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THE IODINE CONTENT IN AREAS WITH ENHANCED LANDSCAPE MANAGEMENT IN THE CZECH REPUBLIC*

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ABSTRACT

Iodine is an essential trace element for animals. The major sources of iodine for animals are contained in feed and water, in which the iodine content depends on its amount in the given environment. The aim of this study was to analyse and evaluate the iodine content in soil, soil water, grass mass, and also to assess the effect of grassland exploitation on the iodine content in the Šumava and Jeseníky Protected Landscape Areas (PLAs) in the Czech Republic. The soil type in both PLAs was Modal Cambisol. Soil samples were collected from two different depths (up to 15 cm, 16-30 cm). Soil water samples were extracted from a depth of 40 cm and grass mass samples were collected from an area of 1 x 1 m. The areas according to exploitation intensity were as follows: EA1 – a meadow mowed twice a year, EA2 – a meadow mowed once a year, EA3 – a meadow was not mowed for 5 years. Iodine in soil and grass mass was determined by a spectrometric method (the Sandell-Kolthoff reaction). Iodine in water was measured by the ICP-MS method. The average iodine content in the Jeseníky PLA was $0.91 \pm 0.18 \text{ mg kg}^{-1}$ in soil, $1.16 \pm 0.79 \text{ } \mu\text{g dm}^{-3}$ in soil water and $0.16 \pm 0.07 \text{ mg kg}^{-1}$ of 100% DM of grass and in the Šumava PLA was $4.69 \pm 0.70 \text{ mg kg}^{-1}$ in soil, $3.12 \pm 0.91 \text{ } \mu\text{g dm}^{-3}$ in soil water and $0.31 \pm 0.13 \text{ mg kg}^{-1}$ of 100% DM of grass. A significantly ($p < 0.01$) higher iodine content in soil ($5.14 \pm 0.55 \text{ mg kg}^{-1}$) was recorded in the most exploited EA1 area. The iodine content in soil water was significantly higher ($p < 0.05$) in the EA2 area. The iodine content in grass mass was not affected by the exploitation of grassland. Significant differences in the iodine content extracted from the two soil depths mentioned above were not observed. The results demonstrated a low iodine content in both PLAs in the Czech Republic (especially in the PLA Jeseníky) and demonstrate complex relationships among individual components of the soil ecosystem affecting iodine bioavailability. The findings also indicated that exploitation may be another factor that can influence the iodine content in soil.

Keywords: iodine, soil, soil water, grass, protected landscape areas, exploitation.

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INTRODUCTION

Iodine (I) is an essential trace element for humans and animals because it is crucial for the synthesis of the thyroid hormones regulating many metabolic processes in the body (NUDDA et al. 2009). Iodine deficiency has multiple adverse effects in humans and animals (ZIMMERMANN 2009). The major I source for both humans and animals is contained in food (feed) and water, in which the I content depends on its amount in the given environment. The optimum biological indicator of an insufficient I concentration in soil and water are ruminants (cattle, sheep, goats) which consume large quantities of roughages and water originating from the area where they are living (HERZIG et al. 2003). Soil is the main I reservoir in the environment, having approximately 99.9% of the total I content of the ecosystem (ROULIER et al. 2018). Iodine retention in soils (sorption) depends on the types of soil and the chemical form of iodine. Iodide sorption is dominant in mineral soils with low levels of organic carbon. Soils rich in organic carbon and acid soils have more beneficial effect on iodate sorption (DUBORSKÁ et al. 2019). Humic acids in soil increase iodide and iodate sorption (ZOU et al. 2018). Higher I sorption in the soil component reduces its transition to the water phase, which affects plant root uptake of iodine or its leaching into surface water or groundwater (FUGE, JOHNSON 2015)

The vegetation cover growing on soils with a higher I content (alluvial soils in river basins, sedimentary soils) is also affected by its higher content. Plants growing on soils with the granite bedrock show the lowest iodine concentration (UNDERWOOD, SUTTLE 2001). Podzolic soils and sandy soils contain less iodine than chernozemic soils. Intensively cultivated soils and soils rich in humus contain more iodine (BOWLEY et al. 2019). Iodine concentration in soils worldwide ranges from 0.10 to 100.0 mg kg⁻¹ (FUGE, JOHNSON 2015). The average I content in the soils of Europe is 5.56 mg kg⁻¹ (SMYTH, JOHNSON 2011). A relatively higher median iodine concentration was recorded in the soils of Northern Ireland – 10.6 mg kg⁻¹ (BOWLEY et al. 2019). In the United Kingdom and Norway, the iodine content in soil ranged from 4.2 to 14.7 mg kg⁻¹, while the value of 9.3 mg kg⁻¹ was measured in a deciduous forest in France (SMYTH, JOHNSON 2011, ROULIER et al. 2018).

The territory of the Czech Republic is formed by three geological groups: the crystalline complex (formed by granite, gneiss, granodiorite) with almost no I content; volcanic rocks in western Bohemia with a higher I content, and Quaternary sediments in southern Moravia comprising Pannonian clay minerals with a relatively higher I content. None of the rock types forming the territory of the Czech Republic contains enough I which would ensure its sufficient entry into the food chain. Areas with the highest I deficiency in the environment, including soil, feature southern and south western Bohemia, south western Moravia, the Jeseníky Mountains in their northern part belonging to Moravia (HERZIG et al. 2003). A low I content in surface

waters in Protected Landscape Areas (PLA) of the Šumava Mountains ($2.58 \pm 0.33 \mu\text{g dm}^{-3}$) and the Jeseníky Mountains ($1.55 \pm 0.33 \mu\text{g dm}^{-3}$) was confirmed by ŠEDA et al. (2017).

Organic and inorganic I compounds emitted from the ocean surface (e.g. methyl iodide or ethyl iodide) form the main sources of I in the atmosphere (SAIZ- LOPEZ et al. 2016). The main anthropogenic sources of iodine in the atmosphere are represented by the burning of fossil fuels. Iodine from the atmosphere is deposited in soil by aerosols and precipitation (BAKER et al. 2000). ŠEDA et al. (2012) observed the augmented I concentration in precipitation in the Czech Republic in response to the Eyjafjallajökull volcanic eruption in Iceland in 2010. Due to the augmented I concentration from fallout from the eruption cloud, the I concentration in water precipitation was up to 6 times higher (the original I concentration of $1.78 \pm 0.04 \mu\text{g dm}^{-3}$ increased up to $6.68 \pm 0.16 \mu\text{g dm}^{-3}$).

The principal objective of this study was to determine and assess I concentrations in soils of permanent grassland, soil water, grass matter, and also to assess the effect of grassland exploitation on the iodine content in PLAs in the Czech Republic (Šumava, Jeseníky).

MATERIAL AND METHODS

Samples collection and their processing

Soil, soil water and grass mass samples were collected from the Šumava PLA in the Arnoštov location (828 m above sea level) and from the Jeseníky PLA from the Rapotín location (345m above sea level) – Figure 1. Soil and grass mass samples were collected in the Arnoštov location (Šumava PLA) twice a year (June and September) between 2011 and 2012 and in 2018. These samples came from 3 permanent grassland experiment areas with different levels of exploitation: a meadow mowed twice a year (EA1), a meadow mowed once a year (EA2) and a meadow which was not mowed for 5 years (EA3). The amount of humus (%) and pH in the two surface horizons in the experimental areas in the Šumava PLA are described in Table 1.

In the Rapotín location (Jeseníky PLA), soil, grass mass and soil water samples were collected from six permanent grassland areas of the same exploitation (meadows) also twice a year (June, September) between 2011 and 2012.

Soil samples weighing 300 g were collected at both locations from 4 designated areas (1 x 1 m) and from two depth profiles at each area (up to 15 cm and from 16 to 30 cm). These soil samples were pre-dried at room temperature (for 1 week) and then finely sieved. A soil batch weighing 0.025 - 0.030 g was used for the actual analysis. Grass mass samples (100 - 500 g) were collected after mowing the area of 1 x 1 m. The grass samples were dried

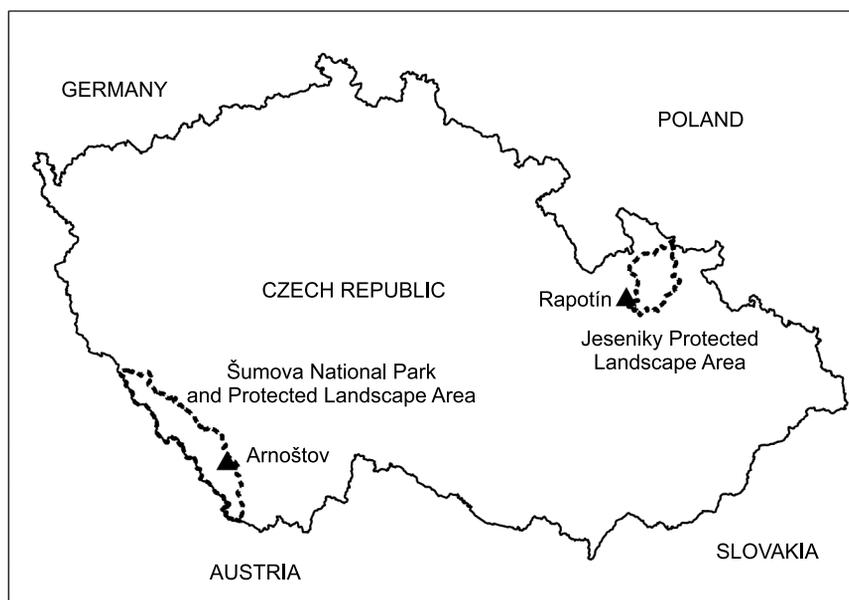


Fig. 1. Location of sampling points PLA Šumava (Arnoštov) and PLA Jeseníky (Rapotín)

Table 1

Amount of humus (%) and pH in two surface horizons in the experimental areas in PLA Šumava

Horizons (m)	Humus (%)			pH in the water soil solution		
	experimental area			experimental area		
	EA1	EA2	EA3	EA1	EA2	EA3
0.00–0.20	8.62	6.03	5.17	5.26	5.80	5.30
0.20–0.50	5.17	5.17	4.31	4.80	5.70	5.40

EA1 – area with a meadow mowed twice a year, EA2 – area with a meadow mowed once a year, EA3 – area with a meadow which was not mowed for 5 years

at 60°C and homogenized prior to analysis. A sample weighing 0.4 - 0.5 g was used for the actual analysis. Soil water samples were collected using lysimeters from a depth of 40 cm.

Iodine in soil and grass mass was determined on the basis of alkaline ashing using the Sandell-Kolthoff spectrometric method. The principle behind determination is the reduction of Ce^{4+} to Ce^{3+} in the presence of As^{3+} due to the catalytic effect of I. Dry mineralisation takes place in the alkaline environment at 600°C (KURSA et al. 2005). The above method was used to determine total I (inorganically and organically bound iodine to proteins). Iodine in soil water was determined by using the ICP-MS method (ŠEDA et al. 2011). Certified samples of soil, hay and water were processed as control samples at the same time as the tested samples.

Statistical analysis

Statistical data processing including the average values (means), standard deviations (SD), minimum and maximum values, median and statistical significance was determined by the ANOVA - Tukey test. The data was evaluated by Statistica 12.0. (StatSoft, Inc.)

RESULTS AND DISCUSSION

The most abundant soil types in the Czech Republic are Cambisols of an average quality (JANKŮ et al. 2016). This type of soil is used intensively for mixed farming, grazing and as forest land (PETRÁŠOVÁ et al. 2009). In both monitored PLAs, Cambisol soil type, Modal Cambisol subtype, was found. The average I content in the Šumava PLA (Arnoštov location) and the PLA Jeseníky (Rapotín location) in grassland soils (permanent grasslands) is shown in Table 2. The I content in soil in the Šumava PLA and the Jeseníky PLA was lower than the European average (SMYTH, JOHNSON 2011). The average value ($4.69 \pm 0.18 \text{ mg kg}^{-1}$) in the Šumava PLA slightly exceeded compared to the average iodine content in Austria (GERZABEK et al. 1999). Compared to the Šumava PLA, the I content recorded in the Jeseníky PLA showed a significantly lower I content ($P < 0.01$), where an average value did not exceed 1.00 mg kg^{-1} and the maximum level reached only 1.30 mg kg^{-1} (Table 2). Furthermore, a significantly lower I content in soil water and grass mass was recorded in this area (Table 3). Based on our previous study

Table 2

Average iodine content (mg kg^{-1} in dry soil) in soil of permanent grasslands in PLA Šumava and PLA Jeseníky in the years 2011-2012

Location	<i>n</i>		Mean	SD	Maximum	Minimum
	area	samples				
PLA Jeseníky	6	192	0.91 ^a	0.18	1.30	0.64
PLA Šumava	3	96	4.69 ^b	0.70	5.71	3.27

^{a,b} $p < 0.01$; *n* – number, PLA – Protected Landscape Areas, SD – standard deviation

Table 3

Average iodine content in soil water and grassland in PLA Šumava and PLA Jeseníky in 2011-2012

Location	Iodine content in soil water ($\mu\text{g dm}^{-3}$)			Iodine content in grassland (mg kg^{-1} 100% DM)		
	<i>n</i>	mean	SD	<i>n</i>	mean	SD
PLA Jeseníky	12	1.16 ^a	0.79	30	0.16 ^c	0.07
PLA Šumava	24	3.12 ^b	0.91	24	0.31 ^d	0.13

^{a,b, c,d} $p < 0.01$; *n* – number of samples, SD – standard deviation

(ŠEDA et al. 2017), these results indicate that the I content in the PLA Jeseníky cannot be a sufficient natural I source in the feed chain (HERZIG et al. 2003) because the amount of I in feeds primarily depends on its quantity in soil (KAPIL 2007, KOROBOVA 2014, KRZEPILKO et al. 2015, CAKMAK et al. 2017). Moreover, our results show that Modal Cambisols contain a variable amount of iodine, depending on a specific area.

In the PLA Šumava, we further focused on the effect of different permanent grassland exploitation on the I content in soil, soil water and grass mass (Tables 4 and 5). The study was conducted in three different areas.

Table 4
Average iodine content (mg kg⁻¹ in dry soil) in soil of permanent grasslands in PLA Šumava by exploitation

Location	2011-2012			2018		
	<i>n</i>	mean	SD	<i>n</i>	mean	SD
EA1	32	5.14 ^a	0.55	16	5.26 ^d	0.63
EA2	32	4.70 ^b	0.48	16	4.87	0.76
EA3	32	4.08 ^c	0.41	16	4.41 ^e	1.01

^{a,b,b,c,a,c,d,e} $p < 0.01$; *n* – number of samples, SD – standard deviation, EA1 – area with a meadow mowed twice a year, EA2 – area with a meadow mowed a once a year, EA3 – area with a meadow which was not mowed for 5 years

Table 5
Iodine content in soil water and grassland in PLA Šumava in 2011-2012

Location	Iodine content in soil water (µg dm ⁻³)			Iodine content in grass mass (mg kg ⁻¹ 100% dry matter)		
	<i>n</i>	mean	SD	<i>n</i>	mean	SD
EA1	8	2.69 ^a	1.11	8	0.33	0.13
EA2	8	4.38 ^b	1.62	8	0.28	0.13
EA3	8	2.25 ^c	1.29	8	0.33	0.12

^{a,b,b,c} $p < 0.05$; Explanations under Tables 1 and 2

The EA1 area featured the most exploited location, i.e. a meadow mowed twice a year. In the EA2 area, a meadow was mowed once a year, and in the EA3 area, a meadow was not mowed for 5 years. Table 4 clearly indicates that the I content was statistically significantly higher (5.14±0.55 mg kg⁻¹) in the EA1 area in the period between 2011 and 2012. Compared to EA1, the I content was lower by 8.56% in EA2 and by 20.62% in EA3. Samples were also analysed in the monitored areas in 2018. The analysis showed that the I content slightly changed (by 2.28% in EA1, by 3.62% in EA2 and by 7.48% in EA3) without statistically significant differences. In 2018, the difference that was statistically significant in comparison to the years 2011 and 2012 was found only between the EA1 area and the EA3 area (Table 4).

The iodine content in soil water and in grass mass is reported in Table 5. Contrary to the I content in soil (Table 4), samples collected from soil water demonstrated a statistically highly significant I content ($4.38 \pm 1.62 \text{ mg kg}^{-1}$) in the EA2 area.

The differences observed in the I content in the experimental areas can be related to different levels of I retention in soil, levels of its leaching, and eventually the or water or gas phase transition (FUGE, JOHNSON 2015, MEDRANO-MACÍAS et al. 2016). Soil I retention depends on many factors (quality and quantity of organic soil mass, pH values of the soil environment and microbial activity) (SHEPPARD et al. 1995, MURAMATSU et al. 2004, DUBORSKÁ et al. 2017, SODERLUND et al. 2017, KÖHLER et al. 2019). BOWLEY et al. (2019) recorded a significant positive correlation ($r=0.64$) between organic carbon and I concentration in soil. JENSEN et al. (2019) notes that soil organic carbon increased I retention in soil. In our study, we also recorded a higher soil I content in the EA1 area with a higher amount of humus, and a lower I content in the EA3 area with a lower amount of humus (Table 1).

According to DUBORSKÁ et al. (2016), the I fixation capacity of organic matter increases with a decreasing pH value. BOWLEY et al. (2019) reported negative correlation between soil pH and I concentration in soil ($r=-0.58$). In the experimental areas (EA1, EA2 and EA3), pH water solution values ranged from 4.80 to 5.70 (Table 1). The lowest pH was determined in the EA1 area, followed by the EA3 and EA2 areas. The pH soil differences may be related to the above mentioned higher I content in soil water in the EA2 area. On the other hand, the lowest (statistically non-significant) I content in grass mass ($0.28 \pm 0.13 \text{ mg kg}^{-1}$ of 100% dry matter) was measured in this area (Table 5). The I content in grass mass from the EA1 and EA3 areas were higher by 18% than from the EA2 area (Table 5). The low I content in grass mass and the higher I content in soil water in the EA2 are indicated the low I utilization by plants and higher I leaching. BOWLEY et al. (2017) and SÖDERLUND et al. (2017) reported a negative relationship between soil pH and the I content in pasture. Our results are not in clear accordance with these authors.

SHETAYA et al. (2012) recorded that the I content in soil changes with depth. ROULIER et al. (2018) in their study observed an increasing I content with increasing depth. The authors explained the vertical distribution of iodine with enrichment of iodine in the deepest soil layers by bedrock weathering and a lower I content in a surface layer by volatilization from the topsoil. The I volatilization from the topsoil is also described by ALLARD et al. (2010). Moreover, the iodine content in the soil profile is affected by rainfall (SHETAYA et al. 2012). This study analysing the Šumava PLA did not demonstrate any statically significant difference in an average I content (composite sample EA1, EA2, EA3) based on the samples taken at a depth of 0-15 cm ($4.69 \pm 0.55 \text{ mg kg}^{-1}$) and of 16-30 cm ($4.72 \pm 0.57 \text{ mg kg}^{-1}$). Figure 2 indicates the I content of two different soil depths in the experimental areas. Based on this result, it is evident that statistically significant differences in the

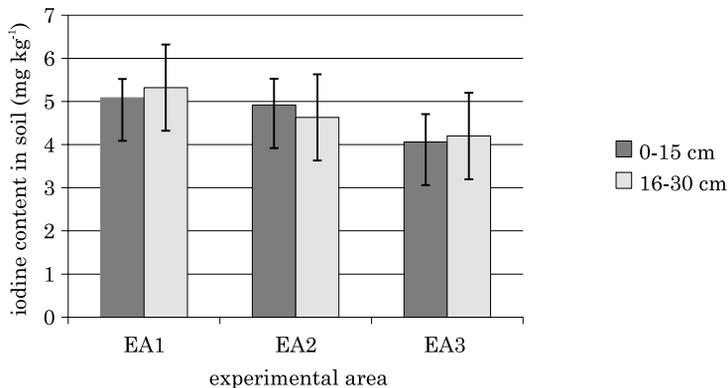


Fig. 2. Iodine content in two layers of soil in experimental locations in PLA Šumava in 2011-2012: EA1 – area with a meadow mowed twice a year, EA2 – area with a meadow mowed a once a year, EA3 – area with a meadow which was not mowed for 5 years

I content between two depths were not found in any experimental area. Except for the EA2 area (a meadow mowed once a year), the I content was higher in those samples collected at a depth of 16-30 cm (EA1, EA3). The differences in the I content according to depth ranged from 3.45 to 6.26%. The highest difference was discovered in the EA2 area.

The results of the I content in soil, soil water and grassland demonstrate complex relationships among individual components of the soil ecosystem and the effect of the exploitation of grassland impacting bioavailability of I. In addition to the absolute I deficiency in soils, its permeability to deeper soil horizons or excessively firm fixation on humus substances negatively contributes to its entry into the food chain of ruminants.

CONCLUSIONS

The results of this study confirm a low I content in soil and grass in the selected PLAs in the Czech Republic. A higher risk of I deficiency can be expected in the PLA Jeseníky. Moreover, our results showed that exploitation may be another factor which can affect the I content in soil. However, this fact shall be supported by other studies.

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