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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.
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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

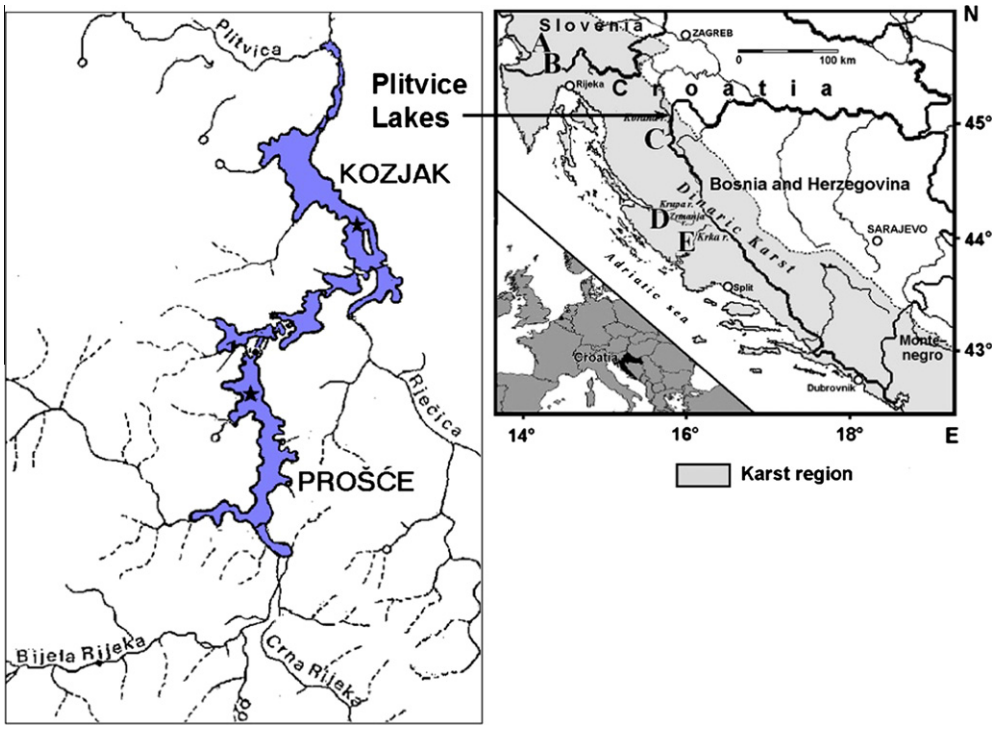

Fig. 1. Map of the Plitvice Lakes with indicated sampling stations.

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