Journal of Elementology ISSN 1644-2296

Šeda M., Konečný R., Fiala K., Hladký J., Švehla J., Trávníček J. 2017. *Iodine content in running surface waters in areas with more intensive landscape management in the Czech Republic*. J. Elem., 22(1): 295-304. DOI: 10.5601/jelem.2015.20.4.1044

**ORIGINAL PAPER**

# IODINE CONTENT IN RUNNING SURFACE WATERS IN AREAS WITH MORE INTENSIVE LANDSCAPE MANAGEMENT IN THE CZECH REPUBLIC*

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## Abstract

The aim of this study has been to make an analysis and evaluation of iodine content in running surface waters in protected landscape areas (PLA) in the Czech Republic. Water samples were taken in 2009-2011 in Jeseníky PLA (Rapotín locality) and in Šumava PLA (Arnoštov and Lipno localities), and in 2009-2010 in the upper course of the Blanice River and its tributaries in and outside of Šumava PLA. Iodine was determined by the ICP-MS method. The average iodine content was 1.55±0.33 μg dm$^{-3}$ ($n$ = 41) in Jeseníky PLA and 2.58±0.33 μg dm$^{-3}$ ($n$ = 24) and 2.29±0.84 μg dm$^{-3}$ ($n$ = 30) in Šumava PLA. The average iodine content in water samples of the Blanice River and its tributaries localized in Šumava PLA was 2.27±0.65 and 2.38±0.66 μg dm$^{-3}$ and outside of Šumava PLA it equalled 2.90±0.68 and 3.26±1.51 μg dm$^{-3}$. The lowest concentration of 1.43 μg dm$^{-3}$ was found out in a sample from the Spálenecký brook (Šumava PLA), and the highest one, 7.63 μg dm$^{-3}$, was determined in a sample from the Živný brook, which flows below the town Prachatice. Higher concentrations were measured in the summer season: 3.05±0.35 (Blanice) and 3.63±1.24 μg dm$^{-3}$ (tributaries), while lower ones were determined in the spring season: 1.48±0.30 (Blanice) and 2.37±1.12 μg dm$^{-3}$ (tributaries). The results confirm the low iodine content in the environment of Jeseníky and Šumava Mts., and the self-purification capacity of the Blanice River even when it is stressed with anthropogenic iodine.

**Keywords:** iodine, water, protected landscape areas, ICP-MS.

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* This study was supported by the project of the Grant Agency of the University of South Bohemia in České Budějovice (GAJU 002/2016/Z; GAJU 152/2014/Z).

# INTRODUCTION

Iodine is an essential element for humans, and its most abundant reservoir is seawater, marine sediments and potentially magma (Muramatsu et al. 2004). Iodine is released from seas and oceans as elementary $I_2$ as well as alkyl iodides which are produced by biochemical and photochemical processes. Transport by air currents from seas towards inland and subsequent deposition on land or the leaching effects of rainfall are very important sources of iodine for inland areas. This element enters groundwater mainly through rainfall or is released from surrounding soils (Bassford 1999, Neal 2007, Šeda et al. 2011). The binding capacity of soils for iodine is varied, namely it is higher in ferruginous and clay soils than in sandy soils (Mackowiak et al. 2005). The iodine bond in soil is relatively strong, its water extractability is usually less than 10% (Fuge 2007). Alkaline pH of soils and a high content of calcium may decrease the biological availability of iodine, and hence its uptake by plants (Oliver 1997).

The Earth's hydrosphere, which contains huge amounts of iodine, dominates in the biogeochemical cycling of iodine on the Earth. Iodides are a dominant form of occurrence in waters, while other forms of occurrence are iodates and less frequent organically bound iodine, elementary iodine, undissociated hypoiodous acid and other compounds. The iodide content in surface waters of the Czech Republic does not usually exceed 5 µg $dm^{-3}$. The highest content of natural iodine in the Czech Republic is present in mineral waters, oil waters from the Hodonín district and spa waters in Karviná-Darkov (Šeda et al. 2011). The amount of iodine is typically lower in rain and snow than in surface waters although a short-time increase in iodine content in precipitation can be observed during volcanic activity (Šeda et al. 2012). Anthropogenic sources and the farm animal sector also contribute to the iodine cycling: disinfection, medicines, mineral supplements, excrements, industrial and chemical production and burning of fossil fuels (Backer, Hollowell 2000, Fuge 2007).

An average iodine concentration in uncontaminated surface waters is generally in the order of micrograms per litre (Muramatsu et al. 2004, Tagami, Uchida 2006, Ren et al. 2008). The iodine content in standing surface waters is usually higher compared to running waters in the same area (Chandra et al. 1999). The iodine content exceeding 150 µg $dm^{-3}$ was found out for example in well waters of the Yellow River floodplain areas (Guo et al. 2005). Phytoplankton activity, oxidation and reduction conditions of the water environment belong to factors significantly influencing the iodine content in water (Shulyarenko 2004).

The objective of the present paper was to determine and evaluate iodine concentrations in surface waters in protected landscape areas (PLA) of the Czech Republic (Šumava, Jeseníky) and in the upper course of the Blanice River, including some of its major tributaries (Šumava PLA).

# MATERIAL AND METHODS

## Collection of samples and their processing

In 2009-2011, water samples were taken from running surface waters at one site in the Jeseníky Protected Landscape Area (Jeseníky PLA): Rapotín locality (the brooks called Pod salaší and U Annova, GPS 49°58′58.31″N, 17°00′39.10″E) and at two sites in the Šumava Protected Landscape Area (Šumava PLA): Arnoštov locality (the brook called Puchéřský, GPS 48°53′43.76″N, 13°59′31.67″E) and Lipno locality (the brooks called Bukovský, Horský and Mlýnský, GPS 48°38′26″N, 14°6′11″E). In total, 24 water samples were collected at Arnoštov, 30 water samples at Lipno and 41 water samples at Rapotín; all samples were taken periodically 4-6 times a year. In 2009-2010, samples were taken from 8 upstream sampling points of the Blanice River at a stream length of 38 km, from the sampling point above the municipality Arnoštov (GPS 48°53′41″N, 13°59′37″E) to the river segment above the Živný brook (GPS 48°57′29.32″E) – Figure 1. The first three sam-

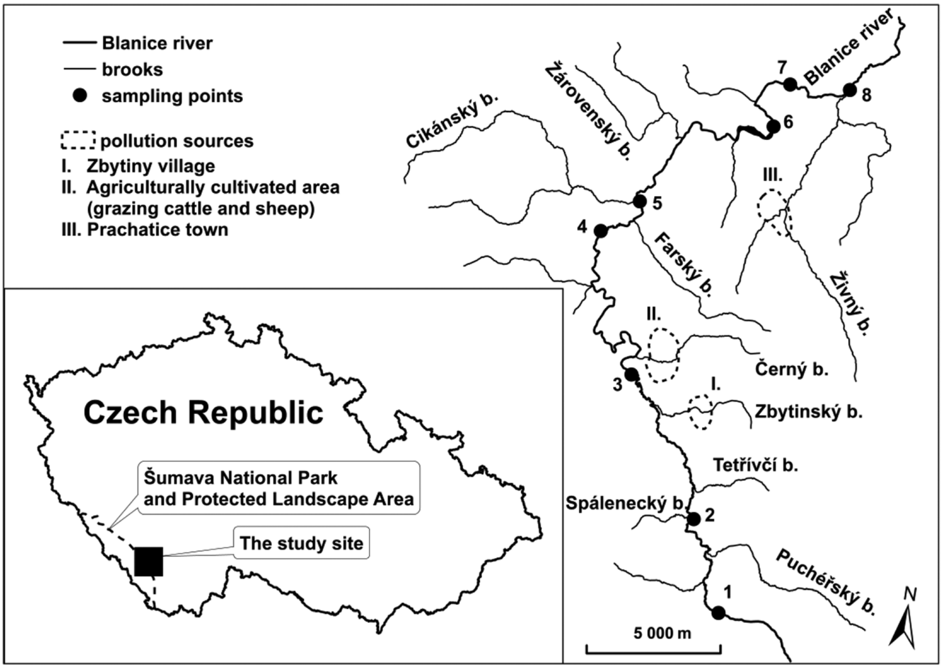


Fig. 1. Sampling sites on the Blanice River and its tributaries: 1 – above the village Arnoštov (river km 90.1), 2 – before the Tetřívčí brook (85.8), 3 – near the village Blažejovice (77.2), 4 – near the village Záblatí (66.6), 5 – near the Zábrdský mill (64.0), 6 – below the Husinec reservoir (55.8), 7 – near the village Těšovice (52.7), 8 – below the Živný brook (50.0)

pling points were localized in Šumava PLA. Water samples were also taken from 11 sampling points on 8 tributaries to the Blanice River. The tributaries Puchéřský brook, Spálenecký brook and Tetřívčí brook belong to the

Šumava PLA and to the National Natural Monument Blanice, where juvenile forms of the freshwater pearl mussel (*Margaritifera margaritifera*) occur. In total, on four dates (November 2009, March 2010, April 2010 and June 2010), 76 water samples were collected from 19 sampling points on the Blanice River and its tributaries.

At each sampling point, 4 individual samples were collected manually from the superficial layer in the middle of water stream to gather a composite sample. 200 ml glass or polyethylene bottles were used, previously treated with nitric acid and deionised water. All composite samples were filtered in a laboratory under reduced pressure through a membrane filter (Pragopor 6) with the pore size 0.45 µm, and then they were kept at a temperature of 4° C in the absence of light until analysis.

**Instrument**

An ICP-MS instrument, PQ-ExCell model, manufactured by VG-Elemental, UK, was used for analysis. The method of external calibration was used in the range of 0 - 50 µg $dm^{-3}$ ($n$ = 4). The repeatedly measured calibration standard included among particular samples provided values with errors in the range within 10%. Before each analysis, the instrument was always rinsed with 0.5% solution of TMAH (tetramethylammonium hydroxide) until the signal on $^{127}I$ dropped below 10% of the value of the lowest calibration standard. In the course of measurements, the internal standard of antimony $^{121}Sb$ solution at a concentration of 100 µg $dm^{-3}$, ensuring the signal stability, was pumped with a peristaltic pump.

**Chemicals**

Demineralized water from a Milli-Q Element instrument (Millipore, USA) with the parameter $R$ > 18.2 MΩ was used. Antimony (CertiPur solution, solution of $Sb_2O_3$ in 7% HCl) at a concentration of 1 000 mg $dm^{-3}$ (Merck, Germany) was applied as an internal standard. Tetramethylammonium hydroxide (TMAH), 10% solution to dilute (Merck, Germany), was employed to rinse the instrument. The calibration series was prepared from the standard of solid potassium iodate, CertiPur standard product for volumetric analysis and iodometry (Merck, Germany), and from potassium iodide solution at a concentration of 1 000 mg $dm^{-3}$ as Acculon reference standard (AccuStandard Ltd., USA).

**Statistical analysis**

The data were processed in the Statistica 7.0. programme (StatSoft, Inc.) and ANOVA test was used.

## RESULTS AND DISCUSSION

Table 1 shows the iodine content in running surface waters in Jeseníky PLA and Šumava PLA. The average iodine content in water did not exceed 3 μg $dm^{-3}$ in any of the studied localities in 2009-2011, and the highest indi-

Table 1

Iodine content in running surface water in Jeseníky Protected Landscape Area (PLA) (Rapotín) and Šumava PLA (Arnoštov, Lipno)

| Locality | Year | *n* | Iodine content (μg $dm^{-3}$) | | | | |
|---|---|---|---|---|---|---|---|
| | | | mean | SD | minimum | maximum | median |
| Rapotín | 2009 | 8 | $1.68^{a,b}$ | 0.54 | 1.07 | 2.99 | 1.60 |
| Rapotín | 2010 | 20 | $1.20^{a,c}$ | 0.30 | 0.67 | 1.72 | 1.18 |
| Rapotín | 2011 | 13 | $2.00^{b,c}$ | 0.32 | 1.36 | 2.54 | 1.96 |
| Total content | | 41 | $1.55^{A,B}$ | 0.33 | | | |
| Arnoštov | 2009 | 8 | $2.36^{d}$ | 0.29 | 1.83 | 2.69 | 2.29 |
| Arnoštov | 2010 | 8 | 2.48 | 0.74 | 1.05 | 3.62 | 2.67 |
| Arnoštov | 2011 | 8 | $2.89^{d}$ | 0.60 | 2.03 | 3.65 | 2.90 |
| Total content | | 24 | $2.58^{A}$ | 0.54 | | | |
| Lipno | 2009 | 9 | 1.84 | 0.46 | 1.22 | 2.72 | 1.72 |
| Lipno | 2010 | 12 | 2.37 | 1.24 | 0.49 | 4.51 | 2.26 |
| Lipno | 2011 | 9 | 2.64 | 1.14 | 1.01 | 3.95 | 2.29 |
| Total content | | 30 | $2.29^{B}$ | 0.84 | | | |

$^{a:a,\ d:d}$ $P < 0.05$; $^{c:c,\ A:A,\ B:B}$ $P < 0.01$; SD – standard deviation

vidual concentrations did not reach the level of 5 μg $dm^{-3}$, which corresponds to the optimum iodine content in the environment. Significantly lower concentrations ($P < 0.01$) were measured in samples from the locality Rapotín in Jeseníky PLA. Similarly, lower iodine concentrations in stormwater in the same locality compared to sites in Šumava PLA were reported by Šeda et al. (2012) and to grassland sites investigated by Trávníček et al. (2004). In all the sites selected for our study, the highest average values were measured in 2011 (Table 1). Presumably, this iodine content elevation in all the water stream localities detected in that year could have been affected by environmental changes caused by the volcanic activity in Iceland in 2010. This assumption may explain the higher iodine content in air and rainwater in the monitored areas (Šeda et al. 2012).

The low content of iodine in surface waters of the tested areas is consistent with the low iodine content in the environment and historically with the occurrence of endemic goitre cases (Kursa et al. 2005, 2010).

The average iodine content in water samples from the upper course of the Blanice River ranged from 1.48±0.30 μg $dm^{-3}$ (April 2010) to 3.05±0.38 μg $dm^{-3}$ (July 2010) – Figure 2. The values were lower in spring

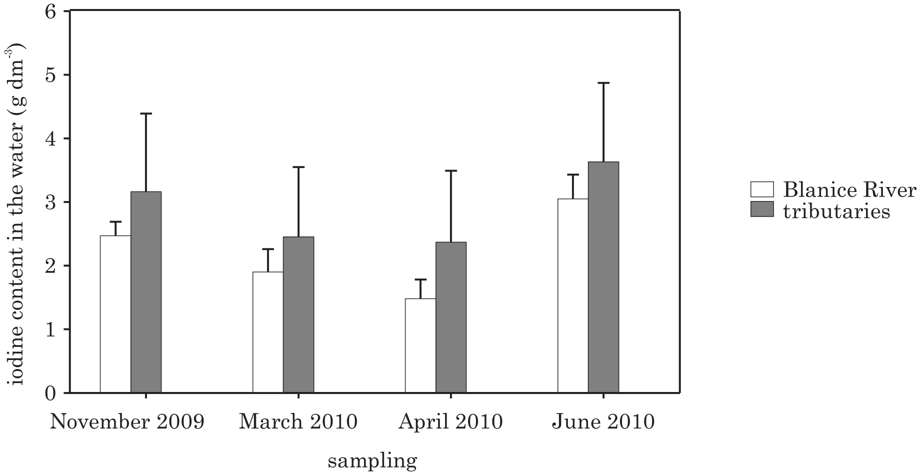


Fig. 2. Iodine content in the water of the Blanice River and its tributaries

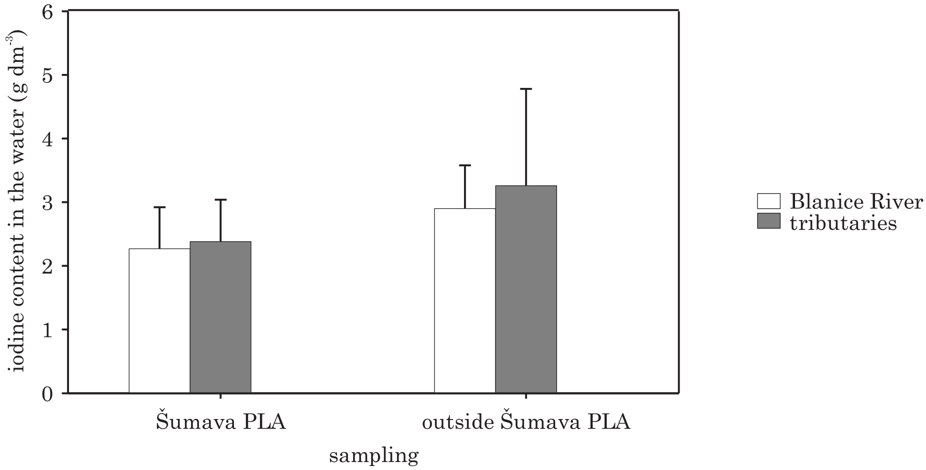


Fig. 3. Iodine content in the water of the Blanice River and its tributaries in Šumava PLA and outside Šumava PLA

while being higher in summer and autumn ($P < 0.05$; $P < 0.01$). Higher concentrations in the summer season in 2010 (Figure 2-3) may be related with the increased microbiological activity accelerating the natural cycling of matter, including iodine, and with the decreased water discharge in rivers in summertime (Šeda et al. 2011). Higher concentrations were found out in sites below Husinec reservoir (2.67±0.61 μg $dm^{-3}$), near the municipality Těšovice (2.57±0.67 μg $dm^{-3}$), and at the beginning of the upper course in a site near the municipality Arnoštov. The iodine content at the beginning of the river course depends on the soil and biological conditions in the Blanice River spring area and in the catchment of its tributary to the Puchéřský brook (Figure 4, Table 2), whereas in the Těšovice locality anthropogenic

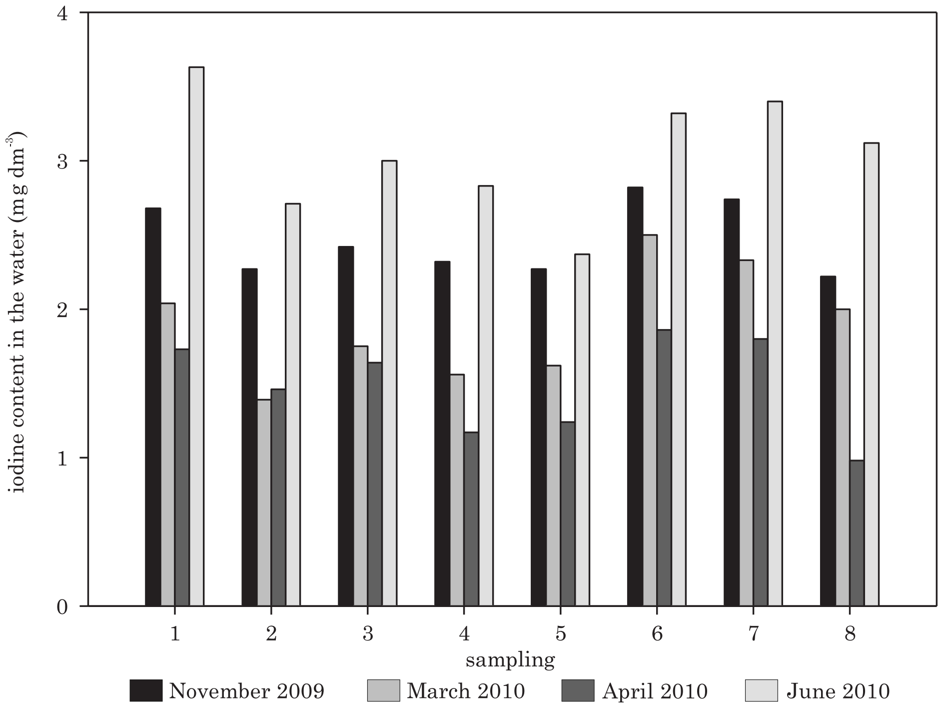


Fig. 4. The dynamics of iodine content in water in the course of the Blanice River. Sampling sites see Fig. 1

factors are responsible for a higher iodine content in a tributary to the Živný brook flowing through the town Prachatice (Table 2).

The identical dynamics of the iodine content in the riverbed (November 2009, March 2010, April 2010 and June 2010) is associated with the river's self-purification capacity to equalize the iodine level in water following its increase due to higher iodine concentrations in tributaries (Figure 3). This occurs, for example, by volatilization to the air, dilution or binding to sediments, the river bottom and banks. The assumption is consistent with the literature data (Stewart et al. 2003, Tagami, Uchida 2006, Ren et al. 2008).

The average concentration of iodine in water samples from the tributaries to the Blanice River was in the range of 2.45±1.10 μg dm$^{-3}$ (March 2010) and 3.64±1.24 μg dm$^{-3}$ (June 2010). Lower values were measured in the spring season (March 2010), which was analogous to iodine concentrations measured in samples collected from the riverbed, while the highest values were determined in June 2010 (Figure 1). Higher concentrations (Table 2) were found out in the water of the Živný brook (7.63 μg dm$^{-3}$, $P < 0.01$) and the Zbytinský brook (6.80 μg dm$^{-3}$), whereas the lowest concentrations were in the water of the Cikánský brook (0.72 μg dm$^{-3}$). The higher iodine content in the Zbytinský brook water is probably caused by treated wastewater that is discharged into this brook from the village Zbytiny (300 inhabitans). The

Table 2

Iodine content in tributaries to the upper course of the Blanice River

| Order of tributaries | Tributary | Locality | Iodine content (μg dm$^{-3}$) | | | |
|---|---|---|---|---|---|---|
| | | | mean | SD | minimum | maximum |
| 1. | Puchéřský brook | PLA Šumava NNM Blanice | 2.35 | 0.76 | 1.75 | 3.62 |
| 2. | Spálenecký brook | PLA Šumava NNM Blanice | 2.04 | 0.61 | 1.43 | 3.01 |
| 3. | Tetřívčí brook | PLA Šumava NNM Blanice | 2.49 | 0.50 | 1.83 | 3.22 |
| 4. | Zbytinský brook | above the village Zbytiny | 2.23 | 0.80 | 1.54 | 3.54 |
| 5. | Zbytinský brook | below the village Zbytiny | 4.17 | 1.52 | 3.08 | 6.80 |
| 6. | Černý brook | near a farmstead | 3.65 | 0.78 | 2.87 | 4.91 |
| 7. | Farský brook | outside the village | 1.86 | 0.30 | 1.49 | 2.29 |
| 8. | Cikánský brook | | 1.66 | 0.68 | 0.72 | 2.48 |
| 9. | Žárovenský brook | | 2.31 | 0.37 | 1.89 | 2.78 |
| 10. | Živný brook | above the town Prachatice | 2.67 | 0.48 | 2.01 | 3.38 |
| 11. | Živný brook | below the town Prachatice | 6.49 | 0.87 | 5.19 | 7.63 |

NNM – National Natural Monument Blanice; PLA – Protected Landscape Area; SD – standard deviation

other tributaries also tend to have a higher iodine content, which corresponds with the local increase of iodine in the Blanice River. The Černý brook flowing through the agriculturally cultivated area (grazing cattle and sheep) also has a higher iodine content than found in the other tributaries (4.91 μg dm$^{-3}$, July 2010). Nevertheless, the latter values are only slightly higher. The highest values were measured in samples from the Živný brook, which was attributed to wastewater discharged from a wastewater treatment plant in Prachatice (11 140 inhabitans) just into the stream concerned. Hence, it is iodine of anthropogenic origin that is not probably completely eliminated in the WTP and which significantly contributes to an increase in the iodine amount in the Živný brook. However, this brook is not very important with regard to iodine amounts carried with water because its water is diluted after its confluence with the Blanice River, so that the iodine content in the Blanice River is only minimally affected. The importance of the Blanice River's self-purification capacity is documented in Figure 3, which shows the average iodine content in the Blanice River and its tributaries.

# CONCLUSIONS

The iodine content in running surface waters in areas with more intensive landscape management in the Czech Republic confirms low levels of iodine in the natural environment. The dynamics of iodine content changes in the course of the Blanice River indicates that the river possesses a significant self-purification capacity even when its tributaries have a higher iodine content. In the basin of the Blanice River, the largest sources of anthropogenic iodine are human settlements, especially Prachatice (11 140 inhabitants) and Zbytiny (300 inhabitants), and the livestock maintained in the basin of the Černý brook.

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