



RESEARCH ARTICLE

Novel dissolved organic ^{14}C analyses method applied in a case study at a LILW waste repository

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Abstract

A routine chemical procedure was developed at the Ede Hertelendi Laboratory of Environmental Studies (HEKAL), in Debrecen which can measure the dissolved organic radiocarbon content of groundwater as well as the inorganic and total fraction. The typical background of this non-purgeable dissolved organic radiocarbon preparation is 0.73 ± 0.14 percent modern carbon (pMC), using a carbon contamination correction on fossil dissolved material (potassium hydrogen phthalate) samples.

Within the framework of this study, the determination of the specific activity concentration of the radiocarbon in inorganic, organic and total carbon of groundwater was performed for selected monitoring wells and surface waters of the Püspökszilágy Radioactive Waste Treatment and Disposal Facility, Hungary. The aim of our extensive investigation was to determine the radiocarbon concentration of the organic carbon fraction as well as the inorganic part in the vicinity of the facility.

The dissolved inorganic ^{14}C results of the analysed samples did not show specific excess anthropogenic ^{14}C around the investigated facility, however, an anthropogenic effect was observed for the organic fraction of every groundwater sample, with ^{14}C activity concentration values significantly exceeding 192 pMC, while the highest value of absolute activity concentration of the organic fraction was found to be only 72.4 ± 3.6 mBq L⁻¹.

Introduction

Environmental monitoring of the radiocarbon emission from nuclear waste disposal facilities into the groundwater has mainly been limited only to the measurement of the inorganically bound radiocarbon (^{14}C) in most of the countries where nuclear waste was stored. However, an exact dose calculation would need the total activity, not just the radiocarbon in the inorganic form. Therefore, in addition to the determination of inorganic radiocarbon, Hungarian monitoring programs have also incorporated the measurement of TD ^{14}C (total dissolved radiocarbon) fraction. As a result, these measurements are becoming more and more widespread during environmental assessments, not only for research purposes, but also are requested by clients and authorities as well.

The migration of organic carbon from soil to groundwater is influenced by the water transport and the structure and composition of soil. Organic materials in groundwater facilitate the solubility of heavy metals and radionuclides, and this is an important rationale for the analysis of this component.



In addition to the naturally occurring dissolved organic materials (humic materials), organic material may also increase from anthropogenic sources, therefore, by analysing this fraction, a more precise image can be obtained about actual anthropogenic contamination (Barisevičiūtė et al. 2020; Wassenaar et al. 1990).

According to UNSCEAR (2000), the global collective effective dose from LILW (low and intermediate level radioactive waste) storage is almost entirely due to ^{14}C . Radiocarbon is one of the most significant radionuclides in the population dose contribution of the LILW disposal facilities. Thus, the ^{14}C inventory limit set by national authorities is always at the centre of assessments, as usually this is the limiting radionuclide. However, real monitoring measurements are rarely performed for the determination of the actual ^{14}C content of the wastes due to difficulties in sampling and difficulties in measuring radiocarbon from such samples. Therefore, the estimated total activity of the ^{14}C in a given waste disposal facility usually has high uncertainty, however, the quantity of ^{14}C in the waste may determine the method of storage and may limit the quantity of waste to be stored in the given facility (Yim and Caron 2006).

As a part of the environmental monitoring program of nuclear facilities and radioactive waste disposal facilities, the calculation of the exact dose can be performed by knowing the total activity of the emission and considering each chemical form of the given radionuclide. The chemical form highly influences the applicable analytical procedures and their selectivity. As a significant quantity of organically bound radiocarbon can be emitted from nuclear waste storage facilities to the environment (Yim and Caron 2006; Veres et al. 1995), the selection of the appropriate analytical procedure is very important to perform precise dose calculation.

The measurement of dissolved inorganic ^{14}C (DI^{14}C) has become a routine technique, as it uses rapid sample preparation, and this carbon species appears in the highest concentration compared to other dissolved species. By contrast, the organic material content of groundwater is significantly lower (less than 1–2 mg L⁻¹ dissolved organic carbon (DOC) concentration) (Wassenaar et al. 1990).

It is important that in case of the ^{14}C escaping from underground waste disposal facilities, it is usually the organic ^{14}C to cause actual radioactive dose contribution due to its high solubility and lack of retention (Johnson and Schwyn 2004; Lindgren et al. 2001; Niemayer et al. 2004). In the case of a surface waste disposal facility, additional important factors can be the unconditioned nature of the waste and significant gas formation.

Therefore, we considered it important to assess the ^{14}C isotope in the total dissolved fraction and the organic fraction, in addition to the DI^{14}C subject to continuous monitoring, as well in the environment of the radioactive waste disposal facility. This, we had to develop a new method to assess these fractions.

Nowadays, several different methods can be used to liberate organic carbon from water samples for AMS measurements, including UV oxidation (Lang et al. 2016; Xu et al. 2022), freeze-drying (Wacker et al. 2013), solid phase extraction (Dittmar et al. 2008), ultrafiltration methods (Benner et al. 2004) and wet-oxidation methods (Leonard et al. 2013).

Our purpose was the most complete and comprehensive possible digestion without any special devices (such as a UV digester); therefore, we have adapted the method in Leonard et al. (2013) and improved on it. In this procedure for the separate analysis of the organic fraction, a wet oxidation for ^{14}C AMS measurement was used, based on our oxidising agent procedure, that has already been already applied for TD^{14}C sample preparation (Molnár et al. 2022).

Materials and methods

Description of the study site

The Püspökszilágy Radioactive Waste Treatment and Disposal Facility (RWTDF) began operation in 1976, and is located about 40 km from Budapest, Hungary, between the villages of Püspökszilágy and Kiszémedi, as shown in Figure 1. The purpose of the construction of the disposal facility was to solve the temporary and permanent disposal of the low and intermediate level wastes, radiation sources,



Figure 1. Location of the Püspökszilágy Radioactive Waste Treatment and Disposal Facility (RWTF), Hungary.

wastewater and other liquid wastes (organic solvents, oily materials, scintillation cocktails) generated during radioactive isotope production, the industrial use of such isotopes, and during the operation of experimental and training reactors and in laboratories.

Following the recommendation of the IAEA, the facility was constructed on a hilltop, on an area of suitably high clay content (as it has good isotope absorption ability; here there is a clay layer of at least 2 m even on the worst location for foundation), on a host rock with low-speed water movement. Groundwater is located at a depth of almost 20 m, therefore, the migration of radioisotopes into groundwater can be avoided or at least restricted. Within the controlled zone, the disposal facility consists of close-to-surface outdoor, reinforced concrete storage vaults (vaults “A” and “C”) and carbon steel and stainless-steel wells (wells “B” and “D”). In the outdoor containers (wells and vaults) of the radioactive waste treatment and disposal facility, up to 5040 m³ radioactive waste can be permanently stored. According to the routine at the time (as there were no waste reception criteria), the wastes were placed in the facility partly unconditioned and without proper characterization.

According to the regulations during the 1970s–1980s, long half-life isotopes and radiation sources were also put into the vaults, without any special conditioning and characterization.

Later safety analyses in Hungary and elsewhere have shown that these containers (of RADON type) are not suitable for the storage of unconditioned long half-life isotopes (such as ¹⁴C) (IAEA 2005; RHK 2023).

To fix this issue, the waste packages are removed from the vaults, selected, suitably conditioned and repacked. In the RWTF, a safety program was launched in 2008 by the selection and reclassification of 4 storage vaults.

The program required the placement of some, or based on a later decision even all, of the wastes into a geological disposal facility with suitable engineering and geological barriers (National

Radioactive Waste Repository, Bataapáti, Hungary), of course after selection, conditioning and suitable classification.

Key safety tasks are repacking, appropriate characterization and safe long-term disposal of these so-called historical wastes according to today's requirements and the thorough monitoring of the waste disposal facilities ensuring the storage of the given wastes so far, which includes the determination of the isotope selective activity concentrations and also the chemical forms. Precise characterization is a precondition for safe and long-term future disposal of the waste and also highly simplifies such disposal.

Sampling of monitoring wells of the RWTF site

As there is agricultural activity at the site of the RWTF and in the surrounding areas, several monitoring wells are operated, and sampled with different frequencies.

The soil in and around the facility is cohesive clay soil of mostly low water conductivity, therefore, groundwater movement and recharge are slow. As a result, the purging (meaning a high quantity of water removal) which is required by the standard for water sampling may highly intervene into the natural hydrological processes, and it may also facilitate the spread of contaminants. Furthermore, due to the high ^{14}C and tritium concentration of the groundwater next to the storage vaults, purging is not always possible, as the water removed by pumping cannot be released into the environment or the drainage system. The wells which can be pumped were sampled after purging, while the wells which cannot were sampled from the filtered layer of the well by a bailer sampler. To avoid cross-contamination, each well had its own bailer.

Samplings were performed in the offsite wells within the framework of an individual sampling campaign in October 2022. During this campaign, samples were taken from 16 monitoring wells and at 4 sampling locations from 4 surface water bodies (3 watercourses and a fishpond), for organic and inorganic carbon analysis, as well as total carbon ^{14}C AMS measurement. The water samples taken (500 and 1000 mL) were stored in the dark at 4°C without conservation, in brown glass containers until processing.

Determination of carbon content

For the calculation of the absolute activity concentration of the water samples, a Shimadzu TOC-TN device was used to determine the dissolved inorganic and organic carbon content of the samples. For the filtration of the samples, the filter types applied during ^{14}C sample preparation were used, depending on chemical form. The sample volume sufficient for the performance of ^{14}C measurement was determined based on the dissolved organic carbon content. Furthermore, the carbon concentration values and the specific activities of DI^{14}C and TD^{14}C made it possible to estimate the NPDO^{14}C (non-purgeable dissolved organic ^{14}C) value. The carbon content results alone also provide information about the extent of organic carbon contamination and occurrence.

Dissolved inorganic carbon (DI^{14}C) sample preparation of water sample

The determination of the dissolved inorganic carbon ^{14}C (DI^{14}C) content from groundwater was performed by releasing the CO_2 by acidification with phosphoric acid.

First, a 20 mL water sample was injected by disposable plastic syringe through a $0.45\ \mu\text{m}$ CA (cellulose-acetate) syringe filter into a pre-evacuated vacuum-tight 2-finger glass (2×10^{-2} mbar) reaction vessel and then 2 mL 85% phosphoric acid was added by plastic syringe. The mixture of water and phosphoric acid was heated to 75°C for 1 hr in a heating block (Molnár et al. 2013).

Total dissolved ^{14}C preparation (TD ^{14}C) of water sample

In our laboratory, we have developed a sample preparation method based on the method for chemical oxygen demand determination, which was achieved by the modification of the procedure defined in the Hungarian Standard MSZ ISO 6060:1991. An Ag_2SO_4 and a $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ solution was prepared (Molnár et al. 2022) for the joint digestion of the organic and inorganic compounds.

For the determination of the total fraction, 10 mL of water sample was sufficient. To this sample, 6 mL of digestion solution was injected into a reaction vessel with PTFE stopcock, which was previously evacuated below 2×10^{-2} mbar. During digestion, the sample was heated at 120°C for 2 hr, and the CO_2 sample generated was treated in the same way as after the DI ^{14}C digestion given above.

With this method, a ^{14}C detection limit of as low as 1–2 pMC can be achieved, and a great advantage of this method is that it is suitable for the joint determination of the organic and the inorganic fraction with the same energy investment as the DI ^{14}C determination, and it can be implemented for more precise dose calculations as well, as it also considers the organic fraction.

Dissolved organic ^{14}C preparation of water sample

The dissolved organic carbon preparation method is quite sensitive to carbon contamination because of the generally low organic carbon concentration in groundwater aquifers. For the determination of dissolved organic ^{14}C , a wet oxidation method was also developed.

Previously, Leonard et al. (2013) had already published ^{14}C blank results obtained by wet oxidation. Their method is similar to ours: they oxidised the remaining organic material after vacuum distillation, however, the key difference is the oxidising agent: we replaced the KMnO_4 used by them to the solution used in our recipe. The reason for this replacement was partially that we were unable to achieve the desirable low and well-reproducible background value using the solvent reported in Leonard et al. (2013).

One of the reasons for this high background standard deviation obtained by the previous method could have been that it was necessary to open the flask to atmosphere, and 150 mg of potassium permanganate had to be manually added to the flask. Although an inert gas (e.g. N_2 or Ar) could have been used to bring the pressure in the vessel up to atmosphere, before adding the potassium permanganate, this step is still quite sensitive and not well controlled. Our modified oxidation process consists of three main steps. Firstly, the inorganic carbon is removed from the sample by adding 2 mL phosphoric acid (85% ACROS, extra pure) to the filtered water sample. The sample volume can vary between 400 and 800 mL, depending on the dissolved organic carbon content. At the filtration step, a $0.7 \mu\text{m}$ pre-baked (450°C , 5 hr) glass filter (GF) is used. The filtered water sample flask is connected to a vacuum evaporation system for overnight (3×10^{-1} mbar 40°C), which is shown in Figure 2. The water and phosphoric-acid mix are concentrated with a lyophilization unit (Leonard et al. 2013). Then, the organic forms are oxidized by Ag_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ solution (Molnár et al. 2022). During the NPDO ^{14}C preparation, we applied the same digestion solution as in case of TD ^{14}C preparation method. A volume of 6 mL dichromate solution is added to the mixture of the phosphoric acid and organic component under vacuum (2×10^{-2} mbar) through the septum by a glass syringe, without opening the flask. Then the flask is heated at 120°C for 1 hr. Finally, the carbon dioxide produced is recovered and purified cryogenically. The extracted CO_2 samples were then heated (12 hr 550°C) with MnO_2 and Ag wool by a sealed-tube combustion (Janovics et al. 2018) and the purified gas sample was converted to graphite using the sealed tube method developed in the HEKAL laboratory (Rinyu et al. 2013). Finally, the graphite was pressed into an AMS target for measurement.

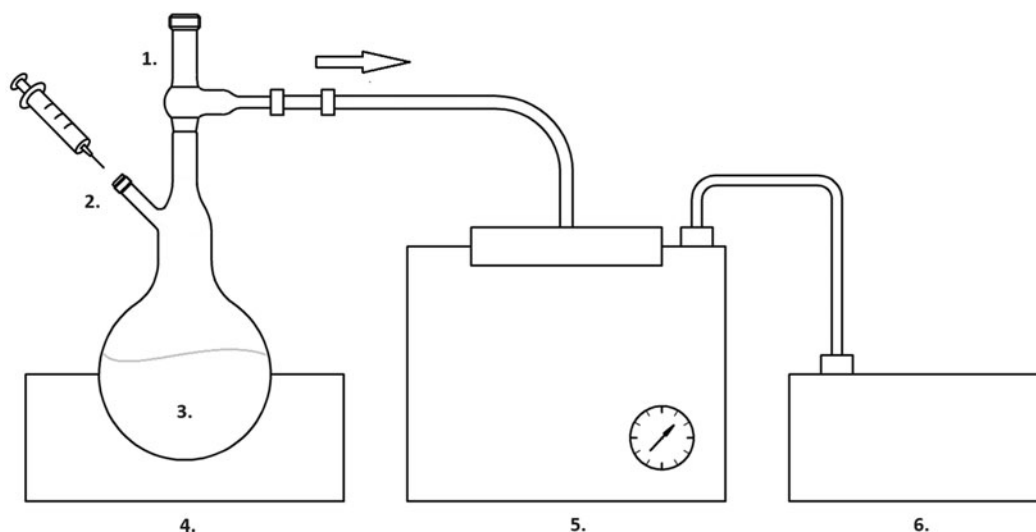


Figure 2. The schematic of the applied vacuum distillation system for NPO¹⁴C extraction. 1. PTFE valve, 2. PTFE septum 3. Sample flask; 4. Heating block; 5. Freeze dryer; 6. dry vacuum pump.

¹⁴C AMS measurements

Radiocarbon measurements were all performed by accelerator mass spectrometry, since it has lower detection limit, and it can also be used to the determination of the organic ¹⁴C component in case of smaller samples.

The specific ¹⁴C content of the sample graphite is measured by MICADAS accelerator mass spectrometer (AMS). Using the MICADAS, a counting statistical uncertainty of ± 3‰ can be achieved for modern samples, with a measurement time of as little as 30 minutes.

During the ¹⁴C AMS measurements, results are compared to international reference materials with known ¹⁴C activity. IAEA-C1 is a marble (¹⁴C free carbonate, blank), IAEA-C2 travertine (41.14 ± 0.03 pMC) was measured in parallel with the samples.

In the case of organic preparation, we used IAEA-C9 (old wood 0.23–0.30 pMC) and IAEA-C6 (sucrose 150.61 ± 0.11 pMC) and the preparation process is done in the same way as the unknown water samples (Molnár et al. 2013).

The suitability of the NPDO¹⁴C method was analyzed by using multiple organic international standards, such as the IAEA-C3 and the IAEA-C5-C9 international standards and potassium hydrogen phthalate (KHP, puriss) which was applied as blank reference material for DOC sample preparation (Murseli et al. 2019).

In a series of tests, the excess carbon introduced by the chemicals used during sample preparation was also determined. The reference materials were tested by 5-5 parallel measurements (sample amount was between 1–2 mg C) by adding 2 mL of H₃PO₄ and 6 mL oxidising agent, in the same way as done for real samples.

The specific activity concentration of the samples, corrected for carbon contamination (Scorr in pMC) was calculated by the Equation (1) below:

$$Scorr = \frac{mx * Rx - mc * Rc}{mx - mc} \quad (1)$$

where *mx* is the total mass of the sample and the contaminant (in mg), *Rx* is the joint specific activity concentration of the sample and the contaminant (in pMC), *mc* is the mass of carbon contamination (in mg) and *Rc* is the specific activity concentration of the carbon contaminant (in pMC).

Table 1. Measured ^{14}C results of the IAEA reference materials (Gröning et al. 2007) using our novel wet oxidation method

IAEA reference material	Material	Reference value (^{14}C activity (pMC))	Carbon yield (m/m%)* (n = 5)	^{14}C (pMC) measured (n = 5) No contamination correction ($\pm 1 \sigma$)	^{14}C (pMC) constant contamination corrected (n = 5) ($\pm 1 \sigma$)
IAEA-C3	Cellulose	129.41 ± 0.06	41.9 ± 0.6	128.02 ± 0.33	130.83 ± 0.81
IAEA-C5	Wood	23.05 ± 0.02	48.8 ± 1.5	24.01 ± 0.14	23.25 ± 0.25
IAEA-C6	Sucrose	150.61 ± 0.11	42.4 ± 0.5	146.72 ± 0.23	149.96 ± 0.33
IAEA-C7	Oxalic acid	49.35 ± 0.12	20.9 ± 0.8	48.94 ± 0.12	49.58 ± 0.28
IAEA-C8	Oxalic acid	15.03 ± 0.17	20.1 ± 0.3	16.96 ± 0.08	14.50 ± 0.59
IAEA-C9	Fossil wood	0.23-0.30	49.6 ± 0.6	2.43 ± 0.04	0.52 ± 0.33
KHP	Potassium hydrogen phthalate, fossil	~ 0*	47.3 ± 1.4	2.54 ± 0.11	0.73 ± 0.14

*Expected value.

A constant contamination approach is based on previous works (Bronk et al. 1990; Ruff et al. 2010; Santos et al. 2007). The hypothesis of the model is that if we apply the same tools, same amount of same chemicals, same recipe in the same Laboratory, when a sample of carbon mass and $^{14}\text{C}/^{12}\text{C}$ ratio is prepared along the preparation process, it is mixed with a contaminant that is constant with respect to its mass and isotopic ratio.

In our study, we have tested the constant contamination approach, using several repetitions of known ^{14}C reference materials in known amount, where we measured the final ^{14}C ratio of the prepared samples. In this way, we have determined our constant contamination parameters: with respect to its mass and isotopic ratio and applied these for correction of unknown samples measured ^{14}C value.

It is to be expected that if one runs several reference material tests to measure the mass and isotopic ratio of the contaminant, there will be some variability. The lower scatter of the mass and isotopic ratio of the contaminant, the better applicability of the constant contamination model and the better/lower final analytical uncertainty when the contamination correction has been applied. That is why it is desired to have stable, constant contamination in the process, even if it means a bit higher, but more stable contamination correction.

Results and discussion

The ^{14}C AMS results of the suitability test series for the NPDO ^{14}C method are summarised in Table 1. During the test, organic IAEA standards and fossil (^{14}C free) materials were used in the range of 0 and 150 pMC. The yield of the digestion can be stated as stable, based on the material.

The obtained ^{14}C results were corrected for background. Carbon contamination was tested by using blank samples, during which the CO_2 released from the phosphoric acid and the digestion solution was directly obtained and measured. From the mixture of chemicals (H_3PO_4 and the sulphuric acid solution with dichromate), an average 70 μg carbon was generated with a specific activity concentration of 50 pMC (\pm rel 10%, $n=10$). The ^{14}C -free fossil samples, such as the IAEA-C9 and the potassium-hydrogen-phthalate gave similar preparation blank values of 2.5 pMC, however, using the applied carbon contamination calculation, this value dropped below 1.0 pMC. In the case of modern samples,

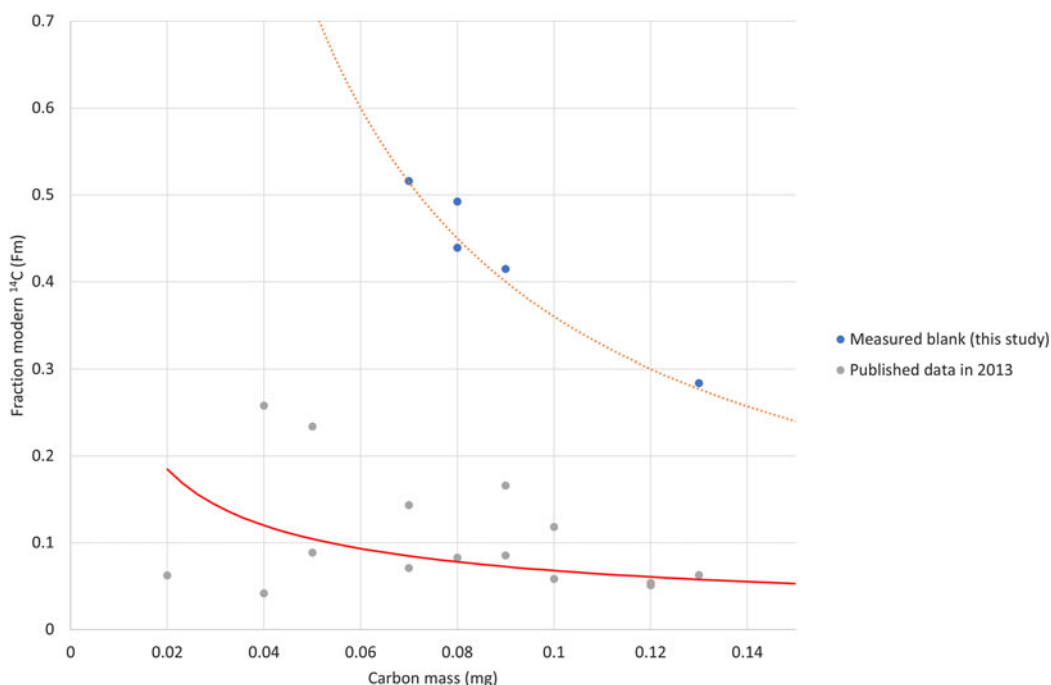


Figure 3. Comparison of ^{14}C values (Fm) of blank samples (0.02–0.15 mg C) with results published by Leonard et al. (2013).

the contamination-corrected measured ^{14}C values did not show any significant deviation from the expected values.

Compared to our TD ^{14}C method (where the background is < 2 pMC without contamination correction), the increase in the background in case of the NPDO ^{14}C method is presumably caused by the organic material content of the phosphoric acid during the DIC step (2 mL). Multiple studies deal with the possible methods of the removal of organic material from H_3PO_4 , since the basic materials from which the phosphoric acid is manufactured are the phosphate minerals that are bound to organic materials, so some excess organic carbon should be expected due to its nature (Anouar et al. 2021; Hamza et al. 2013; Tanaka et al. 2009). The applied phosphoric acid was purified before the dissolved organic radiocarbon process to decrease contamination. In our laboratory, we used ozone purification for this purpose, during which ozone was bubbled through the extra pure phosphoric acid in a closed system, for 3 hr. The organic carbon contaminant in the dichromate sulphuric acid used was determined separately, which was found to be modern, with a specific activity concentration of 103 pMC (Molnár et al. 2022).

To determine the ^{14}C blank level and constant contamination for the method, 5 parallel blank samples were prepared by wet oxidation, with a carbon content between 0.070 and 0.130 mg. These measurement results were compared to the ^{14}C blank results by applying the constant contamination model published earlier by Leonard et al. (2013) in this low sample mass range (< 0.150 mg), which is shown in the Figure 3. By plotting the blank fraction modern ^{14}C values against the carbon content of the sample, it can be seen that although the absolute value of the background of the wet oxidation method applied by us is higher, i.e. 0.50 Fm (50 pMC) for 0.07 mg sample. In the comparison of the two methods, for the same sample mass, 0.07 and also 0.14 fraction modern values were also obtained by the Leonard et al. (2013) method, which means a high uncertainty and high standard deviation, making the constant contamination correction method difficult to apply. For the two 0.08 mg blank samples, 0.47 ± 0.04 ($n=2$) fraction modern (47 ± 4.0 pMC) values were obtained, which is higher than the previously

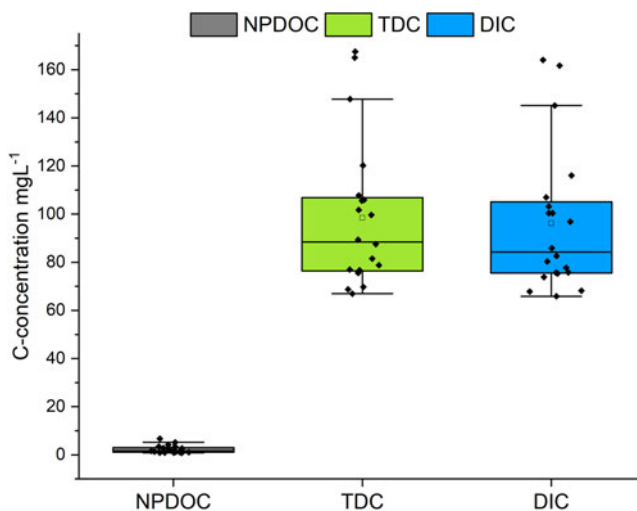


Figure 4. Boxplot diagram of the dissolved inorganic (DIC), total dissolved (TDC) and non-purgeable dissolved organic carbon (NPDOC) content of the monitoring wells.

published values. The more stable value makes in easier to correct for carbon contamination calculation, and it can be used more reliably, especially in case of samples of lower C yield.

Potassium dichromate was used for determination of COD (chemical oxygen demand), using this method the oxidation efficiency of many organic compounds is between 90–100% (MSZ ISO 6060:1991 standard). In contrast to Leonard’s solid potassium permanganate method, our destructive agent is a multicomponent solution that can increase the amount of carbon contamination introduced even with the highest purity, pre-treated chemicals. Since the liquid oxidant can oxidize the carbon content of the applied all chemicals more completely, then the “contaminant C” could also become more digested, leading to increasing blank results and more shifted reference sample results.

The previously reported higher background scatter of Leonard’s method can be due to the way of introducing the solid phase oxidant, since this step requires the reaction cell to be opened to the air. With our modification, we can avoid this opening step and ensured vacuum (10^{-2} mbar) during the entire sample preparation process.

Evaluation of the results of the dissolved carbon concentration of the groundwater monitoring wells

After the determination of the dissolved inorganic, non-purgeable dissolved organic and total carbon concentrations of the 20 water samples, we found that carbon is present mostly in inorganic form in the analyzed samples. The mean concentration of the dissolved inorganic carbon is 96 mg L^{-1} , while the total carbon concentration was 98 mg L^{-1} . In the case of the majority of the wells, the organic fraction is only 1–4 % of the total carbon content ($1\text{--}3 \text{ mg L}^{-1}$), as shown in Figure 4. As regards the total carbon content, samples W-5 and W-14 gave the highest concentration (around $160\text{--}170 \text{ mg L}^{-1}$), while the lowest total dissolved carbon concentration (less than half) was found in the samples W-16 and W-13 ($60\text{--}70 \text{ mg L}^{-1}$).

The dissolved organic carbon content values reflect the values typical for groundwater in this region, i.e. below 2 mg L^{-1} and $2\text{--}10 \text{ mg L}^{-1}$ for surface waters (rivers, lakes) (Thurman 1985). In case of the four monitoring wells (W-5, W-11, W-14 and W-15), higher organic carbon concentrations were found, up to $5\text{--}6 \text{ mg L}^{-1}$. The highest DIC and TDC values were found in the wells W-5, W-11 and W-14. Out

Table 2. ^{14}C results of different C fractions in the water samples from monitoring wells and surface water near the Püspökszilágy RWTF, Hungary

Sample name	DI ^{14}C pMC	TD ^{14}C pMC	NPDO ^{14}C pMC
SW-1	103.23 ± 0.15	104.30 ± 0.10	104.03 ± 0.29
SW-2	94.48 ± 0.14	95.70 ± 0.10	93.39 ± 0.31
SW-3	92.36 ± 0.14	93.60 ± 0.70	85.43 ± 0.27
SW-4	100.85 ± 0.20	101.20 ± 0.21	106.60 ± 0.32
W-1	91.10 ± 0.20	113.35 ± 0.16	2541.65 ± 2.9
W-2	53.90 ± 0.10	58.20 ± 0.10	293.45 ± 0.60
W-3	118.22 ± 0.30	112.40 ± 0.32	322.53 ± 0.61
W-4	87.89 ± 0.30	96.38 ± 0.28	427.53 ± 0.73
W-5	63.20 ± 0.10	75.17 ± 0.51	1177.16 ± 1.5
W-6	206.80 ± 0.40	225 ± 32	3089.3 ± 3.4
W-7	86.90 ± 0.10	89.50 ± 0.13	445.17 ± 0.79
W-8	56.49 ± 0.11	92.19 ± 0.13	764.30 ± 1.23
W-9	87.90 ± 0.10	91.71 ± 0.13	515.60 ± 0.84
W-10	76.10 ± 0.70	76.12 ± 0.12	192.25 ± 0.49
W-11	36.31 ± 0.09	39.87 ± 0.14	193.25 ± 0.44
W-12	78.33 ± 0.13	82.31 ± 0.19	590.35 ± 0.93
W-13	81.93 ± 0.12	84.52 ± 0.19	318.86 ± 0.62
W-14	38.01 ± 0.09	42.58 ± 0.14	457.59 ± 0.89
W-15	65.64 ± 0.16	246.44 ± 0.32	6180.2 ± 6.5
W-16	134.20 ± 0.30	144.91 ± 0.35	764.3 ± 1.1

of the surface waters, the SW-1 was the highest organic carbon concentration (6.7 mg L^{-1}), since this was the water from a fishpond, and it is richer in organic nutrients than the other surface watercourses. In the majority of the cases, 700 mL filtered sample was suitable for initial sample volume, and in case of waters of higher NPOC, even 400 mL proved adequate.

Evaluation of the ^{14}C data of the offsite wells

Table 2 and Figure 5 show the ^{14}C AMS measurement results of the water samples from the different fractions (organic, inorganic and total carbon), in pMC, and the Table shows the same data expressed in absolute activity mBq L^{-1} .

By analyzing the DI ^{14}C values from regular environmental monitoring, it is seen that the samples basically show values between 36- 91 pMC, however, in case of 3 wells (W-3, W-6 and W-16), radiocarbon levels exceeding natural level were found, and the well W-6 showed 206.80 ± 0.40 pMC which has presumably originated from the facility waste.

The specific ^{14}C concentration of the precipitation falling on the ground reflects the current ^{14}C concentration of the atmosphere. This is reflected by the ^{14}C data of surface waters and therefore no effect of the disposal facility can be detected either upstream or downstream the facility.

Concerning the TD ^{14}C values of the wells assessed, multiple samples (5 wells) show increased ^{14}C values related to emissions of facility/anthropogenic origin (W-1, W-3, W-6, W-15 and W-16), however, results between 39 and 246 pMC were obtained. Every sample analyzed shows (except the sample W-3 which requires re-measurement) that the radiocarbon content of the total carbon is obviously higher than that of the inorganic fraction, since the total fraction includes the organic and inorganic carbon content as well.

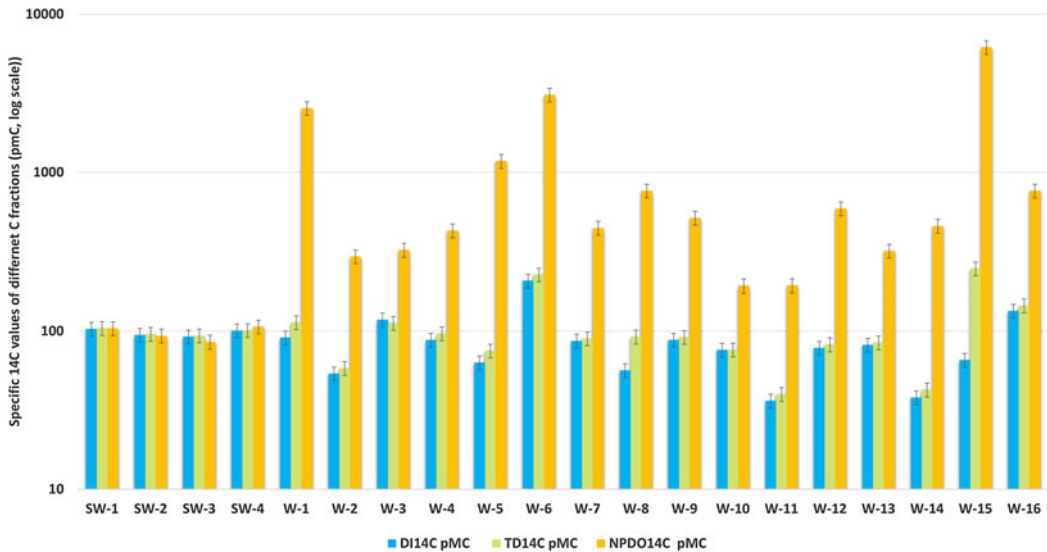


Figure 5. Comparison of the specific ^{14}C activity of different carbon fractions (dissolved inorganic, total and organic) SW: surface water, W: groundwater ($\pm 10\%$ rel. error) from the vicinity of the investigated repository.

By comparing the ^{14}C values of the inorganic and total carbon it can be demonstrated that the measurement of the DI ^{14}C alone is insufficient, and it is much less sensitive for the purposes of environmental monitoring, since there is a significant difference in case of the sample W-15 between the inorganic fraction 65.6 ± 0.2 pMC and the total carbon fraction 246.44 ± 0.32 pMC. In the case of surface waters, the difference between the two components is typically $\leq 1\%$, however, the difference between them in case of groundwater does vary: the total ^{14}C content is usually 3–35 pMC higher, and it was only the sample W-10 (76.10 ± 0.70 pMC) where the specific total ^{14}C activity concentration comes presumably entirely from the inorganic components.

This detected difference in the pMC specific activity concentration is given by the organic fraction which makes up only the 1–4% of the total carbon content. From the results above, one could conclude that the ^{14}C activity of the organic compounds emitted from the disposal facility is orders of magnitude higher than that of the emitted inorganic compounds. However, the inherent carbon content of the soil and groundwater has a significant diluting effect on the different carbon compounds, and the extent of dilution of course depends on chemical form (Geyh 2000). As seen from the composition measurements, the inorganic fraction has overwhelming majority of the water-soluble carbon, therefore, its diluting effect is also more significant. The inherently lower dissolved organic carbon content of groundwater has two orders of magnitude lower diluting effect. This is one of the reasons why the organic fraction has significantly higher specific activity concentration. At the same time, the monitoring of the organic ^{14}C is more sensitive by two orders of magnitude, to show any leakage in a container.

Given the results obtained, we consider it necessary to actually determine the specific ^{14}C activity concentration of the organic carbon component of water samples. The measurement results show that with the exception of the surface waters, almost every assessed well had excess dissolved organic ^{14}C , i.e. there were anthropogenic or facility-based emissions. The sum of organic and inorganic absolute activity concentrations approximately equals to the TD ^{14}C , except for the wells W-6 and W-15 where deviation exceeds three sigma. These exceptions may be due to an error in the determination of one of the constituent component (^{14}C measurement or carbon content). The reason of such deviation needs to be confirmed. In the monitoring wells, the lowest specific ^{14}C activity concentration in the NPDOC fraction was ~ 190 pMC (W-10), while the highest was ~ 6200 pMC (W-15), i.e. it can be stated that ^{14}C

Table 3. Absolute ^{14}C activity concentrations for the different carbon forms of water samples from the vicinity of the investigated repository ($\pm 10\%$ rel. error)

Sample name	DI ^{14}C (mBq L $^{-1}$)	TD ^{14}C (mBq L $^{-1}$)	NPDO ^{14}C (mBq L $^{-1}$)
SW-1	19.3	21.0	1.58
SW-2	22.0	23.0	0.57
SW-3	20.2	21.1	0.54
SW-4	26.5	27.5	0.99
W-1	16.0	20.2	6.10
W-2	12.2	13.4	0.85
W-3	20.2	19.5	0.92
W-4	14.7	16.5	1.68
W-5	23.4	28.5	9.17
W-6	40.1	44.6	11.4*
W-7	14.8	15.4	0.81
W-8	13.7	22.5	1.50
W-9	13.5	14.5	1.82
W-10	13.8	14.0	0.50
W-11	11.9	13.3	1.18
W-12	13.4	14.3	1.22
W-13	12.6	13.1	0.64
W-14	13.9	15.9	3.40
W-15	14.9	58.8	72.4*
W-16	20.0	21.9	1.90

*Deviation beyond the margin of error ($>3\sigma$).

from the disposal facility was detected in all the wells concerned. However, it is important to note that by converting these values to absolute activity concentration (Table 3), these values are not high at all compared to the DI ^{14}C and the TD ^{14}C , due to the very low DOC carbon concentrations. Sample W-15 shows significantly higher absolute activity concentration (~ 73 mBq L $^{-1}$), which significantly exceeds the absolute activity concentration found in the total fraction (~ 59 mBq L $^{-1}$), however, even this cannot be considered as a significant deviation given estimated relative errors of $\pm 10\%$.

We observe that there is no significant correlation between the ^{14}C results and the carbon concentrations, i.e. the higher dissolved organic carbon content does not necessarily come from an anthropogenic source, and a small sample concentration of 1 mg L $^{-1}$ can also have a higher specific ^{14}C value (~ 2500 pMC).

Conclusions

In the present study, we compared three in-house developed preparation method for DIC, NPDOC and TDC accelerator mass spectrometry radiocarbon measurements, and we applied these methods to the measurement the $^{14}\text{C}/^{12}\text{C}$ ratio of groundwater and surface water samples collected at the autumn of 2022 around the Püspökszilágy RWTDF.

The carbon concentrations of the samples collected from the assessed area show that, for each sample, about 96% of the carbon was in inorganic form and only 1–4% was in organic form. Therefore, the ^{14}C analysis of the organic samples was made difficult by such low amounts of organic carbon. A new AMS sample preparation method was developed to make it possible to directly determine the organic ^{14}C activity concentration of water samples.

The wet-oxidation method developed can be used to determine the specific activity concentrations of dissolved non-purgeable organic ^{14}C in environmental water, including in drinking water, surface water and rainwater. The suitability and the stability of the sample preparation method were tested by IAEA international standards and fossil (blank) samples. The results of the standards prepared by the revised wet oxidation technique were subject to constant carbon contamination correction by which the measurement results can be corrected. In the case of organic fossil background sample (IAEA-C9), the specific activity concentration was 2.43 ± 0.04 pMC (0.0243 ± 0.0004 Fm), and by applying the correction, a background of 0.52 ± 0.33 pMC (0.0052 ± 0.0033 Fm) was determined. For blank samples with a carbon content of $80 \mu\text{g}$, the method gave a fraction modern of 0.47 ± 0.04 (47 ± 4.0 pMC), which are higher than those obtained by Leonard et al (2013) by their wet oxidation method, however, we succeeded to achieve more reproducible, more stable and more reliable results.

The ^{14}C AMS results of the groundwater samples from the radioactive waste disposal facility showed that by comprehensively analyzing 16 well and 4 surface water samples, the DI^{14}C only showed excess radiocarbon possibly from the disposal facility in a single well out of the 20 (206.8 ± 0.4 pMC), while in case of TD^{14}C , this effect was observed for two wells. However, for the NPDO^{14}C results there is excess ^{14}C in almost every well, with values between 192 and 6180 pMC. Therefore, even though the measured inorganic and organic ^{14}C do not indicate any excess carbon, the organic form shows excess specific ^{14}C activity concentration in almost every case, which we attribute to the disposal facility. This means that the organic ^{14}C can detect emissions extremely quickly and sensitively and it can be a highly useful early indicator for environmental monitoring and in the water protection as well, as it may give a signal before the inorganic component. In this way, organic carbon can be a more efficient tool of the waste package integrity and contamination model tests and for the verification of engineering and geological barriers. However, it is important to note that as regards absolute activity concentration, the Püspökszilágy RWTDF has only very low emission dose, as even the well with the highest ^{14}C value only showed an activity of 72.39 ± 3.62 mBq L^{-1} .

Our study has demonstrated the possibility to use ^{14}C organic fraction in ground water as a tracer for early detection of radioactive releases from nuclear waste repositories. Practically organic radiocarbon (in addition to tritium measurements) could be used to monitor any unexpected releases from the repository that could cause significant harm to the environment.

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