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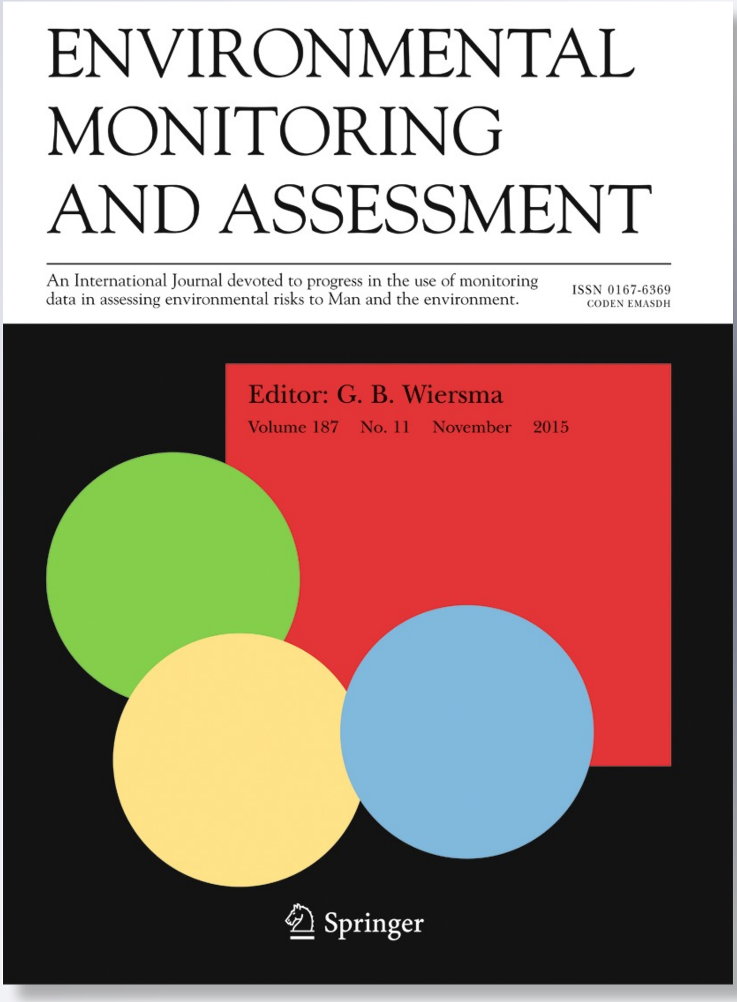

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Abstract The anthropogenic impact on the terrestrial environment of the Plitvice Lakes National Park (PLNP) was investigated through the analysis of three groups of major contaminants (persistent organochlorine pollutants including 15 organochlorine pesticides (OCPs) and 17 polychlorinated biphenyls (PCBs), trace elements/heavy metals (6 major and 23 trace constituents), and anthropogenic radionuclides (^{90}Sr, ^{134}Cs, and ^{137}Cs)) in three terrestrial compartments (soil, air, and bioindicators of air contamination) during 2011–2013. The correlation coefficients of element mass fractions with soil properties indicated that total Fe and Al minerals, soil organic matter (OM), and organic carbon (OC) content affected the mass fractions of most trace elements in the topsoils. The annual and spatial distributions of heavy metals in total deposited matter (TDM) indicated that the metals came from natural sources and long-range transfer of particulate matter. The PCB and OCP levels found in soil and conifer needles corresponded to global environmental pollution levels by persistent organic pollutants and represented the lower end of the mass fraction ranges reported in the relevant literature. Analyses of anthropogenic radionuclides in bioindicators (conifer needles, lichens, and mosses) showed low but measurable activity concentrations of ^{134}Cs (for the first time after the Chernobyl accident), which indicated origin from the March 2011 Fukushima Nuclear Power Plant accident. Our overall results indicated that human activity inside or near the PLNP had no significant impact either on contaminant spread by air or on their content in topsoils.

Keywords Metal(oid)s · Polychlorinated biphenyls · Organochlorine pesticides · Radionuclides · Soil · Total deposited matter

Introduction

The Plitvice Lakes National Park (PLNP) is one of the most popular tourist destinations in Croatia. It was

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included into the UNESCO World Heritage List in 1979, as one of the first natural sites worldwide (http://whc.unesco.org/en/list/98). Due to its specific geology, geomorphology, and hydrology, it is one of the most impressive karst environments in the world. The principal natural phenomenon of the park is a dynamic system of 16 lakes separated by tufa barriers and waterfalls. The natural values of the park also comprise its habitat diversity and exceptional plant and animal biodiversity. Because it is home to various relict, endemic, rare, and protected plant and animal species, the PLNP is considered an exceptionally valuable area for Europe and the world (PLNP 2015). To preserve such a sensitive ecosystem, it is of particular importance to monitor and evaluate the levels of various contaminants in the different compartments of the park.

In the last decades, the PLNP has experienced significant ecological change caused by global climate trends, watercourse regulations, forestry and agricultural activities, leaking wastewater systems, war, and tourism (Sremac et al. 2012). Previous studies of anthropogenic influence in the PLNP focused mainly on the aquatic ecosystem of the lakes and tributaries (water, sediments, and biota), addressing different contamination issues (Dautović et al. 2013; Horvatinčić et al. 2014; Mikac et al. 2011; Srdoč 1992; Vukosav et al. 2014). These investigations revealed the presence of quantifiable levels of anthropogenic pollutants such as metals, hydrocarbons, surfactants, and their metabolites in the aquatic environment of PLNP. However, to the best of our knowledge, simultaneous measurements of multiple anthropogenic contaminants have never been conducted in the terrestrial environment of the park, although it covers almost 99 % of the park's surface (Šikić 2007). The terrestrial environment also undoubtedly deserves careful monitoring, especially in light of the fact that karst areas are susceptible to swift introductions of contaminants and contamination due to the rapid transfer of contaminants by groundwaters (IAHKC 2013).

To bridge this gap in knowledge, this study was designed to be the first to perform a comprehensive analysis of the anthropogenic impact on the terrestrial environment (soil, air, and bioindicators) of the PLNP. Our analyses included soil characterization, determination of the distribution of different organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), major and trace elements, anthropogenic radionuclides (^{90}Sr, ^{134}Cs, and ^{137}Cs), and air quality assessment by measuring deposition particles in the environment of different zones of the PLNP. The contaminants were measured in soil, air, conifer needles (*Picea abies*; bioindicators of average air contamination with organic pollutants and of radioactivity contamination), as well as moss (*Hypnum cupressiforme*), and lichen (*Cladonia rangiformis),* bioindicators of radioactivity contamination. In addition, measurements were also performed at Šumbar, an unprotected area near the city of Karlovac used as a hunting preserve.

The aim of the present study was to investigate the occurrence and temporal and spatial distributions of a combination of compounds (PCBs, OCPs, major and trace elements, and radionuclides) in air, soil, and vegetation of the oldest national park in Croatia and possibly identify their sources. These measurements could be of great interest to park managers and government officials for assessing the impact of the studied contaminants on threatened and endangered natural and wildlife resources.

Material and methods

Study area

PLNP is located in a mountainous region, amidst the Dinaric Alps, covering an area of 297 km^2 and spreading from 367 to 1279 m above sea level. The special geographical location, large difference in elevation (912 m), and specific climatic features have contributed to the emergence of many natural phenomena and rich biodiversity (Šikić 2007). The area of the park is underlined by karstic rocks, mainly dolomite and limestone. The most common in the park are calcocambisol and leptosol (Halamić and Miko 2009).

PLNP is one of the most popular tourist destinations in Croatia; in 2014, it was visited by more than 1.1 million people. Besides tourism, other possible sources of anthropogenic influence in the park could be attributed to the 19 small settlements within the national park area that comprise approximately 1770 inhabitants (CBS 2011) or to the traffic on three state roads (D1, D42, and D52) which pass through or along the border of the PLNP. Traditionally, the local population engaged in animal husbandry, agriculture, milling, and forestry. Since the establishment of the PLNP, almost all commercial activities have been banned within the park's territory.

Sample collection

Samples were collected at four locations within the PLNP (Fig. 1 and Table 1) and at Šumbar, a sampling site outside the PLNP (Table 1). The PLNP sampling sites were carefully selected across the entire park, taking into account different zones of protection within the PLNP's boundaries. Šumbar is situated at an aerial distance of about 70 km northward from the PLNP in an unprotected area.

Topsoil samples (0–15 cm; minimum 500 g of soil) for the analysis of major and trace elements and organic contaminants were collected in April, July, and November 2011 and May 2012. Each of the 16 PLNP soil samples and 8 Šumbar soil samples were composites of 5 subsamples taken from a square area of 1 m^2. The stones and remains of plants were removed manually. Until analysis, the wet soil samples were stored in polyethylene bags and kept at −20 °C.

Air pollution by inorganic contaminants was monitored by collecting and analyzing total deposited matter (TDM) and its heavy metal content. Monthly samples (30±2 days) of TDM were collected from April 2011 to May 2013. Bergerhoff-type samplers were used to collect the bulk deposition according to norm HRN EN 15841 (2009).

Samples of conifer needles (*P. abies*; 1- and 2-year old) for analyses of organic contaminants and radioactivity and lichens (*C. rangiformis*) and mosses (*H. cupressiforme*) for analysis of radioactivity were collected only once, in April 2011. Conifer needles, lichens, and mosses were a composite of subsamples taken in an area of several square meters.

Sample analysis

Soil characterization

Soil samples were defrosted, air dried, and sieved through a 2-mm pore sieve. Fractions smaller than 2 mm were used for the analysis of total carbon (TC), organic carbon (OC), inorganic carbon (IC), organic matter (OM), and moisture content (H_2O) in solid soil samples, as well as of pH, electric conductivity (EC), dissolved total carbon (DTC), and dissolved organic carbon (DOC) in the soil suspension.

OC content was determined as the difference between TC and IC, measured using a total organic carbon analyzer (TOC-V_{CPH}) coupled with the Solid Sample Module SSM-5000A (Shimadzu Europa GmbH, Duisburg, Germany). The moisture content of the air-dried soil was determined by oven-drying samples at 105 °C to a constant mass (for 48 h). OM content was determined in dry samples by gravimetric method, from the loss in mass caused by hydrogen peroxide (30 %) treatment of the samples at 450 °C for 6 h.

The soil pH was measured in the supernatant after overnight equilibration of 5-g air-dried samples with 30 mL of deionized water using a SevenMulti™ pH/conductivity meter equipped with an InLab® Expert Pro pH Electrode (Mettler Toledo, Schwerzenbach, Switzerland). The same supernatant was analyzed for EC using an InLab® 731 Conductivity Probe as well as for DTC and DOC using the TOC-V_{CPH} analyzer.

Organochlorine pesticides and PCBs in soil

Soil samples were analyzed for the following 15 organochlorine pesticides: hexachlorobenzene (HCB), hexachlorocyclohexane isomers (α-, β-, and γ-HCH), DDT isomers (*o,p'*-DDT, *p,p'*-DDT) and metabolites (*p,p′*-DDE, *p,p′*-DDD), aldrin, endrin, isodrin, dieldrin, heptachlor, heptachlor epoxide, and α-endosulfan. Analysis of polychlorinated biphenyls comprised 6 indicator congeners (International Union of Pure and Applied Chemistry (IUPAC) numbers 28, 52, 101, 138, 153, and 180) and 11 toxicologically significant congeners (IUPAC numbers 60, 74, 105, 114, 118, 123, 156, 157, 167, 170, and 189).

Sample preparation and gas chromatographic analysis of purified soil extracts were performed as described by Dvoršćak (2015). Briefly, organochlorine compounds were extracted from wet soil samples with a mixture of *n*-hexane and acetone (SupraSolv, Merck, Darmstadt, Germany) in a 1:1 volume ratio using a microwave-assisted extraction (MAE) on a MARS X system (CEM Corp., Matthews, NC, USA). Extracts were purified using Florisil Bakerbond SPE cartridges (1000 mg, 6 mL) (J.T. Baker, Avantor Performance Materials, Deventer, The Netherlands). When necessary, the eluates were additionally purified by mixing with concentrated sulfuric acid or by treatment with Cu powder and Hg for sulfur removal (Fuoco et al. 1993). The soil extracts were analyzed on two gas chromatographic columns (Rtx-5 and Rtx-CLP, Restek, Bellefonte, PA, USA) of different polarity using a Varian 3380 and a Varian CP-3800 gas chromatographs (Varian, Walnut Creek, CA, USA), both equipped with a ^{63}Ni electron

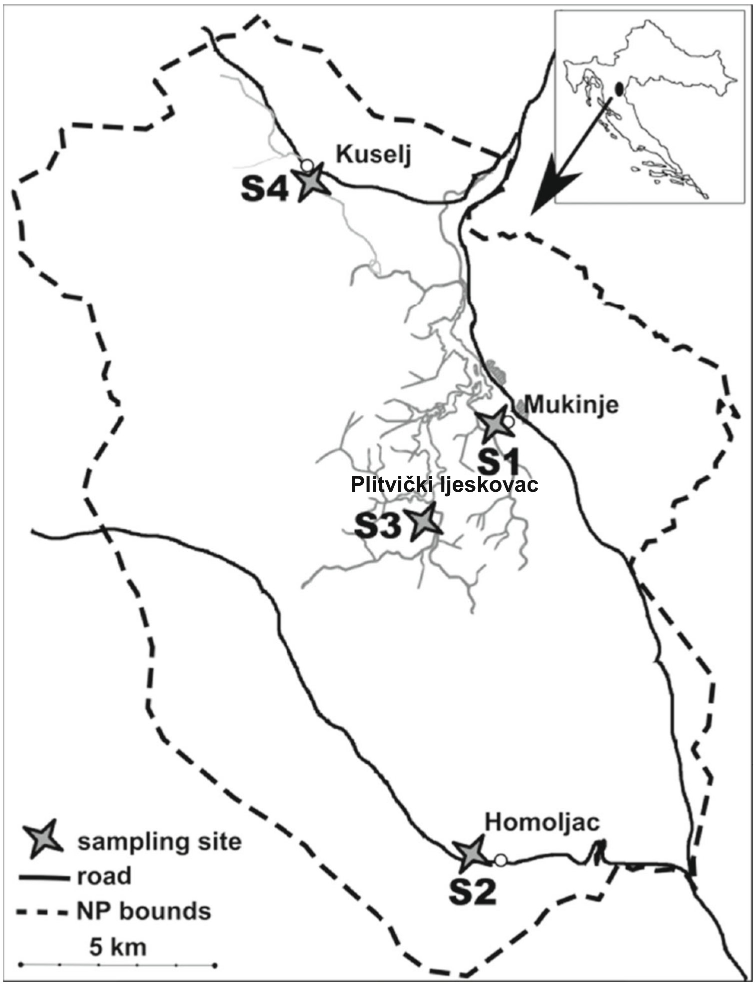

Fig. 1 Locations of the four Plitvice Lakes National Park sampling sites

capture detector. The mass fractions reported are the mean values of the results obtained on two different gas chromatographic columns. The external standard solutions prepared in *n*-hexane were used for daily calibration.

For calculating the mass fractions of organochlorine compounds on a dry mass (d.m.) basis, soil moisture content was determined immediately before extraction by weighing 2-g soil portions before and after drying at 110 °C to a constant mass.

Recovery tests were performed in soils fortified with target analytes at levels between 1 and 3 μg kg^{-1}. Recoveries of all compounds were higher than 72 % with relative standard deviation (RSD) values ranging from 7 to 24 %. Limits of detection (LOD) in soil ranged between 0.01 and 0.02 μg kg^{-1} d.m. for OCPs and between 0.02 and 0.3 μg kg^{-1} d.m. for PCB congeners.

Metals in soil

Soil samples, previously sieved to 2 mm, were milled with an agate mill. Aliquots of the obtained powder (about 100 mg) were wet-digested with a combination of hydrofluoric acid (HF, 48 %, Merck; extrapure) and nitric acid (HNO_3, 65 %, p.a., Merck; purified by quartz sub-boiling distillation using the Milestone SubPUR system) in an UltraCLAVE digestion system (Milestone Srl, Italy) using an application note for digestion of sediments (maximum temperature 240 °C, maximum pressure 160 bars, and maximum microwave power 1000 W). The digest was diluted with Milli-Q water to 50 mL. All of the samples were prepared in duplicate.

All of the analyzed elements were determined by inductively coupled plasma–mass spectrometry (ICP-MS 7500cx, Agilent Technologies, Waldbronn,

Table 1 Sampling locations and type of samples and analytes

Sampling location	Location ID code	Description	Type of sample	Frequency of sampling	Analytes
Mukinje (PLNP)	S1	Zone of settlement	Mosses	One-time sampling	ARNs
44° 52′ 24″ N			Conifer needles	One-time sampling	OCPs, PCBs, and ARNs
15° 37′ 49″ E			TDM	Monthly	TEs
			Soil	Quarterly	TEs, OCPs, and PCBs
Homoljac (PLNP)	S2	Zone of active protection of habitats (grasslands protection and revitalization)	Lichens and mosses	One-time sampling	ARNs
44° 46′ 8″ N			Conifer needles	One-time sampling	OCPs, PCBs, and ARNs
15° 37′ 26″ E			TDM	Monthly	TEs
			Soil	Quarterly	TEs, OCPs, and PCBs
Plitvički Ljeskovac (PLNP)	S3	Zone of the strictest protection	Lichens and mosses	One-time sampling	ARNs
44° 50′ 36″ N			Conifer needles	One-time sampling	OCPs, PCBs, and ARNs
15° 36′ 1″ E			TDM	Monthly	TEs
			Soil	Quarterly	TEs, OCPs, and PCBs
Kuselj (PLNP)	S4	Zone of active protection of forest ecosystems (closest to the city of Slunj)	Lichens and mosses	One-time sampling	ARNs
44° 56′ 53″ N			Conifer needles	One-time sampling	POPs and ARNs
15° 32′ 13″ E			TDM	Monthly	TEs
			Soil	Quarterly	TEs, OCPs, and PCBs
Šumbar	S5	Sampling site outside the PLNP, east of the city of Karlovac, hunting preserve	Lichens and mosses	One-time sampling	ARNs
45° 31′ 47″ N			Conifer needles	One-time sampling	OCPs, PCBs, and ARNs
15° 37′ 56″ E			TDM	Monthly	TEs
			Soil	Quarterly	TEs, OCPs, and PCBs

ARNs anthropogenic radionuclides, *OCPs* organochlorine pesticides, *PCBs* polychlorinated biphenyls, *TE*s trace elements, *PLNP* Plitvice Lakes National Park, *TDM* total deposited matter

Germany). Collision (helium gas) and reaction (hydrogen) mode were used to remove the interferences. Internal standard solution containing Ge, Rh, Tb, Lu, and Ir was used to correct for instrumental drifts and plasma fluctuations. The LODs, expressed in milligrams per kilogram of soil, ranged from 0.00193 mg kg^{-1} for U to 62.6 mg kg^{-1} for Fe (individual LOD values are given in Supplementary material Table 9). Several standard certified reference materials (NIST 2709, NRCC MESS-3, IAEA SL-1, and BCR 320-R) were analyzed as a part of the quality control. The accuracy for most of the analyzed elements in referent soil samples was within ±10 % of the certified values.

Metals in total deposited matter

TDM was determined gravimetrically on analytical balance with readability 0.01 mg (Mettler Toledo AX205, USA), while metallic contents (Pb, Cd, Ni, As, Tl, Mn, Cu, and Zn) were determined by ICP-MS. All of the elements were analyzed in collision mode with helium. Internal standard solution containing Sc, Ge, Rh, Lu, and Bi was used in every analysis. Aliquots of the soluble fraction of TDM (the fraction passing through membrane filter with 8-μm pore size) were acidified with nitric acid, while the insoluble fraction (particulate fraction retained by filter) was digested with nitric acid in an UltraCLAVE digestion system (Milestone Srl, Italy) using an application note for paper filter digestion (maximum temperature 240 °C, maximum pressure 130 bars, and maximum microwave power 1000 W). The metal content sum of these two fractions gave the total monthly flux of metals. Standard reference materials NIST 1643e (trace elements in water) and NIST 1648a (urban particulate matter) were analyzed each time with samples as part of a quality control protocol.

Recovery rates ranged within ±10 % of the certified values. The method LODs were calculated as micrograms per square metre per day from the analysis of individual field blanks as described in HRN EN 15841 and were: Pb 0.02 μg m^{-2} day^{-1}, Cd 0.004 μg m^{-2} day^{-1}, Ni 0.08 μg m^{-2} day^{-1}, As 0.007 μg m^{-2} day^{-1}, Tl 0.001 μg m^{-2} day^{-1}, Mn 0.04 μg m^{-2} day^{-1}, Cu 0.21 μg m^{-2} day^{-1}, and Zn 0.63 μg m^{-2} day^{-1}. Mercury was analyzed only in soluble fraction from aliquot of 800 μL by total decomposition, amalgamation, and atomic absorption spectrometry (TDA-AAS) in a mercury analyzer (AMA 254, LECO, USA). The instrumental LOD was 0.0125 ng mL^{-1}.

Organochlorine pesticides and PCBs in conifer needles

Conifer needles were analyzed for the following seven OCPs: HCB; α-, β-, and γ-HCH; and *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT. Analysis of PCBs comprised six indicator PCBs (IUPAC numbers 28, 52, 101, 138, 153, and 180) and 11 toxicologically relevant PCBs (IUPAC numbers 60, 74, 105, 114, 118, 123, 156, 157, 167, 170, and 189).

Freshly cut needles (10 g) were extracted with 20 mL of a mixture of *n*-hexane and acetone in a 1:1 volume ratio using the MAE system described in "Organochlorine pesticides and PCBs in soil" section. The following temperature program was used: ramping to 115 °C in 10 min, 20-min extraction at 115 °C, and 60-min cooling. Details of the extract cleanup procedure and high-resolution gas chromatography determination of organochlorine analytes have been described by Herceg Romanić and Krauthacker (2004). Recoveries of all compounds were higher than 72 % with RSD values ranging from 0 to 21 %.

Radioactivity in conifer needles, lichens, and mosses

All of the samples were collected and prepared for analysis according to standardized procedures described by the IAEA (1989). The samples were dried at 105 °C and burned to ashes at 450 °C (for gamma-ray spectrometry) and 650 °C (for ^{90}Sr determination). To determine the activity concentrations of ^{134}Cs and ^{137}Cs, gamma-ray spectrometry was used, based on a high-purity germanium coaxial photon detector system HPGe detector (ORTEC, USA), with a relative efficiency of 74.2 % at 1.33 MeV ^{60}Co and resolution (FWHM) 2.24 keV at 1.33 MeV ^{60}Co, coupled to a computerized data acquisition system (HASL-300 1997; Petrinec et al. 2011). For ^{90}Sr determination, some of the lichen and conifer needle samples were prepared as composite samples. The activity concentrations of ^{90}Sr were determined after radiochemical separation, by counting the beta emission of ^{90}Y (decay product of ^{90}Sr) using low-background, anti-coincidence, shield Geiger-Müller counter. The details of the method have been published previously (Franić et al. 2004; HASL-300 1997).

Statistical analysis

The data analysis was performed using the STATISTICA software system, version 10 (StatSoft Inc., Tulsa, USA). Data for Cd, Cu, Mn, Pb, and Tl contents in TDM; As, Hg, and Pb contents in soil; and some characteristics of the topsoils (pH, TC, and OC) were distributed normally. The remaining contaminant mass fraction data had to be transformed to achieve normality and variance homogeneity. Inverse transformation was performed on Ni and Zn contents in soil and air, and Hg content in air, while natural log transformations achieved the best approximation to normal distribution for remaining contaminants. The level of significance was set at $P<0.05$ for all analyses. For calculation of summary statistics, samples with concentrations below LOD were assigned half of the LOD for a specific compound. Simple Spearman's rank correlation (r, P) was used to explore the associations between element concentrations and soil properties and between the elements themselves. Differences between the sampling sites were explored using analysis of variance (one-way ANOVA) followed by Tukey's test.

Results and discussion

Contaminants in soil

Soil characterization

The basic statistical parameters of topsoil characteristics are given in Table 2. TC, IC, and EC were significantly higher at the station located in the zone of the strictest protection (S3) in comparison to the other PLNP stations (Supplementary material Fig. 2). Other parameters such as DOC, OM, and moisture content were similar at all of the PLNP locations. The PLNP soils (pH [H_2O]= 6.3–7.4; median 7.0), and Šumbar soils (pH [H_2O]=

6.1–7.3; median 6.7) were slightly acid to slightly alkaline, which is normal for grassland mineral soils (Alloway 2005). The OC content was higher in PLNP than in Šumbar soils, and the highest values were measured in soils collected in zones of strictest protection (S3) and of active habitat protection (S2).

Organochlorine compounds in soils

The organochlorine pesticides heptachlor, heptachlor epoxide, and α-endosulfan as well as the analyzed PCB congeners were not detected at quantifiable levels in any of the soil samples from the PLNP and Šumbar sites. The mass fraction ranges of other OCPs determined in the PLNP and Šumbar soils are presented in Table 3. The most frequently detected compound at both locations was *p,p*′-DDE identified in all but one of the soil samples. In the PLNP soils, *p,p*′-DDE (median mass fraction 0.68 μg kg^{-1} d.m.) was followed by traces of HCB (identified in more than half of the samples, median mass fraction 0.08 μg kg^{-1} d.m.), γ-HCH and α-HCH (identified in more than a third of the samples), and *p,p*′-DDT (identified in about a third of samples). The number of pesticide compounds detected in the PLNP soils ranged from 3 (HCB, α-HCH, and *p,p*′-DDE) in the zone of active protection of habitats (S2) to 10 (all compounds listed in Table 3 except for β-HCH) in the zone of active protection of forest ecosystems (S4) closest to the northeastern boundary of the PLNP and the city of Slunj. The soils from the zone of strictest protection (S3) contained four compounds (HCB, γ-HCH, *p,p*′-DDE, and *p,p*′-DDT) and those from the settlement zone (S1) contained six compounds (HCB; α-, β-, and γ-HCH; and *p,p*′-DDE and *p,p*′-DDT). *p,p*′-DDD and the cyclodiene insecticides aldrin, endrin, isodrin, and dieldrin were detected only in soils collected at the Kuselj (S4) sampling site. Although dieldrin and aldrin, the latter being readily converted in the environment to the more toxic and persistent dieldrin, have not been used for years (their use in Croatia was banned in 1972), they had a presence in all S4 soil samples. Dieldrin mass fractions were the highest measured of all organochlorine pesticides in PLNP soils (Table 3). Compared to the other PLNP soil sampling sites, the soil samples from the S4 site also contained the highest mass fractions of HCH isomers with mean values of 3.02±1.99 μg kg^{-1} for γ-HCH and 3.61±2.40 μg kg^{-1} for the sum of γ- and α-HCH. In all S4 soil samples, the α-HCH/γ-HCH ratio was significantly lower than 1 and ranged from 0.07 to 0.39. The predominance of the γ-isomer may have partly been a consequence of the locally preferred usage of a lindane formulation in the past (banned in Croatia over a decade ago) containing >90 % of γ-HCH but also of the new inputs to surface soil via atmospheric transport from remote areas.

In the Šumbar soils, only four organochlorine compounds were present in measurable mass fractions (Table 3). In addition to the most abundant *p,p*′-DDE and *p,p*′-DDT, aldrin was present in one and dieldrin in two Šumbar soils but in significantly lower mass fractions than in PLNP soils from the S4 sampling site. *p,p*′-DDE and *p,p*′-DDT mass fractions were comparable with those in the PLNP soil samples. In all of the samples containing both *p,p*′-DDE and *p,p*′-DDT compounds, the DDE/DDT ratio was higher than 1 and ranged from 1.09 to 2.15 in PLNP soils and from 1.11 to 2.41 in Šumbar soils. The prevalence of *p,p*′-DDE indicated an old input of *p,p*′-DDT, which was largely converted to *p,p*′-DDE.

The mass fractions of OCPs detected in the Plitvice and Šumbar soils were at levels of global environmental pollution by these compounds. The values determined for HCH isomers were similar to the levels reported for grassland and forest soils in the Czech Republic (Holoubek et al. 2009) and Taurus Mountain soils in Turkey (Turgut et al. 2012) and were lower than those reported for a background-protected area in Romania (Ene et al. 2012). Maximum mass fractions determined in this work for DDTs were one order of magnitude lower than the lowest values reported by Růžičková et al. (2008) for urban, rural, and background soils in Central Europe (including the Czech Republic, Croatia, Serbia, Montenegro, and Bosnia and Herzegovina). On the other hand, the maximum and mean values of dieldrin mass fractions determined in PLNP soils from the S4 sampling site were significantly higher than values reported for mountain soils (from 0.58 to 2.78 μg kg^{-1}) and background soils (from <LOD to 1.6 μg kg^{-1}) collected in the Czech Republic (Shegunova et al. 2007). Nevertheless, mass fractions of OCPs and PCBs in the PLNP and Šumbar soils were far below the soil screening values in Europe (Carlon 2007) and significantly lower than the maximum permitted value of 0.1 mg kg^{-1} defined by Croatian legislation for the sum of cyclodienes (aldrin + dieldrin + endrin), sum of DDTs, and sum of HCHs in agricultural soil (Official Gazette (OG) 2014).

Table 2 Arithmetic mean (range) of selected properties of the topsoils collected in the Plitvice Lakes National Park (S1–S4) and Šumbar (S5) during the 2011–2012 period

Sampling location	H_2O (%)	OM (%)	TC (%)	IC (%)	OC (%)	pH (H_2O)	EC (µS cm^{-1})	DTC (mg L^{-1})	DOC (mg L^{-1})
Plitvice Lakes National Park (*N*=16)									
S1	3.5	9.8	3.4	1.1	2.3	7.2	102	21.8	8.6
	(0.5–7.8)	(6.5–13.9)	(2.2–5.0)	(0.4–1.9)	(1.8–3.2)	(7.0–7.4)	(83–124)	(15.3–37.4)	(3.5–18.4)
S2	4.9	13.9	6.2	0.011	6.1	6.9	31	12.4	8.3
	(0.2–10.3)	(8.1–19.7)	(4.1–7.1)	(0.009–0.012)	(4.1–7.1)	(6.5–7.4)	(18–40)	(6.7–19.1)	(4.6–11.9)
S3	6.3	10.7	9.0	3.3	5.7	7.1	139	37.8	19.9
	(0.9–15.6)	(7.1–13.5)	(6.6–10.1)	(2.3–3.9)	(3.2–7.7)	(6.8–7.4)	(108–210)	(17.4–90.2)	(5.0–57.5)
S4	3.6	9.1	2.9	0.008	2.9	6.9	19	17.0	13.5
	(0.6–7.4)	(8.0–10.2)	(2.3–4.2)	(0.002–0.012)	(2.2–4.2)	(6.3–7.3)	(15–23)	(7.4–40.4)	(5.1–33.9)
Šumbar (*N*=8)									
S5	5.1[a]	6.1[a]	1.3	0.002	1.3	6.6	17	7.2	5.9
	(1.9–8.6)	(5.7–6.4)	(0.4–2.4)	(0.000–0.003)	(0.5–2.4)	(6.1–7.3)	(11–30)	(2.8–25.6)	(1.9–21.9)

H_2O moisture content, *OM* organic matter, *TC* total carbon, *IC* inorganic carbon, *OC* organic carbon, *EC* electric conductivity, *DTC* dissolved total carbon, *DOC* dissolved organic carbon

[a] *N*=4

Major elements and trace contaminants in soil

The mass fractions of most of the elements in the PLNP soils were similar to those recorded at Šumbar, to those reported for topsoils of mountainous Croatia (Halamić et al. 2012) and Slovenia (Andjelov 1994), and similar or higher than median values for European topsoils (Salminen 2005) (Table 4). When we compared the obtained values against selected European screening values for soil (Carlon 2007), we asserted that the

Table 3 Mass fractions of organochlorine pesticides in topsoil samples collected in 2011 and 2012 in Plitvice Lakes National Park (*N*=16) and Šumbar (*N*=8)

Pesticide	Plitvice Lakes National Park			Šumbar		
	n[a]	Mass fraction (µg kg^{-1} d.m.)		*n*[a]	Mass fraction (µg kg^{-1} d.m.)	
		Range[b]	Mean[b] (SD)[c]		Range[b]	Mean[b] (SD)[c]
HCB	9	0.06–0.26	0.13 (0.06)		<LOD[d]	
α-HCH	6	0.23–1.45	0.45 (0.50)		<LOD	
β-HCH	1	0.23			<LOD	
γ-HCH	6	0.19–4.97	2.09 (2.11)		<LOD	
p,p′-DDE	15	0.10–2.12	0.81 (0.68)	7	0.32–1.56	0.72 (0.40)
p,p′-DDD	2	0.47–0.86	0.67		<LOD	
p,p′-DDT	5	0.35–0.88	0.60 (0.29)	6	0.22–0.84	0.44 (0.27)
Aldrin	4	0.58–2.12	1.02 (0.81)	1	0.28	
Isodrin	2	0.23–0.34	0.29		<LOD	
Dieldrin	4	2.70–35.17	15.48 (14.17)	2	0.16	
Endrin	1	0.35			<LOD	

[a] *n* number of positive samples

[b] Ranges and mean values apply to positive samples

[c] Standard deviation

[d] *<LOD* below limit of detection; detection limits in soil were between 0.01 and 0.02 µg kg^{-1} d.m.

Table 4 Mass fractions of elements in Plitvice Lakes National Park (S1–S4) and Šumbar (S5) topsoils (N=20) (values in mg kg^{-1} d.m., except for Al, Ca, Fe, K, Mg, and Na expressed in %) compared to data from similar studies

Element	Soil S1–S5 (this study)			Mountainous Croatia[a]	Slovenia[b]	Europe[c]
	Min	Max	Median	Median	Arithmetic mean	Median
Ag	0.15	0.60	0.28	–	–	0.27
Al (%)	1.3	5.5	2.4	7.17	6.69	11
As	4.8	25.9	17.4	15	8.17	7.03
Be	1.1	4.4	2.7	–	2.02	1.00
Bi	0.21	0.67	0.43	–	–	0.25
Ca (%)	0.26	15.01	0.58	0.57	2.58	0.92
Cd	0.1	8.0	1.1	0.6	1.16	0.15
Co	5.6	24.9	19.7	14	27.56	7.78
Cr	33	119	96	85.9	90.33	60
Cs	2.8	5.8	3.8	–	–	3.71
Cu	12.7	56.4	22.6	24.6	27.85	13
Fe (%)	1.3	4.3	3.7	3.58	3.75	3.51
Hg	0.04	0.16	0.09	0.105	–	0.037
K (%)	0.43	1.42	0.93	1.3	1.45	1.92
Li	26	75	65	–	–	–
Mg (%)	0.17	7.37	0.53	0.76	1.35	0.77
Mn	326	1636	852	748	1044	3
Mo	0.38	4.05	2.61	–	–	0.62
Na (%)	0.07	0.86	0.45	0.543	0.52	0.8
Ni	28	119	57	52.8	52.9	18
Pb	23.8	56.1	39.0	39	38.3	22.6
Sb	0.49	5.69	1.18	–	–	0.60
Se	0.40	0.76	0.56	–	–	–
Sn	1.49	5.20	3.20	–	–	3.00[d]
Sr	53.3	82.0	66.3	–	–	89.0[d]
Tl	0.74	3.47	1.17	–	–	0.66
U	2.1	4.9	3.7	–	3.3[e]	2.03
V	49	177	135	125	118	60.4
Zn	67	476	109	104	113	52

[a] Halamić et al. (2012)

[b] Andjelov (1994)

[c] Salminen (2005)

[d] Obtained by XRF analysis

[e] Obtained by gamma spectrometry; – no available data

maximum, but not median mass fractions, of some elements (Be, Cd, Co, Cr, Cu, Mo, Ni, Sb, Tl, V, and Zn) were higher than the target (background) levels defined by the Dutch standard. This was probably due to the differences in the background mass fractions between Dutch and Croatian soils owing to the natural enrichment of some elements in the bedrocks of this area, which is at the border of mountainous and central Croatia (Halamić and Miko 2009; Halamić et al. 2012). Nevertheless, it should be stressed that the mass fractions of all heavy metals/metalloids and Se in the PLNP soil defined by these standards did not exceed intervention values for soil remediation.

Mass fractions of Se and Cs did not differ significantly between sampling locations, while total Hg mass fractions were somewhat higher in the PLNP soils (Supplementary material Fig. 3). For all other elements, significant differences were recorded between the sampling locations (Supplementary material Fig. 3). Mass fractions of Ca, Mg, Ni, Zn, Mo, and Cd in Šumbar soils were significantly lower in comparison to PLNP soils, while mass fractions of Li, V, Co, As, Mn, and Cd at sampling sites S3 (located in the zone of strictest protection) and Šumbar were similar and lower in comparison to other sampling locations. In contrast, mass fractions of Ca and Mg were the highest at the location S3, probably because of the strong association with carbon variables (TC, IC, and DTC) and EC. Mass fractions of Na, K, and, in a smaller amount, Sr decreased in the sequence S5≥S4≈S1>S2≈S3. Highest mass fractions of Be, Mn, Ni, Bi, Cu, Zn, Ag, Cd, Sb, Tl, and Pb were recorded at the S2 site, located in the zone of active habitat protection. At the same time, Sr mass fractions at the S2 site were the lowest among all of the studied locations. Mass fractions of Li, V, Cr, Fe, Co, Mo, and Sn at S1, S2, and S4 sampling sites were similar and higher in comparison to site S3. As exceptions, mass fractions of As were highest at location S4 (in the zone of active protection of forest ecosystems), while mass fractions of U were highest at S1.

There are several factors that may influence adsorption-desorption processes in soils, such as concentrations, properties, and speciation of specific trace and major elements in soil; the composition of the soil (abundance of clay minerals; total contents of Fe, Al, and Mn oxides; free $CaCO_3$; and organic matter); and soil physicochemical conditions (pH, redox status, and concentrations of other cations and anions) (Alloway 2005). We used correlation analysis to track similarities between paired data and explore the factors influencing distributions of analyzed elements in PLNP topsoils. Correlation coefficients between trace element mass fractions and soil properties (Table 5) showed that soil pH did not have a significant influence on element distribution in soils, probably because all of the samples had a similar pH, being slightly acidic to slightly alkaline. Almost all of the elements, except for Se, Sr, Cd, Cs, and Hg, were highly correlated to Fe and Al total mass fractions in topsoils. These correlation coefficients were the strongest among all of the 10 variables in Table 5. Except for Ca and Mg, all of the correlations were positive, indicating that the levels of these elements are mainly controlled by Fe and Al minerals present in soils. Most trace elements (Sb≈Zn≈Ni>Cd≈Tl>Cu≈Ag≈Bi>Pb≈Hg≈Mo≈Be>Li≈V≈Mn) were also significantly positively correlated to OM and OC, while mass fractions of Na, K, and Sr decreased with increasing OM content. Electric conductivity of the soil water suspension, as a measure of available salts in the soils, was (except for Mg and Ca) strongly negatively correlated to mass fractions of elements in soils and at the same time positively correlated with IC (r=0.793), DTC (r=0.747), Ca (r=0.743), and Mg (r=0.752). This indicates that the mass fractions of most trace elements in PLNP soils were “diluted” by carbonates.

Air contamination

Total deposited matter

The atmospheric depositions of metals as well as the levels of total deposited matter are presented in Table 6, while spatial distribution is presented in Supplementary material Fig. 4. The results show that the total mass of pollutants transferred from the atmosphere to the surface (water, soil, vegetation, etc.) was low throughout the entire period of measurement and ranged from 62 to 98 mg m^{-2} day^{-1}. The lowest values for TDM were measured in October and November of both 2011 and 2012. The highest contribution of measured metals in TDM was found for Zn; atmospheric precipitation of other measured elements decreased in the sequence Zn>Mn>Cu>Pb≈Ni>As>Cd>Hg>Tl. The atmospheric deposition of Zn measured in January, February, and December of 2012 and January of 2013 was 5 to 10 times higher than those measured during the rest of the sampling period. This can be associated with the differences in the type of precipitation during the winter months (mainly snow). Results of statistical analysis (one-way ANOVA) showed that there was no statistically significant difference in the measured levels between the sampling locations (P>0.05) (results not shown).

The obtained results were similar to those from the Šumbar sampling site. This indicates that heavy metals in the TDM came from natural sources and long-range transfer of particulate matter, on the basis of which we can conclude that human activity inside or near the PLNP had no significant impact on the spread of heavy metals through the air. Results for Pb and Cd in TDM are also comparable with those

Table 5 Correlation coefficients (*r*) of element mass fractions with properties of Plitvice Lakes National Park (S1–S4) and Šumbar (S5) topsoils (*N*=20)

Element	Soil suspension				Solid soil samples					
	pH	EC	DTC	DOC	TC	IC	OC	OM	Fe	Al
Ca	0.15	**0.74**	**0.54**	**0.39**	**0.72**	**0.82**	**0.48**	0.08	**−0.69**	**−0.74**
K	−0.12	**−0.53**	−0.30	−0.17	**−0.79**	**−0.55**	**−0.74**	**−0.39**	**0.33**	0.28
Mg	0.07	**0.75**	**0.61**	**0.48**	**0.72**	**0.77**	**0.52**	−0.02	**−0.72**	−0.83
Na	**−0.33**	**−0.65**	**−0.40**	−0.23	**−0.88**	**−0.64**	**−0.80**	**−0.56**	0.05	0.15
Ag	−0.11	**−0.43**	−0.28	−0.17	0.07	**−0.45**	**0.36**	**0.55**	**0.59**	**0.67**
As	0.08	−0.25	−0.17	−0.14	−0.17	**−0.40**	0.01	0.30	**0.94**	**0.78**
Be	−0.09	**−0.50**	**−0.38**	−0.30	−0.15	**−0.52**	0.11	**0.47**	**0.81**	**0.87**
Bi	0.02	**−0.32**	−0.28	−0.24	0.02	**−0.40**	0.27	**0.57**	**0.84**	**0.87**
Cd	0.12	0.09	−0.01	−0.05	**0.56**	0.20	**0.63**	**0.64**	0.10	0.21
Co	0.10	−0.24	−0.20	−0.19	−0.19	**−0.44**	0.01	0.25	**0.96**	**0.82**
Cr	−0.15	**−0.61**	**−0.43**	**−0.31**	**−0.54**	**−0.75**	−0.28	0.16	**0.92**	**0.91**
Cs	0.07	−0.21	−0.19	−0.16	−0.14	0.06	−0.22	0.09	0.17	0.19
Cu	0.08	−0.22	−0.23	−0.21	0.15	−0.29	**0.39**	**0.58**	**0.65**	**0.72**
Hg	0.01	0.01	0.13	0.15	**0.41**	0.15	**0.46**	**0.48**	**0.34**	0.17
Li	0.23	−0.19	−0.26	−0.29	−0.21	−0.28	−0.12	**0.37**	**0.92**	**0.83**
Mn	0.08	−0.15	−0.14	−0.14	0.06	**−0.33**	0.28	**0.39**	**0.84**	**0.74**
Mo	0.10	−0.04	0.03	0.03	0.11	−0.22	0.29	**0.40**	**0.84**	**0.64**
Ni	−0.13	−0.20	−0.13	−0.10	0.28	−0.25	**0.53**	**0.76**	**0.47**	**0.54**
Pb	0.05	−0.30	−0.26	−0.22	0.10	−0.26	0.29	**0.46**	**0.70**	**0.65**
Sb	−0.19	**−0.31**	−0.19	−0.13	0.24	−0.30	**0.51**	**0.75**	**0.50**	**0.52**
Se	−0.05	−0.06	−0.16	−0.19	0.18	0.27	0.08	**0.31**	0.25	0.28
Sn	−0.10	**−0.62**	**−0.49**	**−0.38**	**−0.41**	**−0.66**	−0.15	0.10	**0.81**	**0.86**
Sr	**−0.34**	**−0.31**	−0.13	−0.03	**−0.66**	−0.26	**−0.73**	**−0.65**	−0.17	−0.19
Tl	−0.09	**−0.36**	−0.22	−0.13	0.19	**−0.37**	**0.48**	**0.65**	**0.61**	**0.69**
U	0.00	−0.19	−0.16	−0.17	**−0.39**	**−0.44**	−0.27	0.06	**0.87**	**0.72**
V	−0.07	**−0.46**	**−0.33**	−0.26	−0.29	**−0.61**	−0.03	**0.34**	**0.97**	**0.94**
Zn	−0.09	−0.17	−0.09	−0.05	**0.34**	−0.23	0.60	**0.71**	**0.44**	**0.51**

Significant correlations ($P<0.05$) are shown in bold

EC electric conductivity, *DTC* dissolved total carbon, *DOC* dissolved organic carbon, *TC* total carbon, *IC* inorganic carbon, *OC* organic carbon, *OM* organic matter

reported for the Kornati National Park, Croatia, for the period of 1999–2004 (Čačković et al. 2009). A comparison of the atmospheric deposition found in our study with data published for other protected areas in Europe or with data from rural or background sampling sites with no influences from industrial or other urban sources is given in Table 6. The lowest values were found in northern Europe by Hovmand and Kystol (2013), who reported results for 10 years of monitoring atmospheric depositions at two rural stations in eastern Denmark. The atmospheric deposition in the PLNP was similar or lower than the ones reported by the authors in Table 6.

According to Croatian air protection legislation, one calendar year is the reference averaging time for air categorization with regard to TDM and metals in TDM (OG 2012). That is why only samples collected during 2012 were processed, and the results are presented in Supplementary material Table 10. They showed that annual values of TDM and Ni, As, Cd, Tl, Hg, and Pb

Table 6 Comparison of atmospheric deposition in the Plitvice Lakes National Park with other European protected areas and background sampling sites

	Location and sampling period	Atmospheric deposition	TDM (mg m^{-2} day^{-1})	Zn (μg m^{-2} day^{-1})	Mn (μg m^{-2} day^{-1})	Cu (μg m^{-2} day^{-1})	Pb (μg m^{-2} day^{-1})	Ni (μg m^{-2} day^{-1})	As (μg m^{-2} day^{-1})	Cd (μg m^{-2} day^{-1})	Hg (μg m^{-2} day^{-1})	Tl (μg m^{-2} day^{-1})
Present study	PLNP, 4 sampling sites, April 2011 to May 2013	TDM (bulk deposition)	84	89	15	5.56	2.40	2.84	0.66	0.25	0.050	0.025
Present study	Šumbar, April 2011 to May 2013	TDM (bulk deposition)	62	120	13	4.50	2.97	2.88	0.60	0.17	0.031	0.022
Čačković et al. (2009)	National Park Kornati, Croatia (Adriatic sea), 1999 to 2004	TDM (bulk deposition)	73	–	–	–	3.99	–	–	0.44	–	2.08
Hovmand and Kystol (2013)	Two rural stations in eastern Denmark, 2002 to 2011[a]	Bulk deposition	–	21	36	3.84	2.47	0.74	0.36	0.11	–	0.019
Avila and Rodrigo (2004)	Montseny Mountains (natural park), NE Spain, two sampling sites (LC and RP), June 1995 to June 1996, weekly samples[b]	Bulk deposition	–	65; 59	12; 9	1.64; 1.37	1.81; 1.73	–	–	2.05; 1.48	–	–
Castillo et al. (2013)	Doñana National Park, Spain, June 2008 to May 2011	Bulk deposition	74–151[c]	115[a]	24[a]	24[a]	1.92[a]	9.77[a]	0.27[a]	0.03[a]	–	–
Rossini et al. (2005)	Lagoon of Venice, Italy, two remote sampling sites (B and C), July 1998 to July 1999	Bulk deposition (modified from Bergerhoff)	31.1; 21.6	54.0; 69.3	11.7; 17.6	8.8; 10.1	5.8; 11.0	2.8; 4.5	0.61; 0.61	0.15; 0.37	0.06; 0.04	–
Azimi et al. (2003)	Morvan's Natural Park, France, May to July 2000, weekly samples[d]	TDM, wet + dry deposition	–	–	–	2.5–14	8–75	–	–	0.4–1.5	–	–

– no data, *PLNP* Plitvice Lakes National Park

[a] Reported as mg m^{-2} year^{-1}

[b] Reported as g ha^{-1} year^{-1}

[c] Reported as g m^{-2} year^{-1}; [a,b,c] recalculated to mg m^{-2} day^{-1} for TDM and μg m^{-2} day^{-1} for metal deposition

[d] Approximate values from figures

in TDM collected during 2012 were all well below the limit values.

Organochlorine compounds in conifer needles

Conifer needles are one of the best passive indicators of environmental pollution by organochlorine compounds because of their global distribution and waxy surface which accumulate lipophilic compounds (such as OCPs and PCBs) from the surrounding air. Out of the 24 analyzed POPs, one organochlorine pesticide (*p,p′*-DDD) and 10 PCB congeners (PCB-60, PCB-74, PCB-105, PCB-114, PCB-123, PCB-156, PCB-157, PCB-167, PCB-170, and PCB-189) were not detected at quantifiable levels in any conifer needle sample. The mass fraction ranges of other OCPs and PCBs determined in the PLNP and Šumbar conifer needles are presented in Table 7. Only seven compounds (HCB, ß-HCH, γ-HCH, *p,p′*-DDE, *p,p′*-DDT, PCB-138, and PCB-180) were detected in all of the samples. The mass fraction medians of these compounds in 1- and 2-year-old needle samples decreased in the following order: ß-HCH>*p,p′*-DDT>γ-HCH≈HCB≈PCB-138≈PCB-180>*p,p′*-DDE. In all of the samples, the DDE/DDT ratio, used to indicate a fresh input of *p,p′*-DDT in the environment, was lower than 1 and ranged between 0.04 and 0.17. Since the usage of *p,p′*-DDT in Croatia was banned more than 40 years ago, the predominance of *p,p′*-DDT in conifer needles is probably simply a consequence of a fresh input of *p,p′*-DDT through atmospheric transfer from remote areas.

Table 7 Mass fraction ranges of organochlorine compounds in one- and two-year-old conifer needles collected in the Plitvice Lakes National Park (S1–S4) and Šumbar (S5)

Location	Mass fraction (ng g^{-1} fresh needles)			
	One-year-old needles		Two-year-old needles	
	OCPs	PCBs	OCPs	PCBs
S1	0.04–0.74	<LOD[a]–0.11	0.07–1.25	<LOD–0.10
S2	0.05–0.93	<LOD–0.09	0.07–1.58	<LOD–0.09
S3	0.05–0.74	<LOD–0.13	0.08–1.46	<LOD–0.09
S4	0.04–0.78	<LOD–0.10	0.08–1.16	<LOD–0.10
S5	0.04–0.63	<LOD–0.07	0.06–0.67	<LOD–0.10

[a] *<LOD* below limit of detection; detection limit for OCPs and PCBs was 0.03 ng g^{-1} fresh needles

Although there have not been many data published about OCP and PCB levels in conifer needles from pristine areas in the last few years, a review of the available literature showed that the mass fractions of the analyzed OCPs and PCBs in the PLNP and Šumbar conifer needles were low, remaining at levels of global pollution. The values obtained in this investigation were similar to the levels reported for spruce needles from Austrian forests (Weiss et al. 2000) and lower than values reported for pine needles from remote mountains of the Central European Alps (Offenthaler et al. 2009), different mountains across Croatia (Herceg Romanić and Krauthacker 2008), or Croatian urban areas (Herceg Romanić and Krauthacker 2006).

Anthropogenic radionuclides

Anthropogenic radionuclides (^{134}Cs, ^{137}Cs, and ^{90}Sr) are present in the environment as a result of atmospheric nuclear weapon testing and the 1986 Chernobyl nuclear accident. ^{137}Cs and ^{90}Sr have been regarded as the fission products of major potential hazard to living beings due to the unique combination of their relatively long half-lives and their chemical and metabolic properties resembling those of potassium and calcium (Franić et al. 2004).

In the period from the 1960s onward, the highest activity concentration of ^{137}Cs deposited by fallout was recorded in 1986 (the year of the Chernobyl accident), causing peak activity concentrations in moss up to 8800 Bq kg^{-1} (Marović et al. 2008b). Since then, activity concentrations have been decreasing. However, in March 2011, a catastrophic earthquake and subsequent tsunami set into motion a series of tragic events in Japan including the severe accident at the Fukushima Daiichi Nuclear Power Plant (NPP). Radioactivity released into the air became involved into atmospheric processes and the transfer of matter in the biosphere, causing global contamination. Mosses, lichens, and conifer needles are good bioaccumulators of radionuclides, particularly caesium isotopes due to its chemical similarity to potassium (Marović et al. 2008a). The activity concentrations of ^{134}Cs ($t_{1/2}$≈2 years) and ^{137}Cs ($t_{1/2}$≈30 years) gradually decreased over the years. However, because of its longer half-life, ^{137}Cs is still present in environmental samples, especially in mosses because of its slow growth, accumulating caesium over longer periods of time (Marović et al. 2013).

Table 8 Activity concentrations of anthropogenic radionuclides (^{134}Cs, ^{137}Cs, and ^{90}Sr) in lichens, mosses, and conifer needles at different locations in Plitvice Lakes National Park (S1–S4) and Šumbar (S5)

Sample	Location	Activity concentration (Bq kg^{-1})		
		^{134}Cs	^{137}Cs	^{90}Sr
Lichens	S1[a]			
	S2	4±1	27±2	
	S3	2.9±0.9	33±1	20.7±0.2[b]
	S4	0.25±0.08	22.0±0.4	
	S5	0.9±0.2	7.4±0.4	
Moss	S1	0.41±0.08	14.7±0.2	
	S2	0.5±0.1	31.3±0.4	12.8±0.3
	S3	0.9±0.2	29.0±0.5	17.2±0.3
	S4	0.24±0.08	321±1	17.0±0.3
	S5	0.4±0.1	36.1±0.4	
Conifer needles	S1	0.05±0.02	1.05±0.05	0.3±0.3[c]
	S2	0.078±0.002	0.74±0.04	
	S3	0.07±0.02	2.95±0.06	
	S4	0.04±0.02	2.88±0.06	
	S5	0.06±0.02	0.14±0.02	

[a] Samples were not available; [b] Composite sample for S2, S3 and S4; [c] Composite sample for S1, S2, S3 and S4

The activity concentrations of ^{134}Cs, ^{137}Cs, and ^{90}Sr in lichens, mosses, and conifer needles from the PLNP collected in April 2011 are shown in Table 8. The activity concentrations of ^{137}Cs in April 2011 ranged from 0.74 Bq kg^{-1} in conifer needles to 321 Bq kg^{-1} in mosses (Table 8). However, we performed an additional sampling of moss in October 2011 at S2, where we recorded significantly higher activity concentrations of ^{137}Cs (1720±1 Bq kg^{-1}) in comparison to April 2011. This was probably the result of radioactive fallout from Fukushima in March 2011. Although ^{137}Cs is still present in the environment from the Chernobyl accident, the half-life of ^{134}Cs is relatively short and the ^{134}Cs from Chernobyl mostly decayed. The fact that the activity concentrations of ^{134}Cs were all above the detection limits and that they could even be measured indicated its recent input into the environment, probably from Fukushima. Regardless of the "new" ^{134}Cs, these values are much lower compared to the post-Chernobyl ones (Marović et al. 2013).

In all of the bioindicator samples, the activity concentrations of ^{90}Sr ranged from 0.3 to 20.7 Bq kg^{-1}, which is within standard range of expected background levels.

Conclusions

We performed a study of the distribution of organic contaminants, major and trace elements, and anthropogenic radionuclides in soil, air, and biological indicators of air contamination (conifer needles, mosses, and lichens), in order to evaluate ecological status and estimate baseline levels of persistent organochlorine pollutants, metals, and radionuclides in the terrestrial environment of the PLNP.

In general, all of the analyzed trace elements in PLNP soils predominantly originated from natural sources. Total Fe and Al minerals, followed by soil organic matter, and organic carbon contents affected the mass fractions of most trace elements in topsoils. Similarly, the annual values of TDM and trace elements in the TDM were significantly below the national limit values for air. Their annual and spatial distributions indicated that the heavy metals in the TDM came from natural sources and long-range transfer of particulate matter.

Overall, PCB and OCP levels found in soil and conifer needles in this study correspond to known global pollution by persistent organic pollutants and represent the lower end of the concentration ranges reported.

Anthropogenic radionuclide analyses in the bioindicators showed a low but measurable presence of ^{134}Cs which indicates its origin from the Fukushima NPP accident in March 2011.

In general, the current level of anthropogenic impact in the terrestrial environment of the PLNP is rather small, as evidenced from our results. The data presented here suggest that human activity inside or near national park had no significant impact on the contaminant spread through the air or on their content in topsoils. The results from this study will serve as a proxy for the calculation and/or estimation of future environmental changes in the PLNP ecosystem.

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