



Method for organically bound tritium analysis from sediment using a combustion bomb



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ARTICLE INFO

Keywords:

Sediments
Organically bound tritium
Parr bomb
Liquid scintillation counting

ABSTRACT

The method consisted in combustion, using a Parr bomb type 1121, of a sediment - tritium free promoter mixture. The proper ratio sediment to promoter in our experiments was between 1:3 and 1:2, higher ratio resulting in unreliable results, due to incomplete combustion of the sample. The described method was used to measure the estuarine sediment sample from the 2nd International OBT Intercomparison Exercise, the average reported value being $163 \pm 12 \text{ Bq kg}^{-1}$ dry matter ($k=2$).

1. Introduction

Tritium and radiocarbon are currently the two main radionuclides that might be discharged in water bodies by the industry and particularly by heavy-water reactors, such as CANDU reactors. Tritium widely integrates into the water cycle and follows the water mass dynamics but it may also be integrated for long term into the organic pool, persisting in aquatic environment according to the recycling rates of organic matter (Eyrolle-Boyer et al., 2015). The experimental data indicated a time lag between concentrations of tritium in water and sediments, reflecting non-equilibrium attributed to the specific dynamics of tissue free water tritium (TFWT as HTO) and organically bound tritium (OBT) forms: TFWT follows the transfer of water while OBT depends on process linked to organic matter (biomass production, degradation and recycling). Tritium persistence through its OBT forms in biomass and aquatic systems may have a major impact on environmental compartments submitted to chronic releases (Eyrolle-Boyer et al., 2014), due to its significant radiotoxicity and contribution to the total dose (Galeriu et al., 2010; UNSCEAR, 2000).

Current measurement of organically bound tritium (OBT) from sediment using liquid scintillation counting (LSC) implies first of all conversion of organic matter in liquid water. In order to convert sediment organic matter to water it is necessary to perform a total oxidation process, which most commonly can be made through wet oxidation (Ware and Allot, 1999; Environment Agency, 2005) or combustion using different type of catalytic furnaces (Cossonnet et al., 2009; Daillant et al., 2004; Eyrolle-Boyer et al., 2014; Fournier et al. 2002; Morris, 2006; Vichot et al. 2005,) or the devices called oxidizers (Kim et al., 2013).

The objective of this study was to develop, optimize and verify a new method for analysis of OBT from sediments, using a Parr bomb type 1121. This kind of apparatus, already available in our laboratory, is considered a versatile device needing limited financial resources and also the duration of the combustion process is significantly shorter compared with the other kind of combustion devices.

The content of carbon and hydrogen in sediments are usually quite low, around 3% for carbon and 1% or less for hydrogen, and the combustion of the organic matter using a Parr bomb has limitations. In order to use this kind of device for sediment combustion we needed to mix the sample with a tritium free combustion promoter.

2. Experimental setup

The sediment samples were collected in the near vicinity of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD), on the Chemical Industrial Estate Rm. Valcea, from the location called Mixing Chamber – the place where the waste water from the entire industrial estate is collected. The PESTD is an experimental installation within the National Nuclear Energy Research Program. The developed technology involves a combined liquid-phase catalytic exchange (LPCE) and cryogenic distillation in order to remove tritium from CANDU moderator (heavy water). PESTD is part of the Institute for Cryogenics and Isotopic Technologies (ICSI), situated at a distance of about 10 km from the Rm. Valcea city. The wastewater from the PESTD is discharged outside the institute, into the sewage system of the Chemical Industrial Estate, which includes electrolysis units and also organic and inorganic synthesis installations. Given that in the vicinity of PESTD tritium level in all environmental compartments does not exceed the limit of 2 Bq L^{-1} , (Vagner et al., 2015) and the

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PESTD has no influence on the tritium level in the environment, we concluded that a sediment sample from the Mixing Chamber, influenced by industrial activities of Chemical Platform, will be suitable for our experiments.

The preliminary experiments involved the use of two fossil tritium free combustion promoters, heavy fuel oil (petroleum derivate) and coal, in order to choose one promoter which ensures complete combustion of the organic matter from sediments. The mixtures were made using one of the two sediments and each of the two combustion promoters, the ratio between sediment and promoter being 1:3 (wt.).

Once the promoter has been chosen, the second set of experiments involved finding the suitable ratio sediment: tritium free promoter, in order to have a complete combustion of the organic matter from sediment.

Both the preliminary test and the optimization of sample: promoter ratios involved preparation of a homogenous mixture of sample and promoter, which was combusted in the Parr bomb type 1121. The obtained combustion water was collected directly from the combustion bomb vessel.

2.1. Sample preparation

The sediment samples were dried at 60 °C in a ventilated oven until constant mass, milled, sieved on a 0.25 mm sieve and kept in the desiccator until use. The samples were collected in June (Sediment 1) and July (Sediment 2) 2014, from the location mentioned above, and they were used exclusively for these experiments.

The necessary step in order to use these sediment samples to measure OBT was to determine hydrogen content using elemental analysis. This type of analysis was made using THERMO analyzer FLASH 2000, which determined, using combustion, pyrolysis and chromatographic separation, the concentration of nitrogen, carbon, hydrogen and sulfur.

2.2. Tritium free promoters

Preliminary experiments involved the use of two tritium free promoters: heavy fuel oil (petroleum derived) and coal. Initially heavy fuel oil and coal were dried, to remove any trace of water that they might have. For this purpose heavy fuel oil was treated with anhydrous sodium sulfate followed by filtration of the solid and coal was dried in an oven at 60 °C until constant mass.

Hydrogen content of the two combustion promoters was also determined, given that combusting these along with the sediment will produce a dilution of the tritium, which must be corrected in the final calculation of the OBT from sediments.

2.3. Combustion water purification

All combustion water samples obtained after experiments were purified, using chemical treatment with sodium peroxide (Na_2O_2) and potassium permanganate (KMnO_4), followed by lyophilisation (Varlam et al., 2015). The water obtained after purification was checked to have a pH value between 5.5 and 8.0 and conductivity under $50\mu\text{S cm}^{-1}$.

2.4. Liquid scintillation counting

Purified combustion water was used for OBT measurements. For this purpose 8 g of water was mixed with 12 g of Ultima Gold uLLT from Perkin Elmer, in 20 ml polyethylene vials. Tritium measurements were performed with ultra low-level liquid scintillation counter Quantulus 1220 from PerkinElmer. Two background samples and tritium standards were simultaneously prepared for each batch. Tritium free water used as background was deuterium depleted water, with a D/(D+H) value below 10 ppm, obtained in our institute from steam by a patented technological process. It must be noticed that the

decision to use this type of water as tritium free water originated from the fact that the removal process of deuterium from natural water (only 15 Deuterium atoms to 10^6 hydrogen atoms) acts on all heavy hydrogen atoms including tritium. Counting efficiency was determined by internal standard method according to ISO 9698:2010 using tritium standard capsules provided by PerkinElmer containing tritium-labeled D-[5- $^3\text{H}(\text{N})$] glucose (reference standard NIST SRM 4947C) with a certified tritium activity of 3360 Bq at 1.4% per capsule, reference date September 6, 2013. Combustion water samples and backgrounds were counted for 1000 min per sample with a counting efficiency between 27.70% and 29.10%. In the same measurement conditions, the background varied between 0.663 ± 0.016 and 0.691 ± 0.016 cpm (counts per minute), following a minimum detectable activity of about 0.40 Bq L^{-1} , evaluated according to ISO 9698:2010. The uncertainty due to the statistical nature of radioactive decay and background radiation was reported at 1σ , but this was strongly influenced by the dilution factors applied to report OBT activity in sediments.

3. Results and discussions

3.1. Hydrogen content analysis

Given the dilution of the tritium during combustion of the mixtures between a sediment and a combustion tritium free promoter, hydrogen content of the two sediments, coal and heavy fuel oil was determined, in order to calculate the dilution factors and to determine the OBT activity from a specific sediment sample (Table 1).

It can be observed that Sediment 1 has higher hydrogen content, providing a lower dilution factor of the OBT in mixture with combustion promoters comparing with Sediment 2. For this reason Sediment 1 was used in preliminary experiments to choose a proper combustion promoter, which can provide a dilution factor lower than the sediment 2.

3.2. Preliminary experiments

In the first stage of our experiments, 4 g of Sediment 1 and 12 g of coal and heavy fuel oil respectively were mixed and combusted and the combustion water was used, after purification, to determine the OBT activity in the studied sediment, calculated with adequate dilution factors. For combustion of the sediment-coal mixture a number of three combustions were performed, in order to obtain the necessary amount of combustion water for one tritium measurement, given the fact that coal has low hydrogen content.

The calculation of dilution factors and tritium activity (OBT) after combustion was made using conversion of the hydrogen content to water. The elemental analysis of the combustion ash remained in the bomb was not relevant, giving the fact that the promoters used has a high hydrogen content and also the combustion water resulted from the combustion bomb has organic compounds as by-products (Paunescu and Galeriu, 2003; Verzezen et al., 2008).

The obtained results from OBT analysis in the studied sample were not the same, although a single sample of sediment was analyzed (Table 2). Activity of the OBT obtained from the combustion water of the Sediment 1 was higher when mixed with heavy fuel oil. This kind of problem is caused by the dilution of the OBT from the sediment, due to

Table 1
Hydrogen content of sediments, coal and heavy fuel oil.

| Component | Hydrogen content, % (wt.) |
|----------------|---------------------------|
| Sediment 1 | 0.79 ± 0.03 |
| Sediment 2 | 0.44 ± 0.03 |
| Coal | 3.42 ± 0.07 |
| Heavy fuel oil | 9.55 ± 0.14 |

Table 2

OBT activity in Sediment 1 measured with corresponding dilution factors, for combustion using mixtures of sediment with coal and heavy fuel oil.

| Combusted mixture | OBT activity in Sediment 1, [Bq L ⁻¹] | Dilution factor, f_{dil} | Number of combustions ^a |
|---------------------------|---|----------------------------|------------------------------------|
| Sediment - Coal | 18.36 ± 2.00 | 14.68 ± 0.63 | 3 |
| | 17.71 ± 1.99 | | |
| | 18.07 ± 1.99 | | |
| Sediment – Heavy fuel oil | 31.09 ± 8.05 | 37.26 ± 1.52 | 1 |
| | 33.81 ± 8.07 | | |
| | 32.13 ± 8.06 | | |

^a Number of combustions to obtain the necessary amount of water for one measurement.

incomplete combustion of organic matter from the sediment when mixed with coal.

Another problem we had to take into consideration was to prepare backgrounds for tritium measurement from the combustion promoters, especially to check if these promoters are free of tritium. The background prepared with combustion water from coal had a tritium activity of 0.85 ± 0.25 Bq L⁻¹, suggesting that this promoter was not tritium free. It must be stated that combustion water resulted from coal has tritium activity to the level of precipitation (IAEA/WMO – GNIP Database), suggesting that the process of mining and storage produces contamination, making it unusable for this type of analysis. Tritium activity of the combustion water prepared from heavy fuel oil was around 0.40 Bq L⁻¹, our value for minimum detectable activity, using as background deuterium depleted water.

The heavy fuel oil was selected among the two combustion promoters because it provides complete combustion of the organic matter from the sediment and also the lowest tritium content, similar to a usual background prepared from tritium free water. This promoter, which has a high viscosity, leads to a good homogeneity of the mixture, preventing the deposition of the sediment on the bottom of the combustion bomb capsule.

Next set of experiments involved the optimization of the sediment: promoter ratio, in order to have complete combustion of the organic matter from sediment.

3.3. Optimization of the sediment:promoter ratio

The experimental setup involved the mixing in different ratios of grounded dried sediments with the heavy fuel oil, directly into the combustion capsule of the combustion bomb. The ratio between sample and fuel oil varied from 1/3 to 1.

In order to obtain sufficient amount of water we combusted mixtures of 12 g heavy oil and 4, 6, 8, 10 and 12 g of Sediment 1 and Sediment 2 respectively.

Due to the use of heavy fuel oil, OBT from the sediment was diluted during the combustion, dilution factors depending on the sediment: heavy fuel oil ratio. Table 3 presents the dilution factors for each of the performed experiments and also OBT activity reported in combustion water of sediments, expressed in Bq L⁻¹.

The obtained results from OBT analysis in the studied samples, using different sediment: promoter ratios, were not the same, although they are the same two samples of sediment that were analyzed. This is due to incomplete combustion of organic matter in the samples for sediment: promoter ratios higher than 2:3, having as result a dilution of the OBT activity.

Similar results for OBT activity in sediments but with different uncertainties were obtained for sediment: promoter ratios of 1:3 and 1:2. Dilution factors are directly influenced by the hydrogen content of the sediment which, together with sediment: promoter ratio, has direct influence over reported uncertainties (Table 3).

Being the fact that a routine procedure of OBT analysis is not

Table 3

Dilution factors f_{dil} for different ratios of sediment: heavy oil used in combustion bomb and OBT activity in combustion water of two sediments, expressed in Bq L⁻¹.

| Sample | Sediment: Heavy fuel oil [g: g] | OBT activity in sediment [Bq L ⁻¹] | Dilution factor f_{dil} |
|------------|---------------------------------|--|---------------------------|
| Sediment 1 | 4:12 | 32.13 ± 8.06 | 37.26 ± 1.52 |
| | 6:12 | 30.90 ± 5.45 | 25.17 ± 1.02 |
| | 8:12 | 26.56 ± 4.19 | 19.13 ± 0.78 |
| | 10:12 | 24.68 ± 3.45 | 15.51 ± 0.63 |
| | 12:12 | 17.28 ± 2.86 | 13.09 ± 0.53 |
| Sediment 2 | 4:12 | 57.77 ± 16.71 | 66.11 ± 4.61 |
| | 6:12 | 41.19 ± 11.26 | 44.41 ± 3.10 |
| | 8:12 | 38.90 ± 8.63 | 33.56 ± 2.34 |
| | 10:12 | 30.87 ± 6.95 | 27.05 ± 1.89 |
| | 12:12 | 9.72 ± 5.59 | 22.70 ± 1.58 |

standardized each laboratory tries to develop a proper way to measure OBT concentration, depending on the laboratory equipment and the wide range of tritium level found in the area of interest. Also a reference material for OBT analysis is not commercially available, the only way to validate the method described above was participation to the 2nd International OBT Intercomparison Exercise 2014. Within this exercise it was sent as sample to be analyzed an estuarine sediment sample, prepared by GAU Radioanalytical Laboratories UK. Hydrogen content of the received sediment was $1.03 \pm 0.03\%$. The preparation technique for OBT analysis from the received sediment implied combustion, purification of the combustion water and measurement using LSC, the sediment: promoter ratio being 1:2 (6 g of sediment and 12 g of heavy fuel oil). Table 4 presents the reported results of the five replicates for this exercise. The average reported value of OBT was 1760 ± 125 Bq L⁻¹ (163 ± 12 Bq kg⁻¹ dry matter), to a confidence level of $k=2$, and it can be considered in according with assigned value reported of 170 ± 1.9 Bq kg⁻¹ dry matter (RADDEC, 2014; Croudace et al., 2015), to a confidence level of $k=1$. The reported values were evaluated by the organizer of the exercise using z score and zeta score. Our laboratory reached a good agreement between the average reported value and the assigned value, z score and zeta score being -0.44 and -1.06 respectively.

4. Conclusions

The new developed method, less expensive (capital equipment cost and operational cost), can be used to OBT measurement in sediment with few precautions.

The combustion water of the promoter must be checked to be tritium free water, the coal sample used in preliminary experiments having around 1 Bq L⁻¹ tritium activity concentration in its combustion water and not being suitable for this type of experiments.

The proper ratio sediment: heavy fuel oil in our experiments was between 1:3 and 1:2, higher ratio conducting to unreliable results, due to incomplete combustion of the sample.

This method was used to determine the OBT activity from sediment received within the 2nd International OBT Intercomparison Exercise, using as promoter heavy fuel oil and sample to promoter ratio of 1:2

Table 4

The reported results for sediment received within the 2nd OBT Intercomparison Exercise.

| OBT activity in sediment [Bq L ⁻¹] | OBT activity in sediment [Bq kg ⁻¹ dry matter] |
|--|---|
| 1712 ± 80 | 159 ± 12 |
| 1680 ± 79 | 156 ± 12 |
| 1821 ± 85 | 169 ± 13 |
| 1775 ± 82 | 165 ± 12 |
| 1813 ± 85 | 168 ± 13 |

(wt.).

The limitations of this method are the low levels of OBT and also low hydrogen content in sediment, due to the fact that mixing the sediment samples with a tritium free promoter conducts to dilutions of the OBT. The dilution factors varied between 37 and 25 for Sediment 1 with a hydrogen content of 0.79% and between 66 and 44 for Sediment 2 with a hydrogen content 0.44%.

Due to tritium dilution during combustion, minimum measurable activity of the OBT was around 13 Bq L^{-1} (0.9 Bq kg^{-1} dry) for Sediment 1 (which for sample to promoter ratio of 1:2 has a tritium activity in sediment combustion water of $30.90 \pm 5.45 \text{ Bq L}^{-1}$) and around 18 Bq L^{-1} (0.7 Bq kg^{-1} dry) for Sediment 2 (which for sample to promoter ratio of 1:2 has a tritium activity in sediment combustion water of $41.90 \pm 11.26 \text{ Bq L}^{-1}$). Also minimum measurable activity of the OBT for the sediment received from the organizers of the OBT exercise was around 6 Bq L^{-1} (0.5 Bq kg^{-1} dry) for a hydrogen content of 1.03%.

More investigations can be made to find another suitable tritium free combustion promoters, especially the ones which have lower hydrogen content and thus a lower dilution factor can be achieved.

Acknowledgments

This work was performed within the framework of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD) from Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea.

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