similar studies from the literature, and Sb was lower than existing sediment quality criteria, proving that the investigated remote lakes can be considered uncontaminated with these elements.

Declarations

Acknowledgements

Support from projects 7555 (TRACESS) of the Croatian Science Foundation, projects with National Parks Krka and Plitvice, and COST action TD1407 are gratefully acknowledged.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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