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Determination of low-level tritium concentrations in surface water and precipitation in the Czech Republic

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Abstract Past tests of nuclear weapons in the atmosphere, nuclear energy facilities and tritium of natural origin are main sources of tritium in the environment. Thanks to its presence in environment and its favourable properties, tritium is used as a radiotracer. Since stopping of atmospheric nuclear tests, tritium in precipitation has been decreasing towards natural levels below 1 Bq l^{-1} and precise analyses of low level tritium activities are necessary. This paper focuses on tritium development at sites not influenced by any technogenic release of tritium in Elbe River basin (Bohemia) in the Czech Republic using liquid scintillation measurement with electrolytic enrichment.

Keywords Tritium · Precipitation · Surface water · LSC · Electrolytic enrichment

Introduction

Tritium (^{3}H) is radioactive isotope of hydrogen with the half-life of 12.32 y [1]. Tritium of natural origin is produced in upper layers of the atmosphere by nuclear reactions caused by cosmic rays. Production of tritium by natural processes is assessed to be 72 PBq y^{-1} and the tritium amount of natural origin is constantly at a level of 1275 PBq [2]. Tritium concentrations are still affected by the atmospheric test of nuclear weapons (1950s–1960s): It has been estimated that 186 EBq (i.e. 186 × 10^{18} Bq) was emitted into the atmosphere [2]. Most tests were carried out in the Northern Hemisphere. Only about 5% of tritium mixed via the stratospheric circulation into the Southern Hemisphere [3]. After the ban of atmospheric nuclear weapons testing in 1963, the global environmental tritium levels have been dropping. Projecting cited data [2], it can be estimated that the remaining tritium activity in 2016 was still 9.6 EBq. By 2051, the remaining tritium activity will be identical to that originating from natural processes (1.3 EBq). Atmospheric nuclear tests introduced tritium directly into the stratosphere. There, tritium is quickly oxidised into tritiated water and transferred into the troposphere, especially by stratosphere-to-troposphere transport in spring, where is rapidly removed by precipitation [4]. This leads to seasonal variation in tritium concentrations in the atmosphere.

Thanks to its presence in environment and its favourable properties, tritium is used as a radiotracer. Tritium from a nuclear power plant was used as a radiotracer for pollutant transport modelling e.g. in Ebro River [5]. It is also widely used for estimation of groundwater mean residence and in modelling of pollutant transport in groundwater [3, 6] or to determinate the origin of waters [7]. It implies that accurate quantification of tritium level is necessary.

Since stopping of atmospheric tests, tritium in precipitation has been decreasing towards natural levels. Typical tritium concentrations detected nowadays in mid-latitude continental precipitation are about 1 Bq l^{-1}. Lower values are observed in the tropics (0.1–0.5 Bq l^{-1}) [8] because of smaller input of tritium into the Southern Hemisphere during atmospheric nuclear weapons tests. In groundwater, higher tritium concentrations, up to several Bq l^{-1}, can be

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observed occasionally. They stem from high tritium levels in precipitation in the 1950s–1960s, resulting from atmospheric nuclear testing [8]. For future hydrological research, natural levels of tritium concentrations in precipitation need to be established [9].

Further, few data about actual tritium concentrations in surface water and precipitation in the Czech Republic are given. There is only one GNIP and GNIR station (Global Network of Isotopes in Precipitation and Rivers, IAEA [10, 11]) in the Czech Republic. They reported annual average values in the range 0.98–1.29 Bq l^{-1} (8.23–10.85 TU) in precipitation in the period 2006–2010 [10] and 0.98–1.12 Bq l^{-1} (8.23–9.42 TU) in rivers in the period 2006–2012 [11]. Hanslík et al. [12] reported values around 1.5 Bq l^{-1} in precipitation in the years 1999–2000 and 1.1–1.5 Bq l^{-1} in rivers in the Czech Republic in the years 2002–2003. The author also stated value of the effective half-life of tritium decrease in precipitation and rivers 7.9 and 8.2 years for the tritium concentration corrected for the residual contamination after the nuclear weapons tests in the period 1993–2001, and 1990–2003 respectively.

This work focuses on tritium development at sites not influenced by any discharge from a nuclear facility in Elbe river basin (Bohemia) in the Czech Republic. The aim of the study was to analyse main tritium components stemming from natural processes and those originating from man activities (residual pollution from atmospheric tests on nuclear weapons in the last century and the atmospheric transfer from nuclear facilities worldwide; and to assess the actual level of tritium in surface water and precipitation in studied sites. There are two nuclear power plants in the Czech Republic (Temelín and Dukovany). Sampling sites without any direct effect (discharges) of nuclear facility were studied. The paper summarizes the assessment of low level tritium concentrations in surface water and precipitation in Elbe River basin in the Czech Republic since 2002. The samples have been pretreated by electrolytic enrichment since 2010.

Experimental

Sampling method

Tritium concentration was monitored in surface water and precipitation at sites not influenced by discharges from any nuclear device. Location of the sampling sites is shown in Fig. 1. The frequency of sampling of surface water was once per month (sampling sites 1 and 2 at the Vltava and Elbe rivers) and four times per year (sampling sites 3–5 at the Vltava River and its tributaries). Monitored period of surface water was 2002–2016. Precipitation samples were accumulated monthly at five sites (A–E). Basic information about sampling sites is in Table 1. Climate is characterized as cool, fully humid, warm summer according to classification used by GNIP [10]. The datasets analysed during the current study aren't available but could be provided by the corresponding author upon reasonable request.

Analytical technique

The determination of tritium was performed according CSN EN ISO 9698 [13] and CSN 75 7600 [14]. The samples were distilled. The measurements were carried out with low level liquid scintillation spectrometer Quantulus 1220. The relative efficiency was about 24%. A mixture of 8 ml of the sample and 12 ml of ULTIMA GOLD LLT scintillator was measured for 800 min (for samples without electrolytic enrichment until 2010) and for 300 min (for electrolytically enriched samples). To avoid chemiluminiscence, samples were stored for at least 12 h in dark before measurement. Certified material No. 1035-SE-4 0339-15 (Czech Metrology Institute) was used for calibration. Dead water with activity lower than 0.07 Bq l^{-1} was used for blank sample. The initial sample volume was 500 ml for electrolytic enrichment. A sample after addition of 1.5 g Na_2O_2 was electrolysed to a volume of 20–25 ml. Subsequently, the sample was neutralized with 6 g $PbCl_2$ [15, 16] and distilled. A set for electrolytic enrichment allows the simultaneous adjustment of 20 samples. There are three spiked samples, two samples of dead water, one control sample and 14 ordinary samples in one series. The total elapsed electric charge is 1400 Ah. The temperature during the electrolysis is kept at 0.5 °C. The tritium concentrations were evaluated according CSN EN ISO 9698 [13], combined standard uncertainties (expressed at 2σ level) and the minimum detectable activity (MDA) according CSN 75 7600 [14]. The MDA at a significance level of 95% was 1.0 (samples without enrichment) and 0.07 Bq l^{-1} respectively. The results are expressed in Bq l^{-1}.

Treatment of data

Annual average values of tritium concentration were calculated. In the case of values lower than MDA, a value equal to MDA was used for the calculations of the average values instead. The mean annual tritium concentration in precipitation has been weighted by the amount of precipitation for given station.

For description of tritium concentration development, effective (observed) decay constant (λ_{eff}) and effective half-life (T_{eff}) of tritium concentration decrease in surface water and precipitation was calculated. For description of

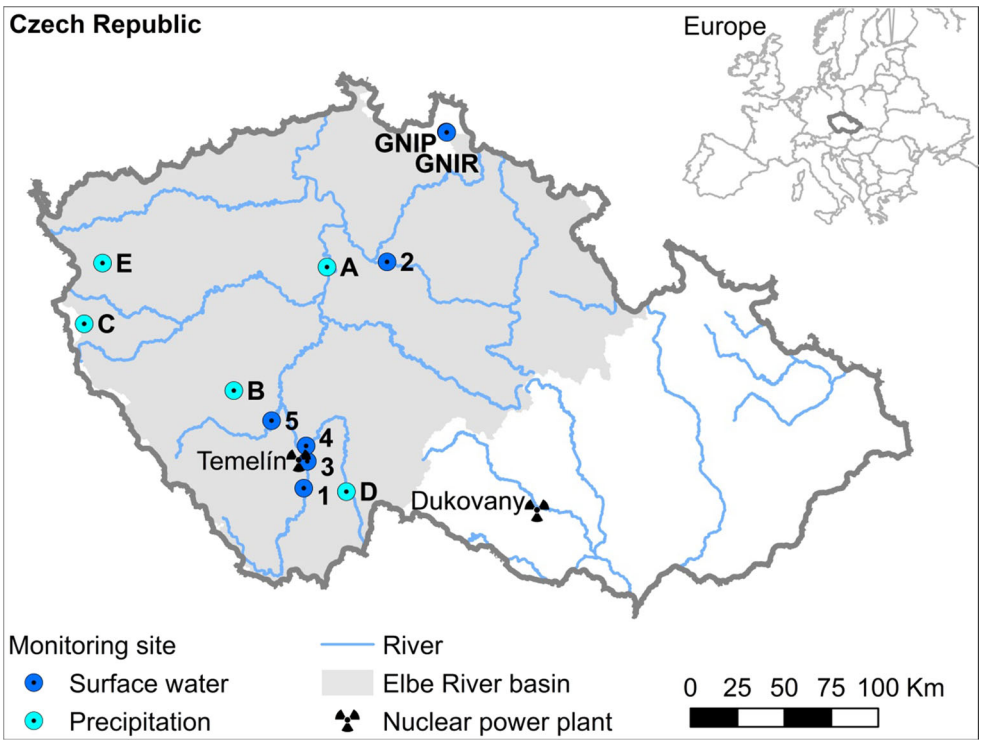

Fig. 1 Map of sampling sites

Table 1 Characteristics of sampling sites

Surface water		Flow rate (m^3 s^{-1})	Frequency of sampling (per year)
1	Vltava Hluboká	27.6	12
2	Elbe Lysá	74.1	12
3	Vltava Hněvkovice	30.6	4
4	Lužnice Koloděje	24.1	4
5	Otava Topělec	23.3	4

Precipitation		Period of record	Frequency of sampling (per year)
A	Prague Podbaba	2001–2016	12
B	Kocelovice	2006–2016	12
C	Přimda	2001–2005	12
D	Lužnice	2001–2012	12
E	Závišín	2001–2005	12

tritium concentration development at the unaffected sites, a first-order kinetics equation was used:

$$\ln c_j = -\lambda_{eff} \times t + \ln c_0 \quad (1)$$

where c_j is the annual average activity of tritium in surface water or precipitation in year j, based on the results of the monitoring (Bq l^{-1}), λ_{eff} effective (observed) decay constant for the decrease of tritium concentration (y^{-1}) and t time of monitoring (y). Statistical significance of dependence (regression curve) was verified using the Pearson coefficient and t test.

Effective half-life (T_{eff}) of tritium concentration decrease in surface water at the unaffected sites was calculated from the assessed effective decay constant (λ_{eff}) using the equation according Smith and Beresford [17]:

$$T_{eff} = \ln 2 / \lambda_{eff}. \quad (2)$$

To examine seasonal variation of tritium concentrations in precipitation, the averages of tritium concentrations weighted by quantity of precipitation were processed for each month and season. We divided the rain samples into four seasons: spring (March–May), summer (June–

Table 2 Annual average values of tritium concentrations in surface water in Elbe River basin (Bohemia) in the Czech Republic (since 2010 the electrolytic enrichment included)

	Surface water, average (Bq l^{-1})	1, Vltava Hluboká	2, Elbe Lysá
2002	1.1 ± 0.5	1.0 ± 0.4	1.4 ± 0.4
2003	1.4 ± 0.6	1.3 ± 0.4	1.4 ± 0.7
2004	1.1 ± 0.5	1.2 ± 0.5	1.2 ± 0.5
2005	1.2 ± 0.5	1.3 ± 0.4	1.3 ± 0.5
2006	1.0 ± 0.4	1.1 ± 0.4	1.1 ± 0.4
2007	1.0 ± 0.4	1.1 ± 0.4	1.1 ± 0.4
2008	1.1 ± 0.4	0.8 ± 0.3	1.1 ± 0.4
2009	1.3 ± 0.6	1.1 ± 0.5	1.3 ± 0.7
2010	1.1 ± 0.2	1.1 ± 0.1	1.1 ± 0.3
2011	1.1 ± 0.2	1.1 ± 0.3	1.1 ± 0.1
2012	0.9 ± 0.1	1.0 ± 0.1	0.9 ± 0.1
2013	0.9 ± 0.1	1.0 ± 0.1	0.9 ± 0.1
2014	1.0 ± 0.2	1.0 ± 0.1	0.8 ± 0.2
2015	0.9 ± 0.2	0.9 ± 0.2	0.8 ± 0.1
2016	0.9 ± 0.2	0.9 ± 0.2	0.9 ± 0.1

August), autumn (September–November), and winter (December–February) [18].

Results and discussion

Tritium concentrations in surface water and precipitation

Evaluated annual average tritium concentrations in surface water are in Table 2. The evaluation was done separately for places with frequency of sampling 12 per year (sampling sites 1 and 2) and for all sampling sites in average (to summary evaluation were taken also sampling sites with lower frequency, sites 3–5), signed as surface water, average.

Annual average values evaluated for surface water in the catchment of Elbe River (Bohemia) varied in range 0.9–1.4 Bq l^{-1}. The uncertainties have been reduced since 2010 when the electrolytic enrichment was included.

We compare our data with those from GNIR [11] and previously published data for the Czech Republic [12] (Fig. 2). There is only one station from Czech Republic in GNIR, we used nearest GNIR stations from Germany for comparison. Only stations not influenced by any technogenic release of tritium where used for comparison. To convert GNIP and GNIR results expressed in tritium units (TU), the relation according Rozanski and Groning [19] 1 TU = 0.11919 ± 0.00021 Bq kg^{-1} was used.

Evaluated annual average tritium concentrations (weighted) in precipitation are in Table 3. The evaluation

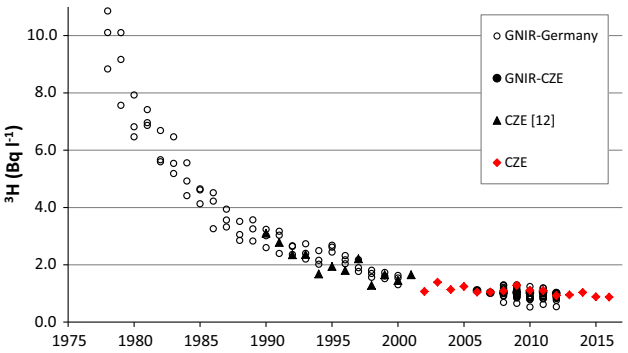

Fig. 2 Comparison of tritium concentrations in surface water in Elbe River basin (Bohemia) (CZE) with data from GNIR [11] and previously published data for the Czech Republic [12]

Table 3 Annual average values of tritium concentrations in atmospheric precipitation in Elbe River basin (Bohemia) in the Czech Republic (since 2010 the electrolytic enrichment included)

	Precipitation, w.m (Bq l^{-1})	A, Prague Podbaba	B, Kocelovice
2002	0.9 ± 0.6	1.4 ± 0.4	
2003	1.1 ± 0.9	1.5 ± 0.5	
2004	1.2 ± 0.7	1.1 ± 0.9	
2005	1.3 ± 0.7	1.6 ± 0.9	
2006	1.0 ± 0.7	0.9 ± 0.7	1.0 ± 0.7
2007	1.0 ± 0.6	1.1 ± 0.7	1.0 ± 0.7
2008	1.0 ± 0.7	1.2 ± 0.7	0.8 ± 0.6
2009	1.1 ± 0.6	1.2 ± 0.7	1.0 ± 0.7
2010	1.4 ± 0.2	1.2 ± 0.2	1.4 ± 0.4
2011	1.2 ± 0.4	1.2 ± 0.2	1.2 ± 0.6
2012	1.1 ± 0.2	1.2 ± 0.2	0.9 ± 0.2
2013	1.0 ± 0.1	1.1 ± 0.1	0.9 ± 0.1
2014	1.2 ± 0.1	1.3 ± 0.1	1.1 ± 0.1
2015	1.1 ± 0.1	1.4 ± 0.1	0.8 ± 0.1
2016	1.1 ± 0.1	1.2 ± 0.1	1.0 ± 0.1

was done separately for places with longest period of record (sampling sites A and B) and for all sampling sites in average, signed as precipitation, w.m.

Mean weighted values in precipitation evaluated for the area of Elbe River basin (Bohemia) varied in range 0.9–1.4 Bq l^{-1}.

We compare our data with those from GNIP [10] and previously published data for the Czech Republic [12] (Fig. 3). There is only one station from Czech Republic in GNIP, we used nearest GNIP stations from Austria and Germany for comparison. Only stations with the similar climate were used for comparison [10].

The observed values of mean tritium concentrations in surface water and precipitation are comparable with other mid-latitude continental GNIP and GNIR stations [10, 11];

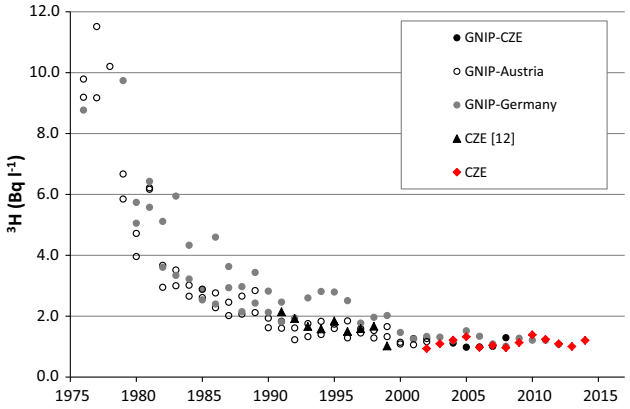

Fig. 3 Comparison of tritium concentrations in precipitation in Elbe River basin (Bohemia) (CZE) with data from GNIP [10] and previously published data for the Czech Republic [12]

they varied around 1 Bq l^{-1}. However, these concentrations are still higher than the natural level, and also higher than the concentrations in the Southern Hemisphere which has already returned to pre-bomb era [3, 8, 20].

Trends of tritium concentrations

Trends of tritium concentrations in surface water were processed using annual average values. The evaluation was done separately for places with frequency of sampling 12 per year (sampling sites 1 and 2) and for all sampling sites in average. We observed statistically significant trend of decrease in all cases but evaluated effective half-lives (Table 4) (T_{eff}) were longer than the physical half-life of tritium (12.32 y, [1]). The reasons for the longer half-life are the other components (contribution by cosmic rays and contribution from nuclear facilities considered constant for the assessed period). These components contribute significantly to relatively low tritium concentrations. For these reasons, the annual average tritium concentrations were corrected for natural component generated by cosmic rays and for the estimated contribution from nuclear facilities worldwide via atmosphere. This component was estimated according Hanslík [12] to be 0.48 Bq l^{-1} together, the component was subtracted from observed concentrations.

Table 4 Evaluated effective half-lives of tritium concentration decrease in surface water (without and with correction for the natural component and the contribution from nuclear facilities worldwide) in the period 2002–2016

	Surface water, average (y)	1, Vltava Hluboká	2, Elbe Lysá
T_{eff}	27 ± 9	29 ± 14	16 ± 6
T_{eff} (corr.)	15 ± 5	17 ± 9	9 ± 4

The values of T_{eff} = 9–16 years were calculated for kinetics of tritium concentrations decrease, corrected for the natural component and the contribution from nuclear facilities worldwide (i.e. for residual contamination from atmospheric testing of nuclear weapons). The obtained T_{eff} were shorter than those for development of uncorrected tritium concentrations (without subtraction). Taking into account their uncertainty, the effective half-lives evaluated for the corrected tritium concentrations correspond to the physical decay.

Trend in tritium concentrations in precipitation was analysed using mean weighted values from all sampling sites. We did not observe any trend in decrease of tritium concentrations after 2002, neither for tritium concentrations with correction for the natural component and the contribution from nuclear facilities worldwide.

From Figs. 2 and 3, the annual mean concentrations in surface water and precipitation (GNIR and GNIP data) decreased over time since the Nuclear Test Ban Treaty in 1963. This trend of decrease was observed also by Hanslík [12] in the Czech Republic in 1990s. We have not observed any trend in precipitation any more since 2002. Significant trend of decrease was observed in surface water, but it is obvious that the tritium component generated by the lasting sources (natural processes and operation of nuclear facilities) begins to predominate over the component of tritium from nuclear bomb testing.

Seasonal trends

Tritium concentrations in precipitation from sampling sites Prague Podbaba (A) and Kocelovice (B) were evaluated for 2010–2016 in detail (the electrolytically enriched samples) (Fig. 4). Seasonality of tritium in precipitation was analysed. Consequently, the weighted averages of tritium were processed for each month and season (Table 5). The determined average values were maximal for spring and summer (1.2–1.4 Bq l^{-1}), and minimal for winter (1.0 and 0.7 Bq l^{-1}). This seasonal variation can be assigned to the Spring Leak phenomenon, which leads to tritium release

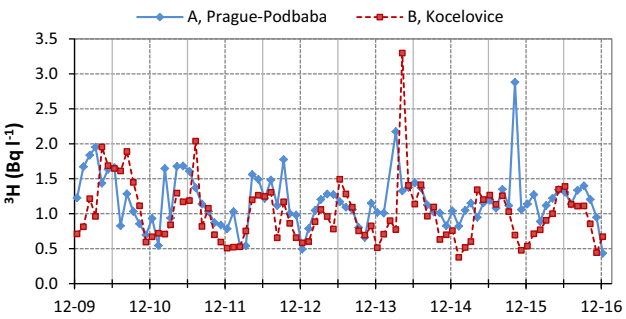

Fig. 4 Tritium concentrations in precipitation from selected monitoring sites in the period 2010–2016

Table 5 Monthly and seasonal average tritium concentrations weighted by quantity of precipitation for the period 2010–2016

		A, Prague-Podbaba		B, Kocelovice	
		(Bq l^{-1})			
Winter	December	1.0 ± 0.3	0.9 ± 0.1	0.7 ± 0.3	0.7 ± 0.1
	January		1.1 ± 0.3		0.6 ± 0.3
	February		1.1 ± 0.2		0.8 ± 0.3
Spring	March	1.4 ± 0.2	1.3 ± 0.2	1.2 ± 0.2	0.8 ± 0.2
	April		1.3 ± 0.3		1.7 ± 0.3
	May		1.4 ± 0.1		1.3 ± 0.2
Summer	June	1.3 ± 0.1	1.4 ± 0.1	1.4 ± 0.3	1.4 ± 0.2
	July		1.2 ± 0.1		1.5 ± 0.3
	August		1.2 ± 0.1		1.2 ± 0.4
Autumn	September	1.1 ± 0.2	1.1 ± 0.1	0.8 ± 0.2	1.1 ± 0.2
	October		1.3 ± 0.2		0.8 ± 0.3
	November		0.9 ± 0.2		0.6 ± 0.1

from stratosphere into troposphere due to heating of continents with resulting rise of the tropopause in spring [21].

Conclusions

This work investigated tritium actual levels in surface water and precipitation at sites not influenced by any discharge from a nuclear facility in Elbe River basin (Bohemia) in the Czech Republic (see Tables 1 and 2). Determined concentrations around 1 Bq l^{-1} correspond to mid-latitude continental location of the catchment. These concentrations are still higher than the natural background and also higher than the values in the Southern Hemisphere but the tritium component generated by the present processes (natural or anthropogenic) begins to predominate over the component of tritium from nuclear bomb testing. We cannot see further decrease of tritium concentrations in precipitation as it was observed in past decades. The seasonal variation of tritium concentrations due to the Spring Leak phenomenon has been clearly seen since year 2010, when we implemented electrolytic enrichment of samples and reduced uncertainties of tritium analyses. This accurate determination of tritium concentrations is essential for other studies using tritium as a radiotracer (for pollutant transport modelling or studies with ground water).

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