DETERMINATION OF THE TOTAL 14C CONCENTRATION OF WATER SAMPLES USING THE COD METHOD AND AMS

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ABSTRACT. Radiocarbon (^{14}C) is the one of the most important radionuclides released from the nuclear facilities to the environment. Currently, inorganic ^{14}C is checked during regular environmental monitoring as part of the groundwater monitoring program of the Paks Nuclear Power Plant. Several studies have shown that organic ^{14}C can be also an important and sensitive tool for detection of possible leakage of nuclear technological systems. For this reason, a wet oxidation method was developed for the accelerator mass spectrometry (AMS) ^{14}C measurement technique to determine the ^{14}C activity concentration of the total dissolved carbon content of water samples, coming from environmental monitoring wells. The overall efficiency of the oxidation was around $94 \pm 5\%$ for different types of tested organic compounds. The typical ^{14}C background (1–2 pMC) is obtained by preparation of blank samples, which allows a detection level of around $5 \cdot 10^{-5}$ Bq L^{-1}. The activity of the organic fraction can be calculated using the formula presented in the study. The method was applied for water samples deriving from environmental monitoring wells of a pressurized-water reactor (PWR) type of NPP. The results of our investigations over the 14 different water samples around the Paks NPP show that DO^{14}C contribution to the total ^{14}C activity concentration was between 5–25%.

KEYWORDS: AMS, COD, groundwater, nuclear power plant, total dissolved ^{14}C.

INTRODUCTION

The total dissolved carbon (TDC) content of environmental water samples is presented as a form of dissolved inorganic carbonates (DIC) and in several dissolved organic forms (DOC) (Bisutti et al. 2004). The dissolved carbon concentration of these waters varies between a few tens to a few hundred mg L^{-1}. Generally, carbon is mainly bound to the inorganic fraction in the water and only few mg L^{-1} is bound to the organic compounds. Using the conventional radiometric ^{14}C measurement methods (LSC or GPC), 30–100 L of water sample is needed to obtain accurate analytical results, even for the measurement of the dissolved inorganic (DI^{14}C) fraction (Varlam et al. 2007). Due to the above, the determination of the ^{14}C concentration of environmental water samples is generally based on the measurement of the DIC fraction only (Geyh 2000; Gonfiantini et al. 2003).

Radiocarbon (^{14}C) has a decisive importance for the environmental monitoring of nuclear facilities and radioactive waste repositories, as it can spread well with groundwater and indicates the propagation path of the contamination (UNSCEAR 2000). However, to monitor the DIC fraction alone is not sufficient to control the emission, as radioactive wastes may also contain significant amounts of organic compounds with high ^{14}C activity concentration. Moreover, the anthropogenic origin inorganic fraction may be diluted by the relatively high amount of dissolved natural carbonate content of the groundwater, which can reduce the sensitivity of these methods for detection of the environmental impact of the monitored facilities. The dilution and reduced sensitivity phenomenon are less significant in case of the organic

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compounds due to the much lower natural DOC appearance in groundwater (Wolstenholme et al. 1998; Povinec et al. 2001; Cook et al. 2004; Huang et al. 2015; Muir et al. 2017).

Previously, several investigations of the organic ^{14}C source mediums were carried out at the Paks Nuclear Power Plant (NPP). Based on previously reported ^{14}C activity concentration values from Paks NPP of samples from the primary coolant and cooling ponds the ^{14}C activity concentration of the inorganic fraction at each reactor block are rather similar: 8–10 Bq L^{-1} (Isotoptech 2016). Veres et al. (1995) published that in the ventilation stacks of the Paks NPP, the carbon dioxide fraction represents only 5–6% of the total airborne ^{14}C release, so the airborne organic forms release is 20 times higher. Their preliminary results showed that the ^{14}C is mostly in the form of hydrocarbons and its concentration is about 4 kBq L^{-1} primary water of Paks NPP (Veres et al. 1995).

Additionally, the analyses of dissolved gases in the water of the spent fuel pool show that in some cases it is not only the inorganic fraction contributes to ^{14}C activity but also other gases in organic and volatile forms. In some cases, it could mean twice the DIC ^{14}C activity. Organic ^{14}C, as one of the most important limiting radionuclide and chemical form for radioactive waste disposal, is also present in low and intermediate level radioactive waste from PWR-type nuclear power plants. Its concentration in the evaporation concentrates of Paks NPP are in the order of between 0.1 kBq L^{-1} and 1.5 kBq L^{-1} in dissolved organic fraction and the ^{14}C activity concentrations of inorganic fraction are between 3.5 kBq L^{-1} and 5.5 kBq L^{-1} (Isotoptech 2018). Consequently, the previous investigations confirm relevance of the organic ^{14}C measurements in the monitoring of nuclear power plants releases, because probably it can also be emitted into the environment.

Several routine methods are available for the determination of the specific ^{14}C content of the DIC fraction of water samples by AMS measurement method. These methods generally use phosphoric acid to recover the inorganic carbon from a 10–20 mL water sample as a form of CO_2. However, in this case the organic compounds remain in the reaction vessel (Gudelis et al. 2010; Molnár et al. 2013a, 2013b). To measure the organic fraction is much more complicated as about 800–1000 mL sample is necessary, since the concentration of the organic fraction is much smaller than the inorganic one. The inorganic fraction should be removed from the sample, before the oxidation of the organic fraction is performed. After removing the inorganic fraction, the sample can be freeze-dried and then the residue combusted, or the oxidation can be done by wet oxidation method by strong acidic reagents or by UV light (Burr et al. 2001; Leonard et al. 2013; Steier et al. 2013; Huang et al. 2015; Svetlik et al. 2017). Due to the complications and difficulties described above it is still very uncommon that the ^{14}C in the DOC fraction is measured as a part of a monitoring program around nuclear facilities.

The aim of the study is to develop an easy-to-use AMS-based measurement method to determine the total dissolved ^{14}C activity concentration (TD[14]C) of water samples. This can be useful for the environmental monitoring of nuclear facilities and radioactive waste repositories, as there is a lack of data in literature related to the concentration of the ^{14}C found under different chemical forms (Svetlik et al. 2017).

EXPERIMENTAL

Instrumentation and Samples

In this study, the specific ^{14}C content of groundwater monitoring in well water (from 12 monitoring wells) collected from the Paks NPP site and the Danube above Paks and the hot water channel were investigated. The activity concentration of inorganic ^{14}C in surface

and near-surface groundwater is considered to be nearly constant for the first two factors and is well known. Thus, around nuclear facility, the study of this isotope is an excellent indicator of uncontrolled releases and their detection.

The ^{14}C AMS measurements and sample preparation were carried out in the HEKAL AMS laboratory in Debrecen, Hungary. The introduce of the MICADAS type AMS was detailed in status report in 2013 (Molnár et al. 2013b). The concentration of the carbon forms in our samples was measured by Shimadzu® TOC-V$_{CPN}$ analyser according to the EN ISO 1484:1998 standard. This device can measure independently the TDC the DIC and also the DOC concentration of the water. The carbon content details were used for DO^{14}C calculation.

Sample Preparation and Measurement

The organic compounds of environmental water samples can be quantitatively oxidised to CO_2 in the presence of the mixture of sulphuric acid, potassium-dichromate and silver-sulphate, a reaction which is used for the determination of the chemical oxygen demand (COD) of water samples (ISO 1989). According to the ISO standard, the reaction is done in an open reaction vessel and the COD is determined by titration. In this way, the released CO_2 escapes from the vessel.

In our case, in order to retain the generated CO_2, the ISO procedure was modified and the reaction was run in a closed glass vessel specially designed for this purpose (Figure 1). The sample injection port was integrated into the stem of the valve and sealed with PTFE coated septum. This way the reagents can only come in contact with the glass and PTFE parts. The volume of the vessel is 70 mL.

The recipe of the ISO standard was further modified in order to add the oxidising agent in a single step. The individual Ag_2SO_4-H_2SO_4 and $K_2Cr_2O_7$-H_2SO_4 solutions were not prepared separately, but all of the reagents were combined in one solution. The recipe for the modified oxidising solution is the following Eq. (1):

$$100 \text{ mL } H_2O + 900 \text{ ml } H_2SO_4 \, 96\% + 18 \text{ g } Ag_2SO_4 + K_2Cr_2O_7. \qquad (1)$$
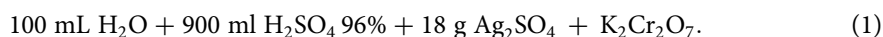
During the sample preparation, 6 mL oxidizing solution is first added into the open reaction vessel by a glass syringe and then evacuated to a $4 \cdot 10^{-3}$ mbar pressure using vacuum line, followed by the sealing of the vessel by the PTFE valve. In the next step, 20 mL water sample is injected through a 0.45 μm syringe filter into the closed vessel through the PTFE coated septum. Then the reaction cell is heated up to 120°C for 2 hr in a heating block to help DOC digestion by the oxidising agents. After the digestion, the cooled reaction vessel is connected to a dedicated gas handling line where the CO_2 can be recovered and purified by cryogenic method. The water vapor is trapped first at –70°C (isopropyl alcohol—dry ice) and the CO_2 is frozen at –197°C (liquid N_2). After the remaining incondensible gases were evacuated, the CO_2 was expanded to a known volume and its quantity was measured with Baratron® 626B pressure sensor (range: 0–500 mbar) (Molnár et al. 2013b).

The recovered CO_2 was converted to graphite by the sealed tube graphitization technique (Rinyu et al. 2013). The ^{14}C activities of the graphite targets were measured by our EnvironMICADAS AMS. The overall measurement uncertainty was calculated including counting statistics, background subtraction and normalization (Synal et al. 2007). The
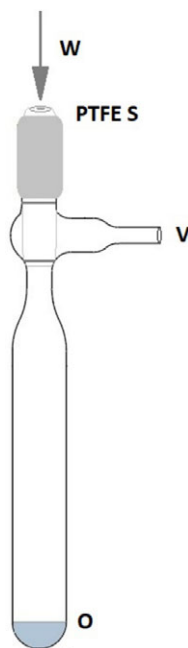
Figure 1   TD[14]C reaction vessel. W: injection of water sample; PTFE S: PTFE coated septum; V: J. Young high-vacuum PTFE valve; O: oxidizing solution.

results were corrected for the $\delta^{13}C$ isotopic fractionation using the Bats software (Stuiver and Polach 1977; Wacker et al. 2010).

RESULTS AND DISCUSSION

Results of the Measurements of Reference Samples

To test for any initial carbon content in the oxidising solution, the COD preparation was executed without the addition of any water sample into the oxidising agent. During these tests significant amount of CO_2 was generated (0.006 ± 0.004 mg/6 mL). To get rid of the carbon contamination of the oxidising solution, it was preheated to 120°C for 6 hr in the reaction vessel and the liberated CO_2 was purged out by N_2 gas flow. We used carbon-free deionized water (MilliQ®, Merck) for making some model solutions during the tests. The possible carbon contribution of the MilliQ water was also tested by the COD method and no measurable CO_2 formation was found.

The solution was tested by organic and inorganic reference material, since the TDC contains these two fractions, which are oxidized during digestion. The efficiency of the oxidation was tested by the preparation of 5–5 parallel model samples made of different types of IAEA ^{14}C reference materials (IAEA-C1 to C9) with known carbon content and ^{14}C concentration (Table 1). The model solutions contained 50 mg L^{-1} of carbon. In case of the insoluble materials, the reference material and the MillQ® water were added to the reaction vessel before the oxidising solution. Independently of the sample type, the carbon content of the model samples was recovered with a yield of 77 ± 2% with good reproducibility. Based on our previous experience, 25–30% of the developed CO_2 remained in the liquid phase in the

Table 1 Results of the tested IAEA reference materials (no chemical blank correction applied).

IAEA reference material[1]	Material[1]	^{14}C (pMC) consensus value[1]	Yield C (%) measured (n=5)	^{14}C (pMC) measured (n=5) (±2s)
IAEA C1	Marble	0	76 ± 3	0.11 ± 0.12
IAEA C9	Wood	0.12–0.21	77 ± 3	1.8 ± 1.2
IAEA C2	Travertine	41.14 ± 0.03	75 ± 2	41.04 ± 0.56
IAEA C3	Cellulose	129.41 ± 0.06	80 ± 2	129.0 ± 1.0
IAEA C6	Sucrose	150.6 ± 0.11	78 ± 1	149.6 ± 1.2

[1]Gröning et al. (2007).

vessel due to the equilibrium solubility of the CO_2 (Molnár et al. 2013a). When the CO_2 extraction was repeated three times, a yield of 75–80% could be obtained. Considering the results, the conversion factor of the samples to CO_2 during the applied oxidation process was close to 100%.

According to the above test results, the applied COD preparation method adds only a negligible contamination with modern carbon (~103 percent modern carbon [pMC]) to the samples, as the results of the fossil (^{14}C free) samples (IAEA-C1 and C9) are very close to their consensus values (close to 0 pMC; Table 1). Contamination of sample preparation for real samples can be taken for correction using the results of the reference (blank) samples. The observed contamination is not higher than 0.01 mg of recent carbon in the case of the applied COD method. For the higher activity IAEA reference material samples (IAEA-C2, C3 and C6), the measured values were in very good agreement with the expected nominal values, within 2 sigma uncertainty level, even without any chemical blank correction. Using the applied COD preparation method, the background is lower than 2 pMC (0.02 fM) for total carbon ^{14}C determination.

Calculating the ^{14}C Activity of the Organic Fraction

With the sample preparation method introduced above, the ^{14}C activity concentration of the total dissolved carbon (TDC) of water samples can be determined as easily as that of the inorganic fraction (DIC). If besides the total dissolved carbon fraction, the ^{14}C activity concentration of the inorganic carbon is also measured and the concentration of all the three carbon fractions is determined, then the specific ^{14}C activity concentration of the dissolved organic carbon ($DO^{14}C$) can be calculated with the formula below (Eq. 2):

$$DO^{14}C \,[pM] = \frac{TD^{14}C \cdot TDC - DI^{14}C \cdot DIC}{DOC} \qquad (2)$$

where $TD^{14}C$, $DI^{14}C$ and $DO^{14}C$ are the specific ^{14}C activities (in pMC units) of the carbon of the total dissolved carbon (TDC), inorganic carbon (DIC) and dissolved organic carbon (DOC, calculated as TDC-DIC) fractions, respectively, whereas TDC, DIC, and DOC are the measured dissolved carbon content concentrations (in mg/L units) for each fraction, respectively.

By considering the propagation of uncertainties, the uncertainty of the calculated specific ^{14}C activity value of the organic fraction ($\sigma DO^{14}C$) can be expressed as below (Eq. 3):

$$\sigma DO^{14}C = \sqrt{\left(\frac{\partial DO^{14}C}{\partial TD^{14}C}\right)^2 \cdot (\sigma TD^{14}C)^2 + \left(\frac{\partial DO^{14}C}{\partial TDC}\right)^2 \cdot (\sigma TDC)^2 + \left(\frac{\partial DO^{14}C}{\partial DI^{14}C}\right)^2 \cdot (\sigma DI^{14}C)^2 + \left(\frac{\partial DO^{14}C}{\partial DIC}\right)^2 \cdot (\sigma DIC)^2} \qquad (3)$$

For the monitoring of the nuclear facilities and for dose calculation, the absolute ^{14}C activity concentration [Bq L^{-1}] of the water is also important which can be expressed using Eq. (4):

$$A = 2.26 \cdot 10^{-6} \cdot pM_x \cdot C_x \qquad (4)$$

where A means the ^{14}C activity concentration of the water sample [Bq L^{-1}]; pM_x means the "absolute" percent Modern of the given carbon fraction which is decreasing with time and depends on the date of measurement (which is August of 2014 in this study), C_x means the carbon concentration of the water sample [mgC L^{-1}].

The "absolute" percent Modern of the sample was calculated as Eq. (5):

$$pM = \frac{A_{SN}}{A_{abs}} \cdot 100\% \qquad (5)$$

where, A_{SN} is the normalized specific activity of the sample, and A_{abs} is the specific activity of the absolute ^{14}C standard (A_{abs}=226 Bq/kg C) (Mook and van der Plicht 1999; Stenström et al. 2011).

Results of Real, Environmental Samples

On the site of the Paks NPP, there is a groundwater monitoring network to check the possible radioactive contaminations entering into the groundwater system. Additionally, the site-specific hydrological and contamination dispersion model is also used to identify any possible uncontrolled discharge points. From the groundwater monitoring wells, water samples were taken to measure TD^{14}C, DI^{14}C and the concentration of the different carbon forms. Table 2 shows the AMS ^{14}C measurement results, where the DO^{14}C values are calculated according to the above method. In some cases of certain monitoring wells, significant anthropogenic ^{14}C content was obtained in the dissolved carbon as it was already reported by Janovics et al. (2010).

If the specific calculated ^{14}C concentration of DOC fraction is plotted in the function of the specific ^{14}C concentration of the DIC, it is clear that the measurement results fit well to the 1:1 line (Figure 2). As it is well visible on Figure 2, on average, DO^{14}C specific activities are slightly higher (8 ± 12%, for the investigated 14 samples) than the DI^{14}C results of the same water sample. Activity concentration of the groundwater samples are highly influenced by the absolute carbon concentrations of targeted fraction. This shows that if we needed a complete picture about ^{14}C distribution in the groundwater system, TD^{14}C and DO^{14}C analyses could be rather useful, besides the commonly applied DI^{14}C measurements.

Based on these measurements it can be stated that the total carbon content of our water samples is within a relatively narrow range. The mean TDC content of the samples were 79 ± 14 mg L^{-1}. The major part, i.e., 75–95% of TDC was bound to inorganic carbonates, while the organic components were only the 5–25% of the total carbon content.

Table 2 ^{14}C results of water samples from different monitoring wells at Paks NPP. The given DO[14]C results are calculated value.

Sample name	TD[14]C (pM)	DI[14]C (pM)	DO[14]C (pM)	DO[14]C/DI[14]C ratio
HWC*	96.2 ± 0.5	95.0± 0.5	113.5 ± 9.9	119%
Danube	96.9 ± 0.5	94.2 ± 0.1	133.4 ± 7.8	142%
Well 1	91.4 ± 0.3	90.8 ± 0.4	99.0 ± 5.9	109%
Well 2	83.9 ± 0.3	83.3 ± 0.4	89.7 ± 4.2	107%
Well 3	93.2 ± 0.2	92.0 ± 0.4	99.2 ± 2.4	108%
Well 4	106.3 ± 0.5	106.2 ± 0.4	106.6 ± 6.6	100%
Well 5	114.4 ± 0.6	115.2 ± 0.5	111.5 ± 3.1	97%
Well 6	148.1 ± 0.5	147.3 ± 0.6	155.2 ± 7.3	105%
Well 7	103.0 ± 0.2	102.8 ± 0.4	103.4 ± 1.6	101%
Well 8	127.3 ± 0.4	125.8 ± 0.5	139.3 ± 5.4	111%
Well 9	127.9 ± 0.5	125.4 ± 0.5	140.7 ± 4.0	112%
Well 10	139.7 ± 0.4	139.1 ± 0.6	142.4 ± 3.3	102%
Well 11	320.4 ± 2.0	330.2 ± 1.2	287.3 ± 9.7	87%
Well 12	513.7 ± 2.7	511.0 ± 1.9	568 ± 68	111%

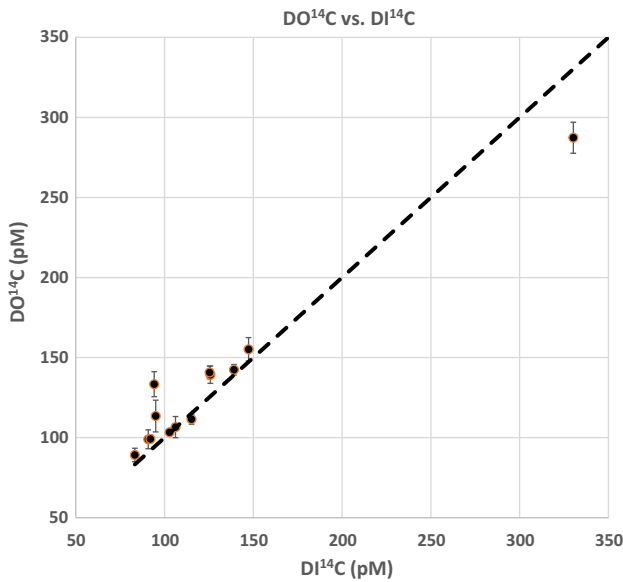*HWC: hot water channel, where the cooling river water returns to the Danube.

Figure 2 Specific ^{14}C concentration of the dissolved organic carbon DO[14]C of the Paks NNP's monitoring wells in the function of the dissolved inorganic carbon values (the result over 500 pMC of well 12 is not presented on the figure).

Using the formula described above, the ^{14}C results can also be expressed as absolute activity concentration of the water samples (Table 3). Because the main part of the carbon is in the inorganic form, the absolute activity concentrations of the TDC and the DIC are close to each other. Regarding the results of our investigations over the 14 different water samples around the Paks NPP (Figure 3), the DO[14]C contribution to the total ^{14}C activity changes between 5 and 25%.

Table 3   Absolute activity concentrations for the different carbon fractions in the monitoring well of the Paks NPP

Sample name	TD^{14}C (mBq L^{-1})	DI^{14}C (mBq L^{-1})	DO^{14}C (mBq L^{-1})	DO^{14}C ratio in TD^{14}C
HWC*	8.1 ± 0.1	7.4 ± 0.1	0.8 ± 0.1	10%
Danube	9.6 ± 0.1	8.8 ± 0.1	0.8 ± 0.1	8%
Well 1	12.0 ± 0.1	11.0 ± 0.1	1.0 ± 0.1	8%
Well 2	14.5 ± 0.1	13.0 ± 0.1	1.5 ± 0.1	10%
Well 2	16.6 ± 0.1	13.7 ± 0.1	3.0 ± 0.1	18%
Well 4	17.0 ± 0.1	15.3 ± 0.1	1.7 ± 0.2	10%
Well 5	21.0 ± 0.1	16.6 ± 0.1	4.5 ± 0.2	21%
Well 6	21.3 ± 0.1	19.1 ± 0.1	2.2 ± 0.2	10%
Well 7	25.3 ± 0.1	19.1 ± 0.1	6.3 ± 0.1	25%
Well 8	26.6 ± 0.1	23.4 ± 0.1	3.3 ± 0.2	12%
Well 9	26.6 ± 0.1	21.8 ± 0.1	4.7 ± 0.2	18%
Well 10	26.7 ± 0.1	21.8 ± 0.1	5.0 ± 0.2	19%
Well 11	63.3 ± 0.4	50.4 ± 0.2	12.9 ± 0.9	20%
Well 12	75.6 ± 0.4	71.6 ± 0.3	4.0 ± 2.5	5%

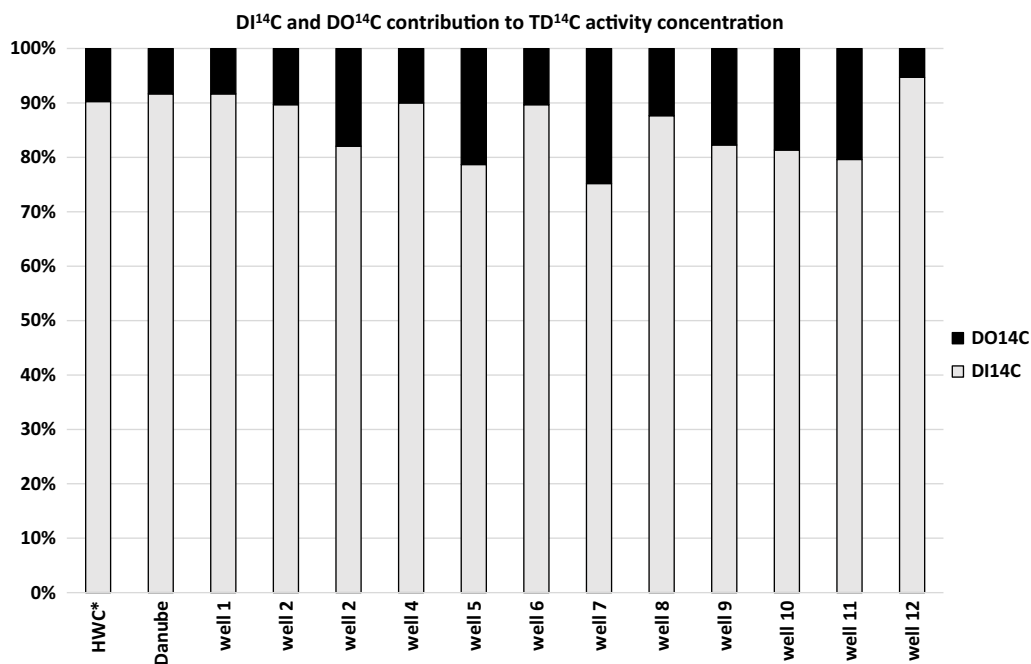*HWC: hot water channel, where the cooling river water returns to the Danube.

Figure 3   Contribution of DI^{14}C and DO^{14}C to the total dissolved carbon ^{14}C activity of the measured groundwater samples.

CONCLUSION

Previous studies have demonstrated the importance of organic ^{14}C measurements in the environmental monitoring of PWR NPPs, as a condition of the technological system, engineering barriers can be controlled and assessed by analyses of organic fraction. One of disadvantages of the only inorganic carbon determination is that the DIC concentration has a significant dilution effect by the natural ^{14}C content of the groundwater on any discharged pollution surrounding the power plant. The total amount of ^{14}C contamination released to groundwater, and hence the exact radiation dose contribution, can be assured with detection and measurement of the total amount of the released (radio)carbon.

Monitoring of uncontrolled ^{14}C emissions of nuclear facilities into groundwater is nowadays performed mainly on the basis of the measurement of the inorganic fraction, nowadays. Within the framework of this study, a simple wet oxidation method was developed for the AMS ^{14}C measurement technique to determine the ^{14}C activity concentration of the total dissolved carbon content of water samples. By the separate measurement of the inorganic and total ^{14}C content in the groundwater in the monitoring wells of the Paks Nuclear Power Plant it was experienced that the ^{14}C contamination getting into the groundwater of the power plant is emitted mostly in inorganic form but can be significant ^{14}C contribution (up to 20%) from the organic fraction which increases the total uncontrolled ^{14}C release. DOC contribution to the TDC ^{14}C activity concentration might be rather higher for the groundwater around radioactive waste storage facilities, especially if significant amount of ^{14}C labelled organic waste is restored in them. During the investigation was obtained between 83.9 and 513.7 pM in TD14C value in monitoring wells of Paks NPP. The calculated DO^{14}C results show that organic fraction can be higher than inorganic fraction. The results of our investigations over the 14 different water samples around the Paks NPP show that DO^{14}C contribution to the total ^{14}C activity concentration was about 5–25% in average.

The elaborated method may be especially useful for environmental monitoring analyses of nuclear facilities and radioactive waste disposal facilities, as with the help of this method, the total ^{14}C activity of groundwater can be determined as easily as the commonly applied DI^{14}C analyses. This way, detection of ^{14}C contaminations becomes possible also in the dissolved organic fraction having been rarely analyzed.

ACKNOWLEDGMENTS

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