QUANTIFYING THE ORGANICALLY-BOUND TRITIUM LEVELS IN THE ENVIRONMENTAL SAMPLES AROUND THE CERNAVODA NUCLEAR POWER PLANT

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This paper is presenting the results of the organically-bound tritium (OBT) determinations, in the 2021 ÷ 2023 period, as part of a supplementary monitoring program around the Cernavoda Nuclear Power Plant, to quantify the OBT concentration levels in different types of environmental food samples (fish, vegetables, fruits and grains). The OBT concentrations are then added to the tissue free-water tritium concentrations (TFWT) to quantify each contribution to the total tritium levels in these samples. The OBT determinations are performed by the Environmental Control Laboratory of the Radioprotection Department of the Cernavoda NPP, using analytical methods validated through international inter-laboratory comparison exercises, organized by the OBT International Working Group.

Keywords: organically-bound tritium, tissue free-water tritium, environmental samples, radioactivity monitoring program, nuclear power plant

1. Introduction

Romania started to build, in the early '80s, the first nuclear site with 5 reactors (Fig. 1), located at about 2 km from the Cernavoda town, near the Danube River and the navigable Channel Danube – Black Sea. The nuclear design of the Cernavoda Nuclear Power Plant (Cernavoda NPP) is CANDU 6 (CANada Deuterium Uranium) technology, which is characterized by natural uranium fuel and heavy water used as moderated and coolant. Unit 1 of the Cernavoda NPP was commissioned in 1996 and Unit 2 in 2007, each with 700 MWe installed power. The two reactors alone ensure about 20% of the internal energy production of Romania.

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Fig. 1. View of the Cernavoda Nuclear Power Plant site.

2. The Environmental Radioactivity Monitoring Program

Tritium (H-3) can be produced in the nature through the interaction of cosmic rays with elements in the upper atmosphere [1]. Tritium isotopes then combine with oxygen to produce tritiated water (HTO), that enters the hydrologic cycle and then into biota and finally to the human body. Tritium decays (with a half-life, $T_{1/2}$=12.3 years) to a rare, stable isotope of helium (^3He) by $\beta-$ emission with a maximum energy of 18.6 keV.

For a typical CANDU reactor, about 97% of tritium is produced in the heavy water moderator system (${}_0n^1 + {}_1H^2 \rightarrow {}_1H^3 + \gamma$), and most of the remaining tritium production occurs in the heat transport system [2].

Considering tritium as the main contributor to the radioactive effluents from the Cernavoda NPP, measurements of ^3H in all the environmental media have been performed for a 10-year period, before the first operation of Unit 1, to establish the background levels in the monitoring area.

To meet the requirements of the regulatory body in the nuclear field (National Commission for Nuclear Activities Control) and the legislation for environmental protection, the Cernavoda NPP is ensuring the environmental radioactivity monitoring for natural and artificial radionuclides from a 30 km area around the plant. The results of the annual report of the Cernavoda NPP are compared with the reference background levels to assess the radiological impact.

The Environmental Radioactivity Monitoring Program of the Cernavoda NPP started in 1996 in the Environmental Control Laboratory, located in the Cernavoda town, as part of the Radioprotection Department.

The purpose of the routine environmental radioactivity monitoring program is to provide reliable and accurate data, which includes statistically valid data sets per nuclide per environmental media combination on an annual basis [1].

The Environmental Control Laboratory is committed to perform determinations for the radioactivity in the environmental samples, according to its quality management program designed based on international standards, and is participating in proficiency tests and intercomparison exercises schemes to validate the analytical and measurement methods, as a mandatory condition for the certification of the laboratory according to ISO/IEC 17025 "General Requirements for the Competence of Testing and Calibration Laboratories".

Although tritium is not a particularly toxic radionuclide, its presence in the environment is a radiologic concern because it is converted to tritiated water (HTO), which is metabolic conversed to organically-bound tritium (OBT), having a longer residence time in the organisms than HTO.

Measurement of tritium activity in its various forms is an important step to evaluate the health risks and to assess the dose for the representative person from the population [3]. The routine methods for tritium monitoring in liquid samples are based on the standard method described in the standard ISO 9698 "Water Quality. Determination of tritium activity concentration. Liquid scintillation method". For the food samples, determination of tritium refers to the tritium activity in the free-water fraction (TFWT) extracted by azeotrope distillation of fresh samples.

3. Development of the OBT monitoring program

Determinations of OBT concentrations in the environmental samples around the Cernavoda NPP were included in a supplementary monitoring program, that was implemented after many years of research and development in this field.

The first research & development OBT project, conducted through the CANDU Owners Group (COG) members, started in 2012; three different dried environmental samples (fish, Swiss chard, and potato) were prepared and measured to evaluate the methods used at that time by the COG members [4].

Due to the interest in the OBT analysis, expressed by many laboratories from the radioactivity measurement field, the OBT International Working Group was created in 2012, devoted to OBT analysis [5]. The founding members of this group are laboratories from Atomic Energy Commission (France), Canadian Nuclear Laboratories (Canada), Southampton University (UK) and Cernavoda NPP (Romania). The main goal was to organize each year an inter-laboratory comparison (ILC) exercise for OBT analysis followed by a workshop to discuss the evaluation of the results and to propose recommendations for improvement. The initial context was the lack of reference materials for OBT determinations and no standard method available for OBT.

Quantification of the OBT levels became important to estimate more accurately the dose for the public, according to the Canadian standard CAN-CSA N288.1-20 „Guidelines for modelling radionuclide environmental transport, fate, and exposure associated with the normal operation of nuclear facilities".

For this reason, the Environmental Control Laboratory of the Cernavoda NPP was committed to the OBT International Working Group, since its formation, and organized two of the six ILC exercises: the 4th OBT exercise (grass sample) in 2017 [6] and the 6th OBT exercise (quince sample) in 2019 [7]; and also two of the nine OBT Workshops (in 2015 and 2019).

The evaluation of the results reported by the participating laboratories, at each ILC exercise for OBT analysis, was performed by the organizing laboratory, according to the robust method (Algorithm A) described in the standard ISO 13528 "Statistical methods for use in proficiency testing by interlaboratory comparison".

In Fig. 2, the results of the Environmental Control Laboratory and the assigned values (reference values) – provided by the organizers of the OBT ILC exercises (2013 ÷ 2019) are presented; these are the OBT concentrations calculated in units of Bq/L water of combustion and Bq/kg dry weight.

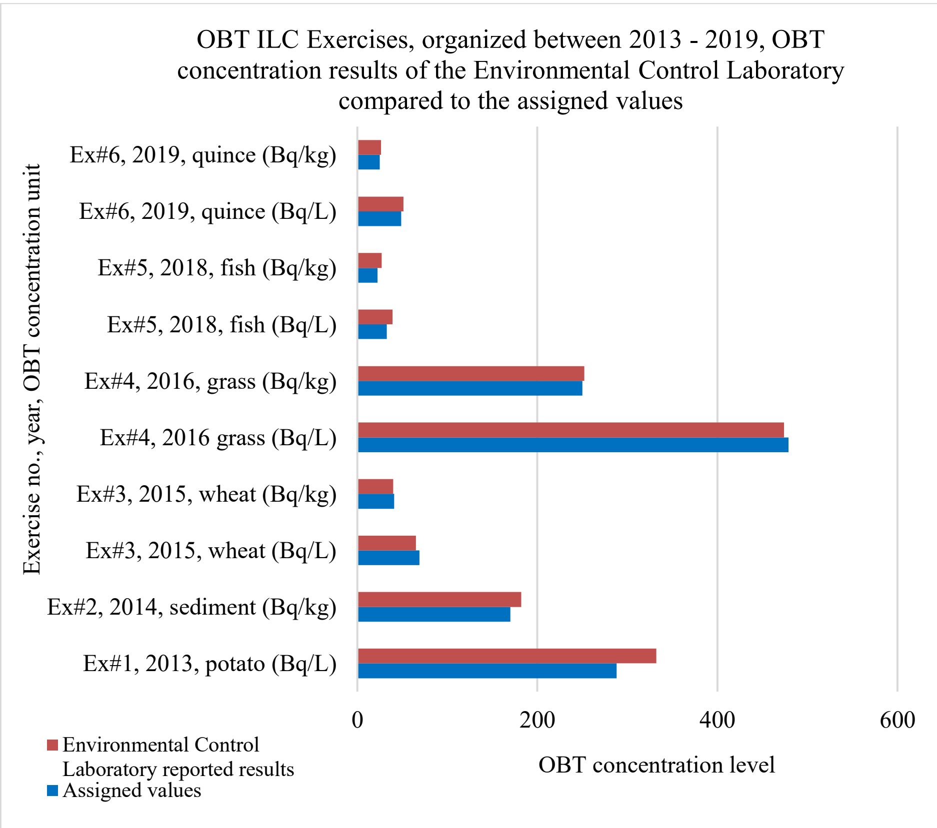

Fig. 2. The results of six OBT ILC exercises, organized during 2013 ÷ 2019 period.

There was a continuous improvement of the sample preparation methods (combustion of the dry sample) and OBT measurements (by liquid scintillation counting) in the Environmental Control Laboratory, reflected in the laboratory's results for these six ILC exercises; all the results were accepted according to the evaluation criteria of the organizing laboratories.

4. Analytical methods for OBT analysis

The sample preparation methods for OBT analysis, implemented at the Cernavoda NPP, include the dehydration process of the fresh samples at 105 °C in a drying oven, followed by the combustion of the dry matter at 800 °C in a Pyrolyser-6 Trio System (Raddec Ltd. from the UK) – Fig. 3.

The Pyrolyser-6 Trio System includes six quartz tubes crossing three zones (sample zone, intermediate zone, and catalyst zone), Eurotherm 3504 and Nanodac controllers, AGS (automated gas changing), Platinum-Alumina catalyst (10 g/tube), quartz wool, air and Oxygen supply. Heating profiles are set up from room temperature to 800 °C in steps.

Fig. 3. Sample combustion – Pyrolyser-6 Trio System for ^{3}H and ^{14}C, Raddec.

Fig. 4. Sample measurement – LSC, Tri-Carb 3180TR/SL, Perkin-Elmer.

The combustion water resulted during a 6-hours procedure, is collected directly into 20 ml high-density polyethylene vial, placed in a glass trap to prevent back suction. The combustion water is weighed and then mixed with 10 ml Ultima Gold™ scintillation cocktail. The vials are counted for 500 min in a Tri-Carb 3180 TR/SL (Perkin-Elmer) liquid scintillation counter (LSC) – Fig. 4. The OBT activity concentrations in the combustion water (Bq/L water of combustion) and in the dehydrated matter (Bq/kg dry weight) are calculated.

5. Results of the OBT monitoring program

This paper is presenting the OBT concentration results of the OBT monitoring program at the Cernavoda NPP from the 2021 ÷ 2023 period (Fig. 5) for fish, apricot, wheat grains and potato samples; harvested in the most representative period of the year, from two of the monitoring locations selected from the routine program: fish from Danube – Black Sea Channel (LII-05) and Danube River (LII-09), ground food samples from Cernavoda (AII-03) and Seimeni (LII-08).

It can be observed from Fig. 5, that OBT concentration levels have quite large variations from one year to another and have also variations towards the samples. The smallest OBT concentrations were measured in the fish samples and larger concentrations were found in potato and apricot samples. The OBT concentrations in Bq/L water of combustion are, in general, almost double the OBT concentrations in Bq/kg dry matter, depending on the Hydrogen percentage (H %) in the dry sample.

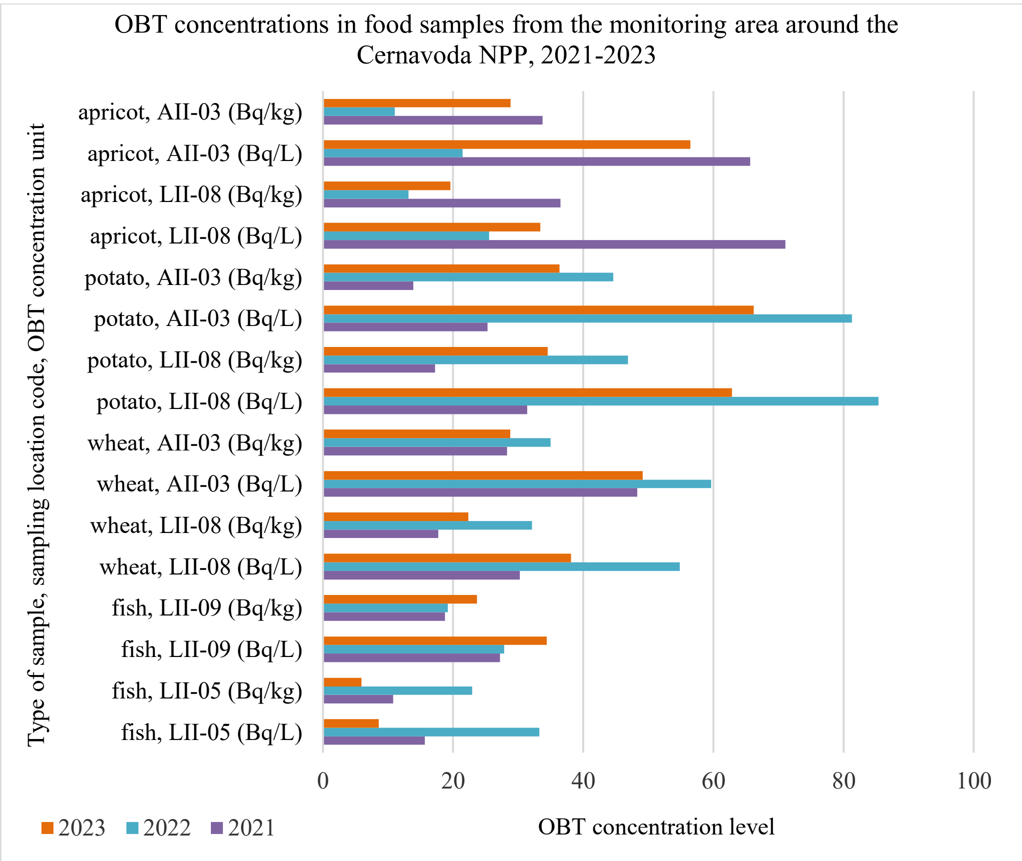

Fig. 5. Results of the OBT monitoring program at Cernavoda NPP, 2021 ÷ 2023 period.

In Figs. 6, 7 and 8 are represented the TFWT concentrations and the OBT concentrations in units of Bq/kg fresh weight (f.w.), calculated as contributions to the total tritium concentrations in the fresh samples, for 2021, 2022 and 2023 respectively.

The OBT contributions (%) to the total tritium concentrations varied from 20 % for fish samples from the Danube-Black Sea Channel to 60 % for fish from the Danube River; for apricot samples – varied around 30 %; for potato samples – varied around 50 % and for wheat samples – varied around 95 % (due to the very low content of water in the grains). There were relatively low variations between the two monitoring locations (Cernavoda – about 2 km from the plant, and Seimeni – about 10 km from the plant).

The development of the OBT monitoring program at the Cernavoda NPP will be focusing on new matrices of environmental samples, chosen from the routine program, to have a bigger picture about the contribution of the OBT concentrations to the total dose of a representative person from population.

Tritium concentration levels in 2021 – 2023 period were compared to the preoperational levels of tritium ("net zero levels") – around 5.0 Bq/L, determined by Institute IFIN-Horia Hulubei, Bucharest to assess the contribution of the Cernavoda NPP operation to the environment [8].

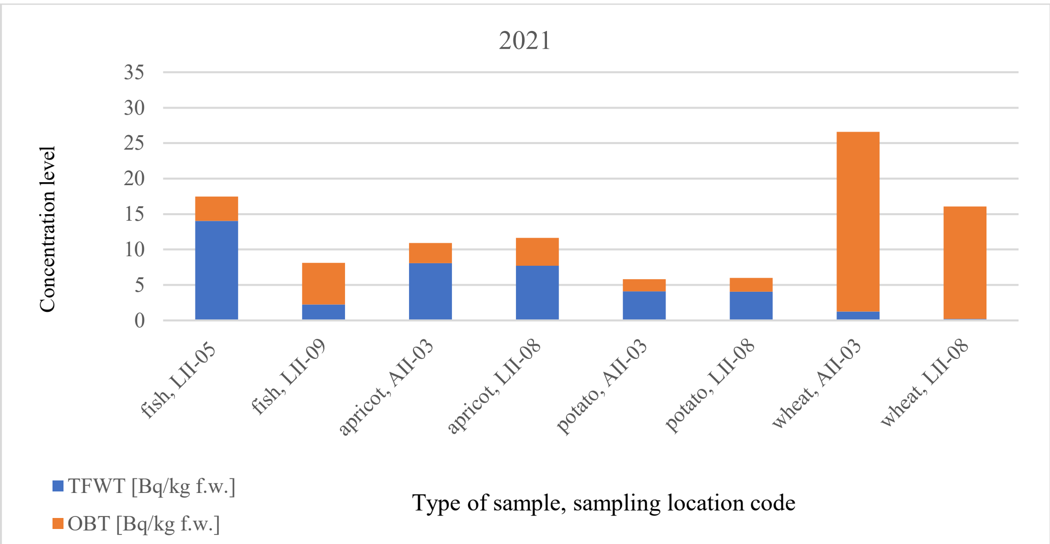

Fig. 6. TFWT and OBT levels in the environmental samples around the Cernavoda NPP, in 2021.

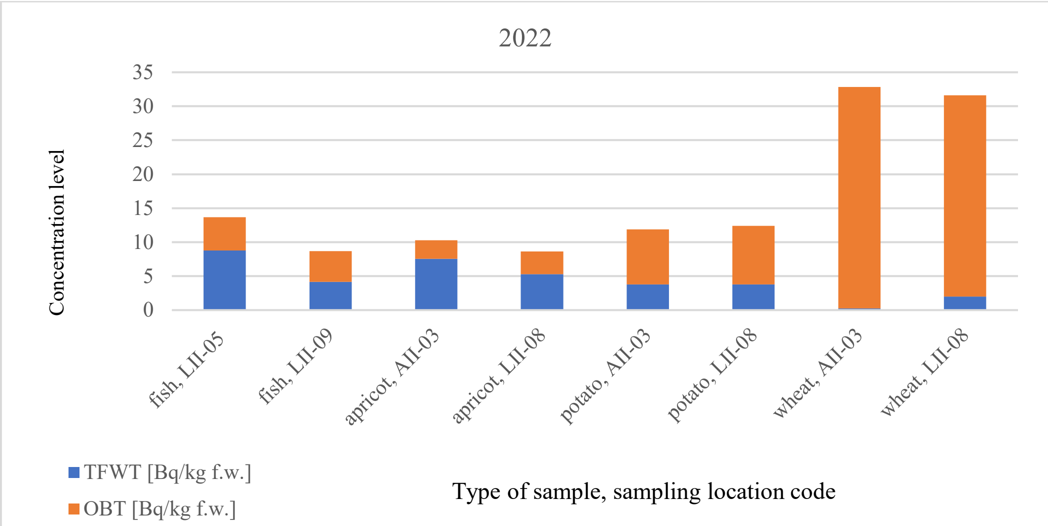

Fig. 7. TFWT and OBT levels in the environmental samples around the Cernavoda NPP, in 2022.

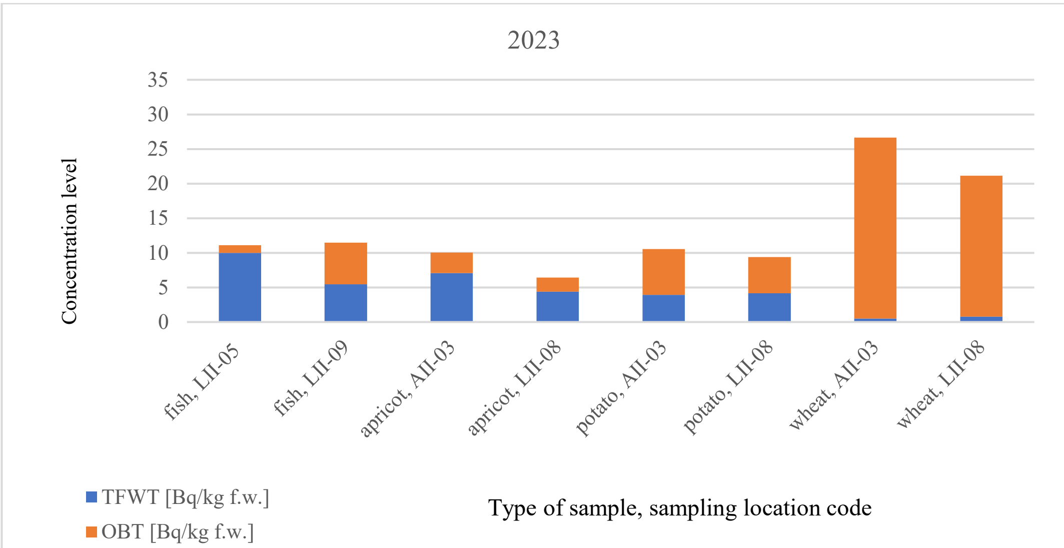

Fig. 8. TFWT and OBT levels in the environmental samples around the Cernavoda NPP, in 2023.

6. Conclusions

The OBT determination became an important component of the environmental radioactivity monitoring program of the Cernavoda NPP that will be correlated with the implementation of the Canadian standard CAN-CSA N288.1-20 „Guidelines for modelling radionuclide environmental transport, fate, and exposure associated with the normal operation of nuclear facilities”.

The results of the OBT inter-laboratory comparison exercises are proving the quality of the analytical procedures and the effectiveness of the Environmental Radioactivity Monitoring Program and are considered as a strength for the international missions that are evaluating the performance of the Cernavoda NPP.

The Cernavoda NPP is completely engaged in maintaining excellence in relation to radiation protection and safety standards in the nuclear industry [3]. As a member of the OBT International Working Group, the Environmental Control Laboratory is dedicated to improve the analytical methods for OBT determinations, which can only be validated though ILC exercises, according to ISO/ IEC 17025, due to the lack of OBT certified reference material for environmental samples.

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