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#### ▶ To cite this version:

Anne-Laure Nivesse, Nicolas Baglan, Gilles F Montavon, Olivier Peron. Tritium speciation in environmental matrices by isotopic exchange. MIGRATION 2019: 17th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Sep 2019, Kyoto, Japan. in2p3-02291303

#### HAL Id: in2p3-02291303 https://hal.in2p3.fr/in2p3-02291303

Submitted on 8 Jul 2021

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# Tritium speciation in environmental matrices by isotopic exchange A-L. NIVESSE<sup>1,2\*</sup>, N. BAGLAN<sup>3</sup>, G. MONTAVON<sup>1</sup>, O. PÉRON<sup>1</sup>

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# Background

Tritium (<sup>3</sup>H) the radioactive isotope of hydrogen is a beta emitter with a half-life of 12.312 (25) years [1]. It can integrate organics molecules of living organisms by following the water cycle and form the organically bound tritium fraction (OBT). In 2017, the IRSN published a report on the update of knowledge on tritium in the environment [2], taking up some of the questions that have been waiting to be answered since the publication of the Livre Blanc du Tritium by ASN in 2010 [3]. Among these, those concerning the behavior, fate and speciation of this radionuclide in the environment are still relevant. The existence of two forms of OBT is commonly accepted: a non-exchangeable fraction (NE-OBT) and an exchangeable fraction (E-OBT) with the near environment. However, there is no consensus on their 9.000-980 definition, therefore several one can be found in the literature.



**OBJECTIVE** : The main goal is to improve the global understanding of tritium exchange mechanisms in environmental matrices, to validate the E-OBT and NE-OBT information and to develop the knowledge about tritium migration processes in the environment.

## **Experimental approach**

## Isotopic exchange « hard way »

In a tritium free water bath, tritium atoms in the exchangeable position are exchanged with the hydrogen atoms of the bath : E-OBT fraction is removed from the sample. E-OBT is measured in the exchange bath and NE-OBT remaining in the sample after combustion [4].



## Isotopic exchange « soft way »

The samples are exposed to different tritiated atmospheres in order to set up a tritium vapor phase line, with controlled and stable temperature and relative humidity parameters. This method makes it possible to determine the fraction of exchangeable hydrogen  $(\alpha_{iso})$  in the sample [5].



The method leads to a potential solubilisation of a part of the sample. A proportion of the NE-OBT fraction may contribute to the E-OBT fraction measurement, which can induce an analytical bias. Solubilisation is currently estimated by elemental CHNS-O analysis of the sample before and after exchange.

# **Results and discussion**

### **1. Humic substances :**

Humic substances (HS) are part of the soil organic matter. Their molecular structures complexity favors the presence of BT [6].



## HS functional groups characterizations

Stevenson (1982),  $\alpha_{th}$  = 42 %



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ELSEVIER         journal homepage: www.elsevier.com/locate/chemosphere           Towards speciation of organically bound tritium and deuterium:	journal homepage: www.elsevier.com/locate/chemosphere         Towards speciation of organically bound tritium and deuterium:         Quantification of non-exchangeable forms in carbohydrate molecules         O. Péron <sup>a,*</sup> , E. Fourré <sup>b</sup> , L. Pastor <sup>c,1</sup> , C. Gégout <sup>a</sup> , B. Reeves <sup>a</sup> , H.H. Lethi <sup>a</sup> , G. Rousseau <sup>a</sup> ,         N. Bardan <sup>d</sup> , C. Landersman <sup>d</sup> , E. Sickler <sup>c, c</sup> , Montavon <sup>a</sup>	6	Chemosphere
Towards speciation of organically bound tritium and deuterium:	Towards speciation of organically bound tritium and deuterium: Quantification of non-exchangeable forms in carbohydrate molecules O. Péron <sup>a,*</sup> , E. Fourré <sup>b</sup> , L. Pastor <sup>c,1</sup> , C. Gégout <sup>a</sup> , B. Reeves <sup>a</sup> , H.H. Lethi <sup>a</sup> , G. Rousseau <sup>a</sup> , N. Bardan <sup>d</sup> , C. Landerman <sup>a</sup> , E. Sicket <sup>c,C</sup> , C. Montyan <sup>a</sup>	ELSEVIER	journal homepage: www.elsevier.com/locate/chemosphere
Quantification of non-exchangeable forms in carbohydrate molecules	O. Péron <sup>a,*</sup> , E. Fourré <sup>b</sup> , L. Pastor <sup>c, 1</sup> , C. Gégout <sup>a</sup> , B. Reeves <sup>a</sup> , H.H. Lethi <sup>a</sup> , G. Rousseau <sup>a</sup> ,		

 $\rightarrow$  The  $(\alpha_{iso})$  parameter determination highlights the BT form in a matrix by confrontation with the  $(\alpha_{theoretical})$  parameter obtained from molecular models of the matrix constituents.

### 2. Myriophyllum Spicatum (La Loire, France) and wheat carbohydrates (OBT WG) :

	Previous works [5]		This work	
	Wheat grains (OBT WG)	Alpha and microcristalline cellulose	Carbohydrates* (wheat grains OBT WG)	<i>Myriophyllum Spicatum (</i> La Loire, France)
$(\alpha_{th})$	30 %	30 %	31.6 %	30 %
$(\boldsymbol{\alpha}_{iso})$	31 ± 1 %	21 ± 1 % and 13 ± 1 %	31.1 ± 1.0 %	26.4 ± 0.5 %
$(\pmb{lpha_{th}})$ vs $(\pmb{lpha_{iso}})$		#		#





bohydrates :
bohydrates :

- 85 % of starch ( $\alpha_{th}$  = 30 %)
- 15 % of maltose ( $\alpha_{th}$  = 36.4 %)

Molecular model of cellulose

- Exchangeable capacity model based on major constituent is validated for cereals matrices type.



Method

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Andreux et al. (1994),  $\alpha_{th} = 22-30 \%$ 

α <sub>depro</sub>	Calculated	15 ± 11 %	16 ± 7 %
$\alpha_{total OH}$	ISO14900:2017 method	15 ± 7 %	15 ± 6 %
$\alpha_{carboxyl}$	Ca(OAc) <sub>2</sub> method	0.14 ± 0.07 %	0.56 ± 0.03 %
$\alpha_{total \ acidity}$	Ba(OH) <sub>2</sub> method	14.3 ± 2.0 %	14.5 ± 1.3 %

HS-Li

Richard (2002),  $\alpha_{th} = 19 \%$ 

<u>Conclusion</u>: Humic substances (HS) isotopic exchange demonstrates a higher exchangeable capacity than characterizations of functional groups, pointing out the limitations of the standard methods in evaluating accessibility, reactivity and migration of the hydrogen element in soils.

HS-Le

- Molecular structure and conformation are responsible for the buried tritium (BT) form.

	Wheat grains (OBT WG)	Alpha and microcristalline cellulose	Carbohydrates* (wheat grains OBT WG)	<i>Myriophyllum Spicatum</i> (La Loire, France)
NE-OBT (Bq.L <sup>-1</sup> ) « soft way »	30.3 ± 2.6	_	24.3 ± 2.1	26.5 ± 2.3
NE-OBT (Bq.L <sup>-1</sup> ) « hard way »	33.1 ± 2.6	_	32.7 ± 2.5	33.7 ± 3.1
<b>NE-OBT</b> deviation	8.5 ± 1.0 %	-	25.8 ± 2.9 %	<b>21.3 ± 2.7 %</b>

<u>Conclusion</u>: Analytical bias leaded by « hard way » isotopic exchange is verified according to the solubility properties of the studied matrix.

— Perspectives	References
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**Conclusions:**