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Chemical indicators of anthropogenic impacts in sediments of the pristine karst lakes

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ABSTRACT

The anthropogenic impact on the pristine karst lakes was investigated using combination of specific parameters, including multielemental analysis of major inorganic constituents (Al, K, Fe) and trace metals (Li, Ag, Cd, Sn, Pb, Bi, Cr, Co, Ni, Cu, Zn and Sb), polycyclic aromatic hydrocarbons (PAHs) and anionic surfactants of linear alkylbenzene sulfonate (LAS) type. The study was performed in the Plitvice Lakes National Park, situated in a sparsely populated area of the northwestern Dinarides, central Croatia. Dated cores of recent sediments from the two biggest lakes, Lake Prosce and Lake Kozjak, were analysed for the selected contaminants using highly specific methods, involving inductively coupled plasma mass spectrometry (ICP/MS), gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem mass spectrometry (LC/MS/MS). The concentration of inorganic constituents reflected primarily the geological background of the area as well as geomorphological and geochemical characteristics of the Plitvice Lakes. Due to the higher terrigenous input, the concentration of all elements was significantly higher in the Lake Prosce. The concentration of toxic metals was relatively low in both lakes, except for Cd (>1 mg kg^{-1}) and Pb (up to 40 mg kg^{-1}). The vertical profiles of these metals suggested that elevated concentrations of Cd were of natural origin, derived from the erosion of the Jurassic dolomite bedrock, while Pb was predominately of recent anthropogenic origin. A similar distribution pattern, suggesting the same prevailing mechanism of input, was observed for pyrolytic PAHs. The characteristic diagnostic PAH ratios revealed that higher PAHs prevailingly originated from the combustion of biomass and fossil fuels. LAS, which represent highly specific indicators of untreated wastewaters, were found in rather high concentrations in the recent sediment layers (up to 4.7 mg kg^{-1}), suggesting that contaminated household and hotel wastewaters reach the Lakes, very probably by leaking through the porous karst rocks.

1. Introduction

Lakes are highly vulnerable aquatic ecosystems, which are exposed to significant inputs of various materials from their watersheds. Even in the remote pristine areas such as high mountains or arctic areas, lakes are exposed to an increasing contamination through a passive or active long-range transport of various inorganic and organic contaminants (Shotyk et al., 1998; Fernandez et al., 2000; Evenset et al., 2007; Pozo et al., 2007). In addition to natural eutrophication, the anthropogenically-enhanced discharges of nutrients and toxic contaminants into the lakes pose a major challenge for their environmental sustainability and management.

Lake sediments represent a major sink for many natural and anthropogenic constituents and may serve as excellent model systems for the study of biogeochemical behavior of inorganic and organic contaminants and organic mater cycling. The accumulation rate of various contaminants is governed by specific water–sediment interactions and is highly dependant on the input dynamics. Consequently, undisturbed sediments represent natural archives for the identification of different environmental sources of individual contaminants as well as for the reconstruction of the past environmental changes, in particular long-term and recent changes in the anthropogenic inputs (Bindler et al., 2009; Thevenon et al., 2011). Sediment cores have been widely used for the assessment of historical trends of trace metals (Bindler et al., 2009; Zaharescu et al., 2009; Thevenon et al., 2011), PAHs (Wakeham et al., 1980; Fernandez et al., 2000; Muri and Wakeham, 2009), persistent organic contaminants (POPs) (Rapaport and Eisenreich, 1988; Muir et al., 1996), and surfactants (Reiser et al., 1997).

The lakes situated in densely populated areas receive very complex inputs, including wastewater discharges, erosion by runoff water and atmospheric deposition, which is reflected in a complex composition and enhanced concentrations of different types of sediment contaminants (De Bartolomeo et al., 2004). Pristine areas

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such as mountain lakes, Arctic lakes or National park areas show much lower concentrations of individual contaminants. Therefore they are highly vulnerable to additional anthropogenic inputs and represent ideal systems to study relative importance of individual routes for the overall contaminant loading into the lakes (Fernandez et al., 2000; Evenset et al., 2007; Muri and Wakeham, 2009; Thevenon et al., 2011).

The Plitvice Lakes (central Croatia) are a pristine hydrological system of sixteen karst lakes, separated by travertine barriers. Owing to their natural amenities, since 1979 they are included on the UNESCO World Natural and Cultural Heritage List. The unique geomorphological, hydrological, biogeochemical and biological characteristics of the Plitvice Lakes have been a continuous challenge for many researchers and environmental managers. Most of the studies, so far, were focused on understanding the basic phenomenon of the Lakes, i.e. the formation of tufa barriers (Srdoc et al., 1985; Horvatincic et al., 1989), in particular the role of the biological factors on the calcium carbonate precipitation (Chafetz et al., 1994). More recently several reports addressed the issue of the anthropogenic influence on the Plitvice Lakes, including both eutrophication and input of several types of anthropogenic contaminants (Srdoc et al., 1992; Ahel and Terzic, 2006; Horvatincic et al., 2006). The study by Horvatincic et al. (2006) suggested that eutrophication in the Plitvice Lakes showed an increasing trend due to the significant input of allochtoneous plant debris from the surrounding forests, while there was no clear evidence of recent pollution by organic and inorganic compounds of anthropogenic origin.

The aim of this investigation was to demonstrate the advantages of using multiple highly specific inorganic and organic constituents in decoupling natural and anthropogenic sources and to assess their relative impact on the sediment quality of the remote pristine karst lakes. The goal was achieved by combining multielemental analysis of trace elements, with a special emphasis on those reflecting specific anthropogenic inputs, with the determination of two classes of complementary molecular marker compounds, polycyclic aromatic hydrocarbons as molecular markers of the pyrolytic processes and detergent-derived linear alkylbenzenesulfonates (LAS) as markers of wastewater inputs.

2. Materials and methods

2.1. Study area and sampling

The Plitvice Lakes, situated in the Dinaric karst in the central Croatia, consist of a cascade system of 16 lakes of different sizes, interconnected by channels, cascades and waterfalls (Fig. 1). The lakes receive water from the two main springs, situated in the upper region of the lakes, which are the source of the surface streams Bijela Rijeka and Crna Rijeka. The two streams join to form the Matica River, which represents the main supply of the Plitvice Lake system. Two additional tributaries, Rjecica and Plitvica Brooks, situated in the lower reaches of the lakes, are less important for the overall hydrology of the Lakes. The lakes are characterized by intense precipitation of authigenic calcium carbonate, forming tufa barriers and fine-grained lake sediments (Srdoc et al., 1985). The details on the chemistry and biology of the Plitvice Lakes have been described by Srdoc et al. (1986). In this work a special emphasis was put on the two largest lakes, the Lake Prosce and Lake Kozjak, situated at the end of the Upper Lakes region. It should be pointed out that there is a significant difference between these lakes with respect to their exposure to modern anthropogenic sources. The Lake Prosce is situated in the upper area, away from the major roads and tourist routes, while the Lake Kozjak, which marks the end of the upper and beginning of the lower lakes section, is exposed to more intensive tourist activities, including three hotels located near its shore.

Sediment cores from the Prosce and Kozjak Lakes were retrieved in 1990 and 2003 by scuba-divers in the central part of the lakes from the depth of 19 and 21.5 m, respectively. The sediment cores (about 30 cm long) of lake marl were obtained using a 100 mm i.d. plastic coring device. Undisturbed sediment cores

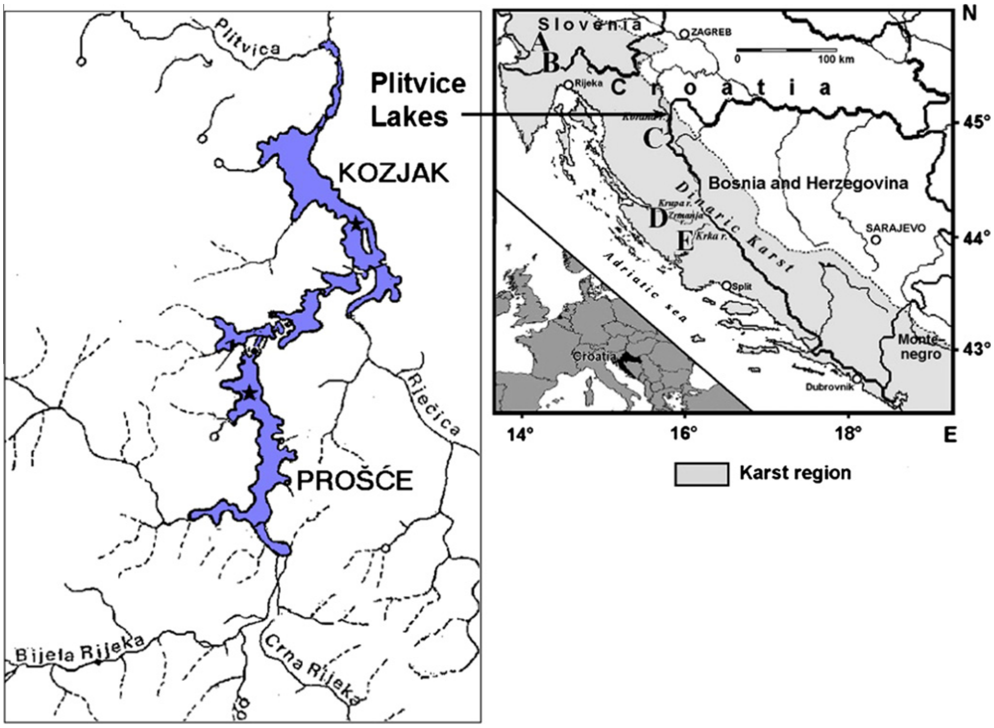

Fig. 1. Map of the Plitvice Lakes with indicated sampling stations.

Table 1
The main characteristics of investigated sediments from the Plitvice Lakes.

Parameter	Lake Prosce	Lake Kozjak
Calcite (%)	65–72	80–87
Dolomite (%)	2.5–4.7	1.7–2.7
Quartz (%)	8.7–11.1	3.4–4.5
Authigenic carbonate (%)	96	96
Organic matter (%)	7–10	3.7–6.7
Authigenic OM (%)	78	84

were frozen immediately after sampling and transported to the laboratory. The cores were carefully extruded with a piston and cut into 1–5 cm layers. Prior to analysis, all sediments samples were air-dried, gently disaggregated using mortar and pestle and homogenized. The main sediment characteristics of the examined cores are presented in Table 1.

2.2. Analyses

For metal analysis, sediment subsamples (0.1 g) were digested with 10 mL of aqua regia (mixture 1:3 of nitric and hydrochloric acid) in the microvawe (MW) oven (Multiwave 3000, Anton Paar, Graz, Austria). The analysis of several certified reference materials (marine sediment MESS-3, NRC Canada and stream sediment NCS DC 73307, Beijing, China) revealed that almost quantitative recovery (80–100%) was obtained for all analyzed elements. Taking into account that sediments from the Plitvice Lakes are composed mainly (80–95%) of carbonates (Horvatincic et al., 2006), which are easily dissolved in aqua regia, the results obtained by the applied digestion method are probably not very different from the total concentrations, but formally should be regarded as aqua regia soluble concentrations. Upon digestion, the samples were diluted with Milli-Q water to achieve a concentration optimized for ICPMS measurements. Prior to the ICPMS determination. Indium (1 $\mu g\ L^{-1}$) was added to the final solutions as an internal standard. Multielemental analysis of the prepared samples was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICPMS) using an Element 2 instrument (Thermo, Bremen, Germany). The measurements of the selected isotopes were performed at three different resolutions: low resolution (^{7}Li, ^{107}Ag, ^{111}Cd, ^{120}Sn, ^{208}Pb, ^{209}Bi), medium resolution (^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{121}Sb) and high resolution (^{27}Al, ^{39}K, ^{56}Fe). External calibration in the range of 1–10 $\mu g\ L^{-1}$ was used for the quantification. Standards were prepared by appropriate dilution of a multielemental reference standard (Analytika, Chech Republic). Quality control of analytical procedure was performed by simultaneous analysis of the blank and certified reference material with each group of sediment samples. Details of the analytical method were described elsewhere (Fiket et al., 2007; Cukrov et al., 2008).

Determination of polycyclic aromatic hydrocarbons (PAHs) followed a modified procedure by Giger and Schaffner (1978). Briefly, aliquots of 5 g of sediment samples were extracted with a mixture of methylene chloride and cyclohexane using accelerated solvent extraction. The total extract was purified using gel-permeation chromatography using EnvirogelTM GPC (Waters, USA) clean-up column. The purified extracts were further cleaned up on a column of fully active silica gel. The aromatic fraction, containing all PAHs, was obtained by elution with methylene chloride. The eluate was evaporated to dryness, reconstituted in cyclohexane and analysed by high-resolution gas chromatography/mass spectrometry (HR GC/MS) as described earlier in Krca et al. (2007). Briefly, the GC/MS analyses were performed using a Varian CP-3800 gas chromatograph, equipped with a 20 m × 0.2 mm × 0.25 μm HP-5 fused silica column, and interfaced with a Varian Saturn 2200 ion trap GC/MS system. The column temperature was programmed from 50 °C to 300 °C at 5 °C min^{-1} and the samples were acquired in full scan mode. The PAHs were quantified from the reconstructed mass chromatograms using their corresponding molecular ions. The quantification of the individual PAHs was performed using suite of deuterated PAH as internal standards, which were added to the extracts before the GPC clean-up. The accuracy of the method was tested using standard reference material RTC-CRM 105 (RT Corporation Ltd., UK). The detection limits for all individual PAHs were below 5 ng g^{-1}, while reproducibility varied from 10% to 20%.

For the determination of anionic surfactants of linear alkylbenzene sulfonate (LAS) type, air-dried sediments were extracted with methanol using an ultrasonic bath and centrifuged to enhance the removal of the suspended particles from the extract. The extracts were analyzed by high-performance liquid chromatography tandem mass spectrometry (LC/MS/MS) using the method described by Ahel et al. (2009). The LC/MS system consisted of a Surveyor HPLC system coupled to a triple quadrupole mass spectrometer TSQ Quantum (Thermo Electron Corporation, San Jose, CA, USA). LAS analyses were performed in the negative ionization (NI) mode using the selected reaction monitoring (SRM) technique (Ahel et al., 2009). Individual LAS homologs were separated on a 3 × 100 mm column filled with 3.5 μm Zorbax SB-C18 particles. The eluent A was water containing 1 M ammonium acetate, while the eluent B was methanol containing also 1 mM ammonium acetate. A binary gradient was applied for the elution at a flow rate of 0.4 mL min^{-1} as follows: the percentage of eluent B increased from 30% to 95% B in 3 min, followed by an isocratic hold of 3 min. For quantitative determination octylbenzenesulfonate was used as internal standard. The quantitation limit of individual LAS homologs was 10 ng g^{-1} and reproducibility was 7–8%.

3. Results and discussion

3.1. Major elements and trace metals

Multielemental analysis proved to be an appropriate tool to study the sources and extent of anthropogenic impact on the Plitvice Lakes. The distribution of selected elements in sediment cores from the Lake Prosce and Kozjak, collected in 2003, are shown in Fig. 2. All elements typical of terrigenous material (Al, Fe, K, Li) revealed uniform vertical concentration profiles in both lakes. This indicated a relatively constant ratio of the authigenic and terrigenous input in the time period, covered by the cores. Concentrations of major elements (Al, Fe, K) were very low in the Lake Kozjak and relatively low in the Lake Prosce, which reflects a low percentage of terrigenous clay materials in these sediments. For comparison, concentrations of Al and Fe in sediments of the karst Krka River estuary are in the range of 20 000–40 000 for Al and 10 000–25 000 for Fe (Cukrov et al., 2008), which is much higher than the concentrations in the Lake Kozjak, but similar to those in the Lake Prosce. This is in agreement with previous research, which showed that Plitivice Lake sediments were mainly composed of authigenic carbonates as a result of intensive calcite precipitation from the water column (Srdoc et al., 1985; Horvatincic et al., 2003). The percentage of calcite in sediments from the Lake Prosce varied between 65% and 72%, and in the sediments from the Lake Kozjak between 80% and 87% (Table 1). The concentration of the major geochemical elements was about two times higher in the Lake Prosce than in the Lake Kozjak, which indicated possible difference in the terrigenic inputs between the two lakes. The Lake Prosce receives the material from the springs of the two largest brooks, Bijela and Crna Rijeka, which join to form the major stream in the area of upper lakes the Matica River (Fig 1). The Matica River represents the most important source of terrigenous material to the Lake Prosce, characterized by enhanced concentrations of

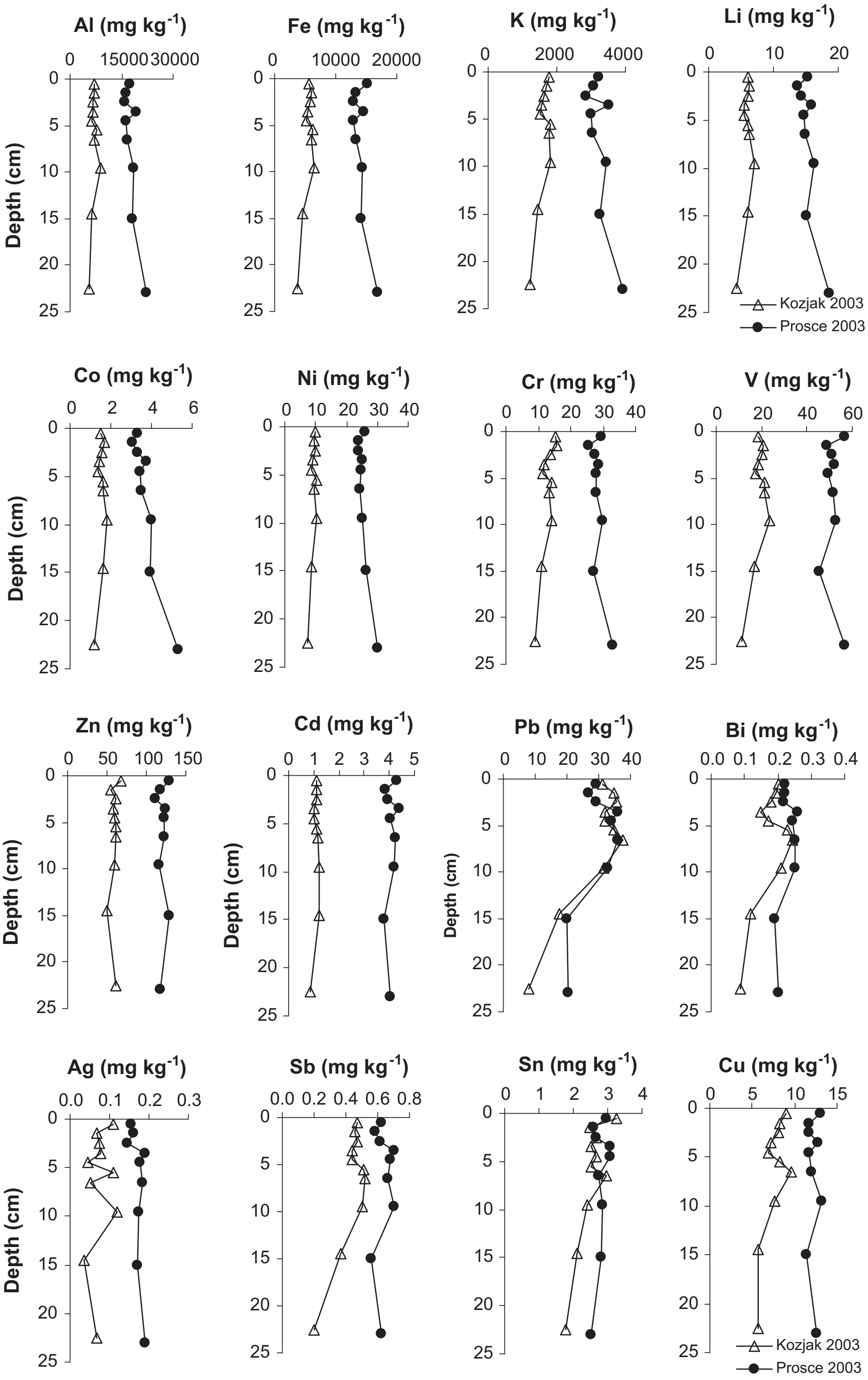

Fig. 2. Distribution of selected major elements and trace metals in undisturbed sediment cores of the Lake Prosce and Lake Kozjak, collected in 2003. Legend: Lake Prosce – closed circles; Lake Kozjak – open triangles.

major and trace elements (Terzic et al., 2007). Rapid precipitation of this material in the upper lakes (Spoljar et al., 2007) prevents its efficient transport downstream, through the cascade system of the Plitvice Lakes so that only a small percentage of this input reaches the Lake Kozjak. A number of trace elements (Co, Ni, Cr, V, Zn, Cd) show the same distribution features like the major elements: a uniform distribution along the depth profiles and more than two times higher concentration in the Lake Prosce than in the Lake Kozjak (Fig. 2). This indicated a predominately natural origin of these elements as well as their rather constant input to the lakes over the time-scale, covered by the sediment cores. It should be pointed out that the concentrations of the determined elements in both lakes were relatively low and can be regarded typical for carbonate deposits, except for cadmium. If concentrations of ecotoxic metals are compared with sediment quality guidelines for freshwater sediments (MacDonald et al., 2000) one can see that in both lakes measured concentrations were much lower than the Probable Effect Concentration (PEC). In the Lake

Kozjak, the concentrations of Ni, Cr, Zn, and Cu are even lower than the Threshold Effect Concentration (TEC). The only exception was Cd, which concentration in the Lake Kozjak was higher than TEC and in the Lake Prosce it was close to the PEC value (4.98 mg kg^{-1}). However, a rather constant Cd concentration in sediment depth profiles suggested that the high Cd content was very probably of the natural origin. Namely, high concentrations of Cd were found in both sediment and water (up to 50 ng L^{-1}) from all springs and tributaries feeding the Prosce and Kozjak Lakes (Terzic et al., 2007), which supports the assumption that Cd also reflects the geological background of the catchment area. Possible specific source of Cd are, very probably, Jurassic dolomitic rocks, which represent the main feature of the geological background in the upper area of the Plitvice National Park (http://np-plitvicka-jezera.hr/hrv/). Namely, it was recently shown (Quezada-Hinojosa et al., 2009) that Jurassic carbonates in Switzerland, and France contained anomalously high Cd concentration and we assume that the same phenomenon can explain our observations in the Lake Prosce. The ratio between the Cd concentrations in the Lakes Prosce and Kozjak was about 4, which is significantly higher than for most of the other elements (Fig. 2). Higher ratio (around 4) was also obtained for V, which showed a significant correlation ($r^2 = 0.4501$) with Cd in the Lake Prosce, indicating that material rich with Cd was also enriched with V. This indicated differences in terrigenous material composition between the two lakes (Table 1). Further research is needed to confirm this hypothesis and to explain the exact geological origin of Cd in the area of the Plitvice Lakes.

Normalization of trace metal concentrations to Al as a conservative parameter provided a better distinction between variations in metals inputs from the variations in sediment composition. These relationships, presented for selected elements in Fig. 3, clearly indicated that there was no significant anthropogenic input of metals in the Lake Prosce, except for Pb, as the concentrations were either well-correlated with Al (Ni, Cr, Ag) or were rather constant (V, Cd, Sb, Cu). However in the Lake Kozjak, there is a clear indication of an additional source, other than the natural geological background, of Pb, Sb, Ag, and Cu (Fig. 3) as well as Bi and Sn (not shown). These elements, which are generally considered typical indicators of anthropogenic sources, showed distribution features that were

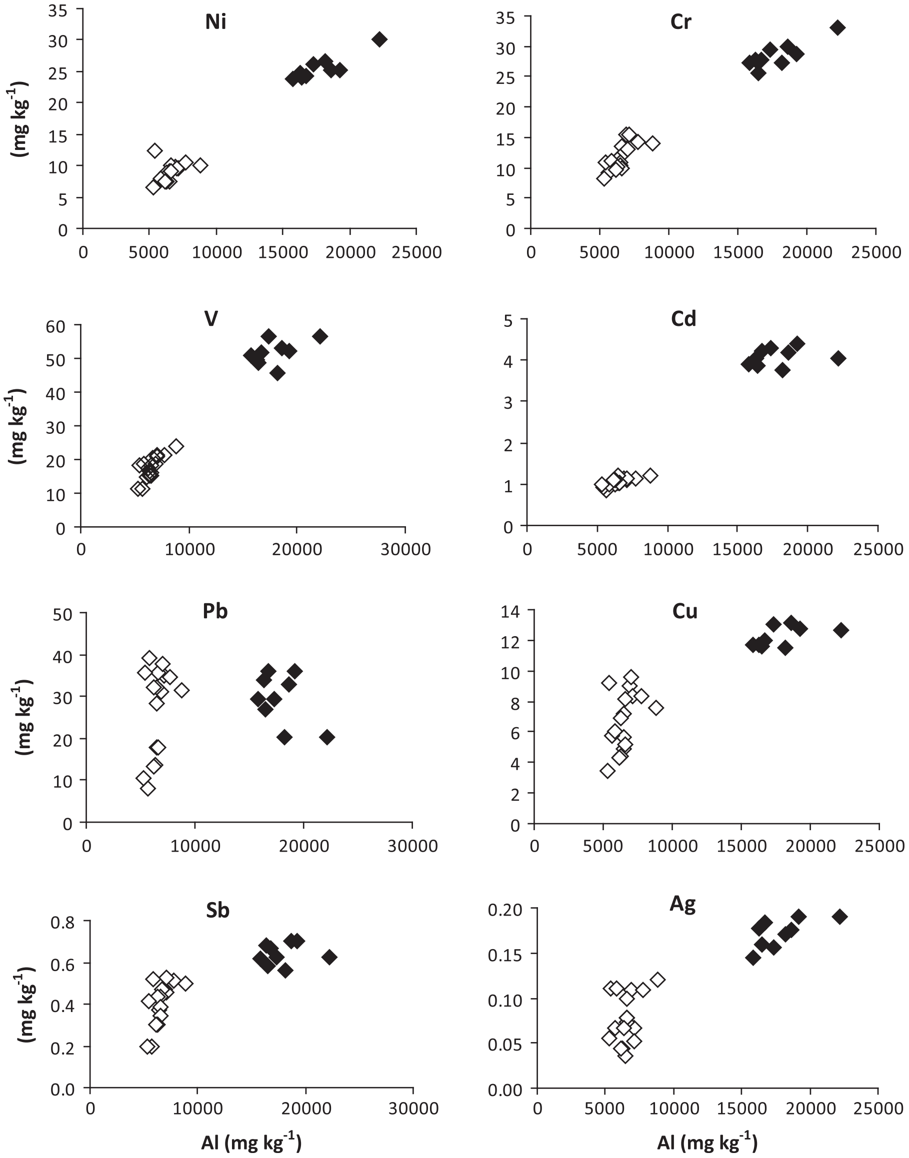

Fig. 3. Relationship between Al and selected trace metals in sediments from the Lakes Kozjak and Prosce, collected in 1990 and 2003. Legend: Lake Prosce – closed symbols; Lake Kozjak – open symbols.

markedly different from those observed for the major elements or Cd (Fig 2). Concentration of these elements in the deepest sediment layers was about two times lower in Lake Kozjak than in the Lake Prosce, which probably reflected the situation in the sediments deposited before the modern time, i.e. before the onset of a significant anthropogenic input. However both cores from the Lake Kozjak revealed that the concentration of metals having anthropogenic origin increased significantly towards the most recent layers. The concentration of Sn, Cu, Sb, Ag and Bi in the surface layer was about two times higher than that in the deepest layer. For Pb, the enrichment factor in the surface sediments reached almost 4. Furthermore, a common feature of the depth profiles for Pb, Bi, Sb and Cu was the concentration maximum in the layer between 5 and 15 cm, while the concentration slightly decreased towards the uppermost layer. On the contrary, the relative enrichment factors of the same metals (Pb, Bi, Sb, Ag, Sn and Cu) in the surface layer of the Lake Prosce were lower, suggesting that the modern anthropogenic sources are mainly located in the drainage area of the Lake Kozjak. Since the input of terrigenous material remained pretty constant over the time period studied, the explanation for the comparatively higher recent anthropogenic inputs into the Kozjak Lake must be interpreted as the consequence of higher concentrations of anthropogenic metals in the recently eroded terrigenous particles. Indeed, the concentrations of Pb in sediments collected near the inflow of the Rjecica Brook into the Kozjak Lake reached elevated levels up to 100 mg kg^{-1} (Terzic et al., 2007). The part of the Pb input is of the atmospheric origin. The atmospheric deposition rate of Pb in the area of Zagreb, Croatia, in 1980s was estimated at 8 mg m^{-2} y^{-1} (Mikac and Branica, 1994a). We assumed that the atmospheric deposition of Pb in the area of Plitvice Lakes, which is situated far from urban areas, must be much lower. Comparison of the atmospheric Pb deposition rate with the average mass accumulation rates of Pb in the Lakes Prosce and Kozjak of 34 and 25 mg m^{-2} y^{-1}, respectively, indicated that the atmospheric contribution to the total Pb input to the Lakes Kozjak and Prosce should be lower than 30% of the total.

3.2. Historical trends in metal concentrations

In order to assess the history of anthropogenic influence on the Plitvice Lakes it was essential to provide a correct dating of the sediment layers. On the basis of the radiocarbon dating of 12 m-long cores, the average sedimentation rates in the Lake Prosce and Lake Kozjak were estimated at 1.4–1.5 and 0.8–1 mm y^{-1}, respectively (Srdoc et al., 1986). A more detailed dating was performed on sediment cores collected in 2003 by three independent, dating methods using ^{137}Cs, ^{210}Pb and ^{14}C as tracers (Horvatincic et al., 2008). The depth profiles of all measured isotopes showed that the cores from the Lake Prosce and Lake Kozjak were undisturbed. In addition, newly obtained estimates of the average sedimentation rates were in good agreement with the data obtained in 1986 but only for the deeper, i.e. compacted sediment layers. Due to the very high water content in the upper layer of the sediment cores (Horvatincic et al., 2008) the apparent sedimentation rates in the surface sediment (1–10 cm) were much higher than in the deeper layers, containing fully compacted sediment. For that reason, dating of sediment layers based on average sedimentation rate leads to significant errors when estimating the age of deposition, in particular in the uppermost sediment layers. The dating of the sediment cores collected in 2003 by ^{210}Pb method (Horvatincic et al., 2008) revealed that 25 cm-long sediment cores cover a time period of about 70 years in the Lake Prosce and about 110 years in the Lake Kozjak. For the core sampled in 1990, which was not dated with ^{210}Pb, we estimated the age of discrete layers in analogy with the sediment core from 2003. The ^{210}Pb dating was applied to reconstruct the history of anthropogenic impact on the Plitvice Lakes using the elements that showed an increase in the surface sediment layers (Pb, Bi, Ag, Sb, Sn, and Cu). The distribution of these elements in dated sediment cores is presented in Fig 4.

For most of the metals presented in Fig. 4, a significant increase in concentration can be noted in sediment layers deposited after the Second World War. This also coincides with the period when the area of Plitvice Lakes was proclaimed a National Park (1949), which was accompanied by increasing traffic and tourist activities around the lakes. These activities were clearly reflected in increasing concentrations of anthropogenic metals in recent sediments and can be linked with some characteristic milestones of the National Park management. The historical trends in lead contamination are the best illustration of these processes. The main anthropogenic source of Pb worldwide in the studied period was the use of tetraalkyllead, a popular anti-knock additive of gasoline. Its intensive use started after 1950 and peaked in the period 1980–1990. In Europe, alkyl-Pb was phased out put in force in 2000, while in Croatia it was banned only in 2006. Measurements performed in Croatia, showed indeed a significant emission of alkyllead compounds into the atmosphere in the period 1985–1990 (Mikac and Branica, 1994a) with a consequence of a significant contamination of surface waters by lead and organolead compounds (Mikac and Branica, 1994b). The profiles of Pb presented in Fig. 4 seem to be in a good agreement with the history of use of tetraalkyllead: the increase starts in the layers corresponding to 1950s, shows the maximum in the 1980–2000s, while after 2000 a slight decrease can be noted. A decrease in the Pb concentration in the Lake Kozjak during the war period (1991–1995), when tourist activities were stopped, was not observed.

Similarly like for Pb, the related metals such as Bi, Ag and Sb show an increase in sediments from the Lake Kozjak after the Second World War. Smelting of lead sulfide ores, which are rarely monomineralic, also releases other elements, which are usually enriched in sulfide minerals, such as Zn, Cu, Sb, Bi, Ag and Tl (Krachler et al., 2009). It was shown that lead pollution in atmospheric particles is regularly accompanied by these elements (Krachler et al., 2008, 2009).

For Cu and Sn, the increase in the most recent layers was less expressed and started only in early eighties. The origin of these elements could be local, for example antifouling paints used on tourist boats and/or wastewater discharges from the hotels, situated on the shore of the Lake Kozjak. As organic tin compounds (tributyl and triphenyl derivatives) are used as biocides in Sn-based antifouling paints (Oliveira and Santelli, 2010), analysis of organotin compounds in sediments from the Lake Kozjak should be preformed in order to get a clue about the predominant source of Sn.

3.3. Organic contaminants

The analyses of organic marker-compounds provided also a valuable indication on the importance of some specific inputs into the Plitvice Lakes. Previous reports on hydrocarbon molecular markers in the Plitvice Lake sediments revealed three distinct sources of hydrocarbons: phytoplankton, higher terrestrial plants and pyrolytic processes (Ahel and Terzic, 2006). Among different hydrocarbon species, the nonsubstituted PAHs, which have a predominately pyrolytic origin, have been selected as the best diagnostic compounds to illustrate recent changes in the anthropogenic pressure on the lakes. The distribution of the most prominent PAHs in the sediment cores, collected in 2003 is presented in Fig. 5.

The most abundant PAHs in the Plitvice Lake sediments were the 5-ring PAH, including benzo(k)fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene, while 3-ring and 4-ring PAHs were present in much lower concentrations. This is in accordance with the comparatively lower solubilities and consequently higher affinities of 5-ring PAH to accumulate on the suspended particles.

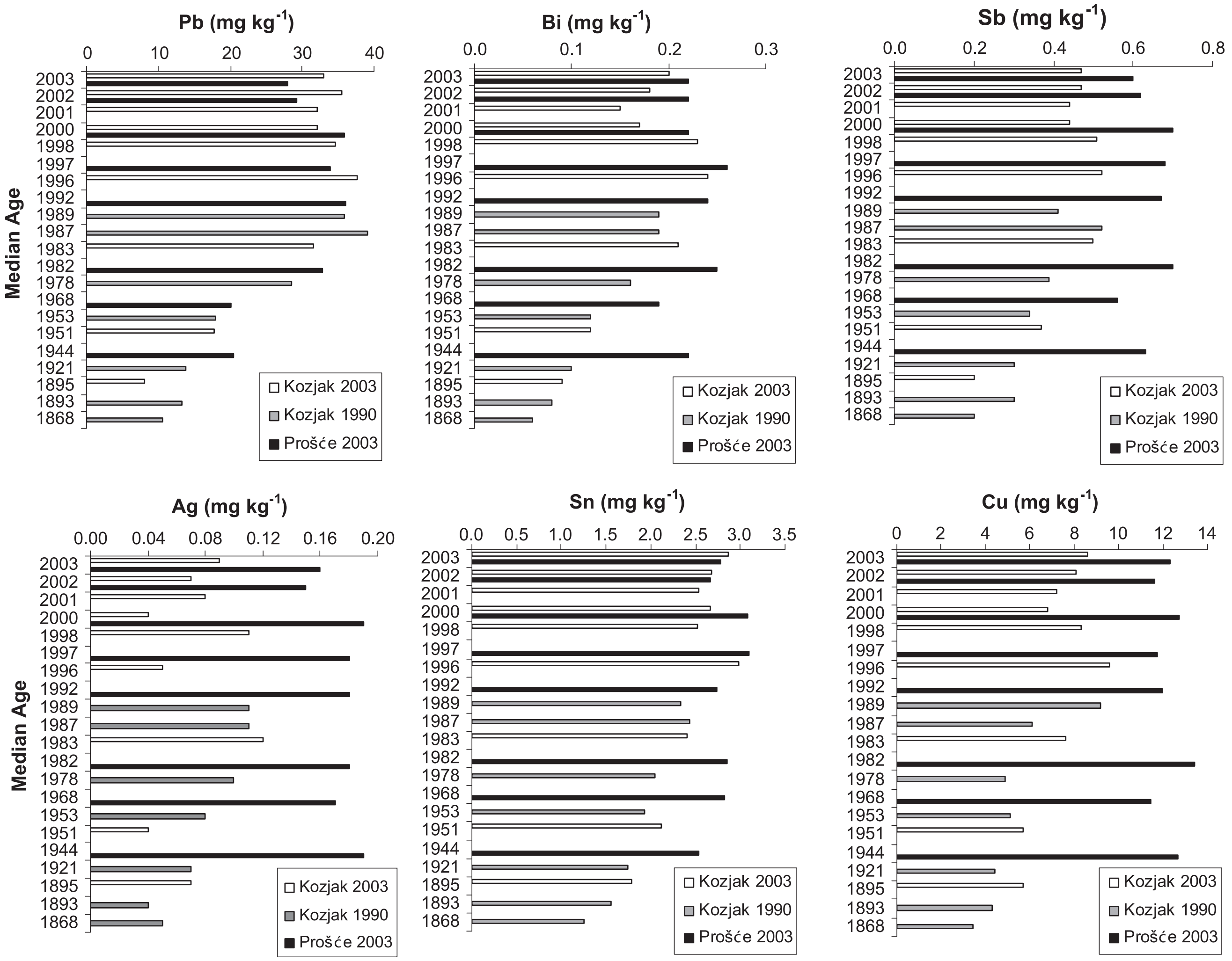

Fig. 4. Concentration of selected trace metals in dated sediment cores from the Lakes Prosce and Kozjak, collected in 1990 and 2003.

The concentration of individual higher PAHs varied in the ranges from 10 to 90 ng g^{-1}. The total concentration of the 16 EPA PAH in the Lake Prosce (285–407 ng g^{-1}) was significantly higher than the concentrations in the Lake Kozjak (167–301 ng g^{-1}), which is very similar to the feature described above for inorganic constituents. This confirmed the assumption that the observed contaminant levels were mainly governed by the input of eroded terrigenous material. Regarding comparison with the typical PAH concentrations in mountain lakes across Europe (Fernandez et al., 2000; Muri and Wakeham, 2009) the concentration in the Plitvice Lakes was lower, which probably reflects the preserved pristine character of the area in the Plitvice Lakes National Park.

As to the sources of polycyclic aromatic hydrocarbons, the characteristic diagnostic ratio Fluorathene/(Fluoranthene + Pyrene) of 0.542–0.587 (Wagener et al., 2010), suggested that most of the PAH originated from the combustion of biomass or coal. Since the area is traditionally known for timber-cutting, the use of firewood for heating in households is quite common, which probably explains the observed diagnostic ratio. However, the diagnostic ratios Benzoanthracene/(Benzoanthracene + Chrysene) and Indeno(c,d)Pyrene/(Benzo(ghi)Perylene + Indeno(c,d)Pyrene) were much lower (0.33–0.38 and 0.32–0.35, respectively) and suggested possible contribution of the combustion of fossil fuels (Aceves and Grimalt, 1993; Wagener et al., 2010).

An attempt to correlate PAH concentrations with the concentration of fossil fuel-derived Pb gave significant positive correlations for the 1990 core from the Lake Kozjak ($r^2 = 0.580$) (Srdoc et al., 1992) and for the 2003 core from the Lake Prosce ($r^2 = 0.598$). This indicated that, at least partly, the two contaminant classes might have originated from the same source, most likely from the fossil fuel combustion. A similar correlation was reported for the Trasimeno Lake, Italy (De Bartolomeo et al., 2004). The reason for the relatively modest correlation can be partial degradation of PAHs in sediments (DeBruyn et al., 2009), especially in the uppermost, less anoxic layers, due to the relatively slow sedimentation and consolidation of the sediments.

The reconstruction of historical trends of the total nonsubstituted PAHs in the Lake Prosce and Lake Kozjak (Fig. 6) revealed a significant dynamics along the recent history of the lakes. The concentrations in the Lake Prosce are less variable and show a gradual decrease from mid-eighties to 2003. The decrease is much more pronounced in the Lake Kozjak and corresponds to the period 1996–2002. This reflects very probably the fact that during the 1991–1995 war in Croatia and immediately after this period, the area was depopulated and closed for the massive tourism. With the revival of the traffic and the tourist activities, the concentration in 2003 increased again to the pre-war levels. This feature was not observed in the Lake Prosce.

Determination of surfactant-derived compounds provided very useful information about an additional less known anthropogenic input into the Lake. The concentration LAS reached high levels with the maximum concentration of 4.7 mg kg^{-1} in the uppermost layer

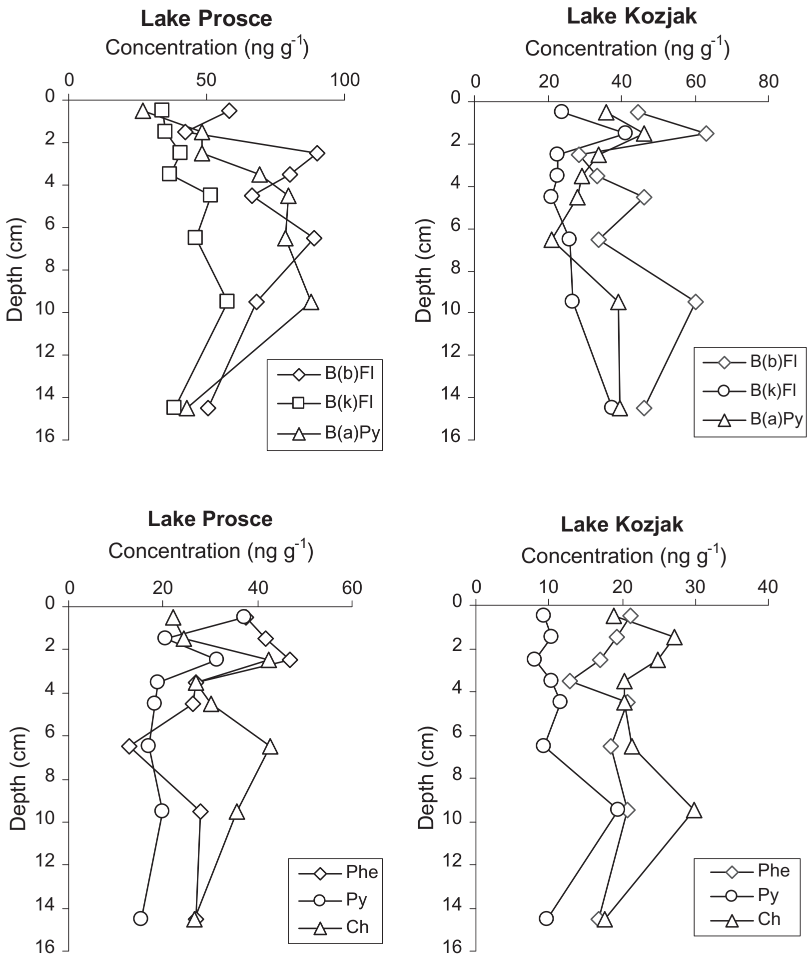

Fig. 5. Vertical profiles of the most prominent 3–5 ring polycyclic aromatic hydrocarbons in the recent sediment cores of the Lake Prosce and Lake Kozjak, collected in 2003. Legend: B(k)Fl: benzo(k)fluoranthene, B(b)Fl: benzo(b)fluoranthene and B(a)Py: benzo(a)pyrene, Phe: phenanthrene, Py: pyrene, Ch: chrysene.

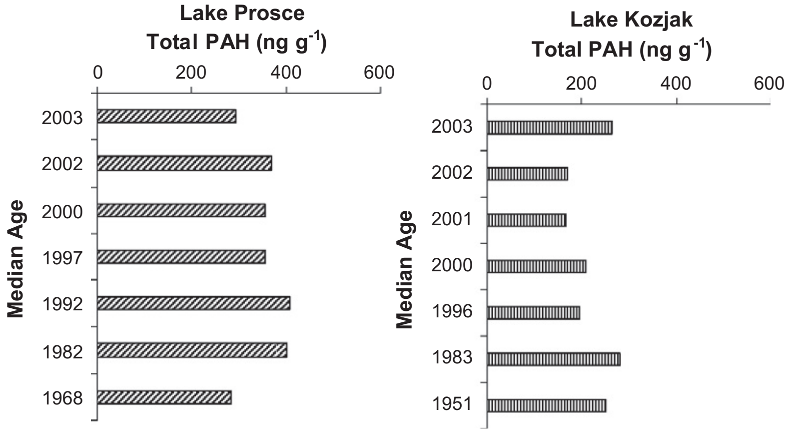

Fig. 6. Concentration of the total unsubstituted PAH in dated sediment cores from the Lakes Prosce and Kozjak, collected in 2003.

of the Lake Kozjak (Fig. 7). The distribution of individual LAS homologs in the examined sediments was significantly altered in comparison with their relative abundance in detergents, showing a conspicuous enrichment in C12 and C13 LAS. The studies on LAS distribution in lakes are very rare (Reiser et al., 1997; De Bartolomeo et al., 2004). The LAS concentration in Plitvice Lake sediments is higher than that reported for the Swiss lake sediments (Reiser et al., 1997), and lower than in the Trasimeno Lake in Italy (De Bartolomeo et al., 2004). However it should be stressed that the results for the Trasimeno Lake were obtained by a comparatively non-specific MBAS method.

The vertical profiles of the total LAS concentration in both lakes clearly indicated a significant input of synthetic surfactants from laundry detergents in the last few decades. The observed distribution was assumed to reflect the impact of untreated wastewaters released from the hotels, situated on the shore of the Lake Kozjak,

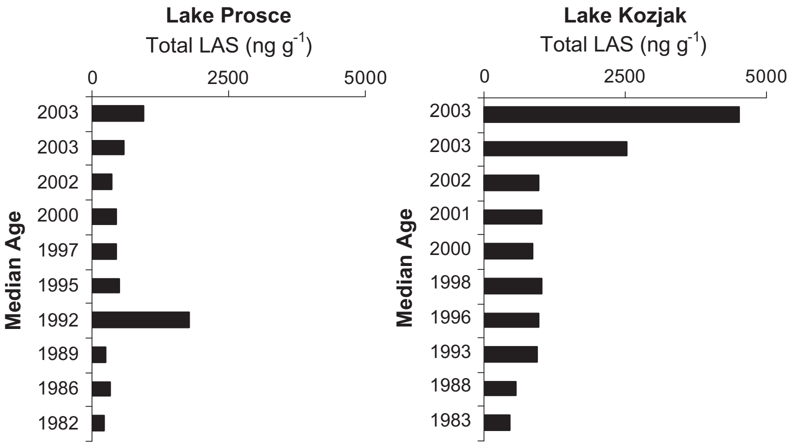

Fig. 7. Vertical profile of the total linear alkylbenzenesulphonates (LAS) in dated sediment cores of the Lake Prosce and Lake Kozjak, collected in 2003.

and households in the upper reaches of the National Park. As opposed to other contaminant classes in this study, the LAS concentrations in the Lake Kozjak (4.7 mg kg^{-1}) largely exceeded those in the Lake Prosce (up to 1.3 mg kg^{-1}), which was a strong indication that main source was in the area near lake Kozjak, most probably the hotel wastewater. We have no clear indication on what could have been the cause for the enhanced concentration of LAS in the Lake Prosce in 1992, as this occurred during the war in Croatia. It should be emphasized that such a concentration increase can be caused by only few kg of LAS, which illustrates high vulnerability of small lake systems. To our knowledge, there were no direct wastewater discharges from the hotels into the Lake Kozjak. Moreover, the concentration of LAS in the surface sediments near the inflow of the Rjecica Brook (1.3 mg kg^{-1}, Terzic et al., 2007) were lower than in the Kozjak sediment core, which indicated that this cannot be the main route of LAS input. The concentration of LAS in the surface layer of the water column of the Plitvice Lakes also showed only a modest presence of these contaminants (<100 ng L^{-1}). Therefore, it has to be assumed that untreated wastewater enters the lake and, subsequently, the bottom sediments, by leaking through the porous karst rocks.

The importance of this observation consists not only in revealing LAS as major class of contaminants in the Plitvice Lakes, but also implies that uncontrolled input of nutrient-rich wastewaters, including P as the limiting nutrient in the Plitvice Lakes, may trigger an accelerated eutrophication, which represents probably the main problem for the lake conservation (Horvatincic et al., 2006, 2008). Indeed, the profiles of *n*-heptadecane/*n*-octadecane ratio (Giger et al., 1980) in both lakes revealed that this process has been significantly intensified over the last few decades (Srdoc et al., 1992; Ahel and Terzic, 2006).

4. Conclusion

Assessment of the anthropogenic pressure on the pristine karst lakes using multiple chemical indicators provided a useful tool for the decoupling anthropogenic and natural sources and created a basis for a better understanding of their relative importance for lake conservation.

It was shown that all trace metals had predominately terrigenous origin and reflected the geological background of the area, which included an interesting Cd anomaly, leading to rather high Cd levels in all sediments. Among different metals, the best indicator of anthropogenic processes was Pb, which showed a high concentration in the most recent sediments. Pb levels remained high despite the gradual phase-out of leaded gasoline started in 1995. Moreover, the Pb was positively correlated with PAHs, indicating fossil fuels as an important common source. High levels of anionic surfactants indicated possible uncontrolled leakage of the untreated wastewaters into the Lakes. This issue warrants further attention, in particular because this input might be responsible for an accelerated eutrophication of the Lakes.

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