Tritium speciation in environmental matrices by isotopic exchange

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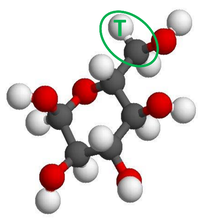
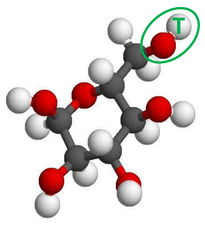
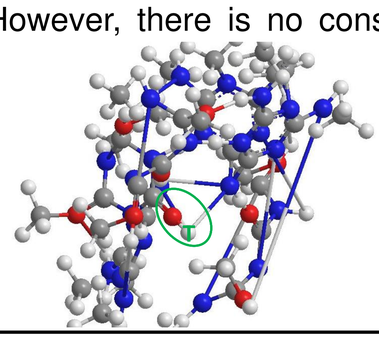
Background

Tritium (^3H) 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 definition, therefore several one can be found in the literature.

NE-OBT 

E-OBT 

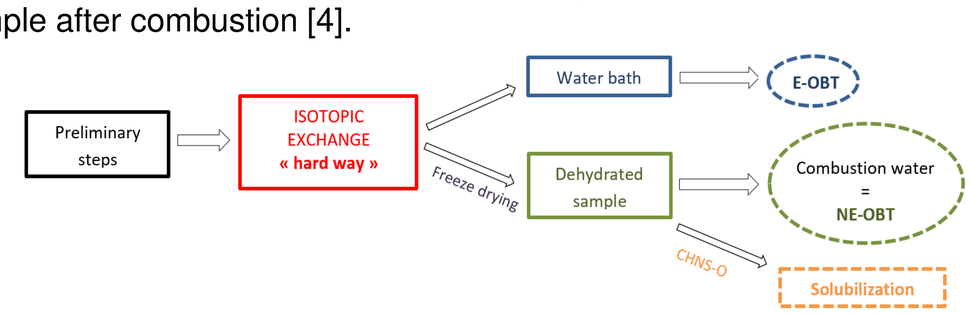
BT (Buried Tritium) 

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 »

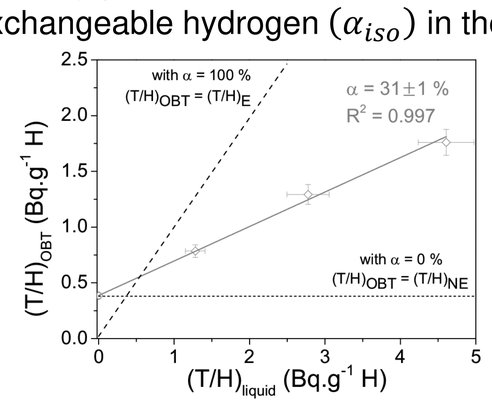
In a tritium free water bath, tritium atoms in the exchangeable position are exchanged with the hydrogen atoms of the bath : E-OBT fraction is removed from the sample. E-OBT is measured in the exchange bath and NE-OBT remaining in the sample after combustion [4].



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.

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 (α_{iso}) in the sample [5].



$$\left(\frac{T}{H}\right)_{OBT} = \alpha \times \left(\frac{T}{H}\right)_{E-OBT} + (1-\alpha) \times \left(\frac{T}{H}\right)_{NE-OBT}$$

$$\left(\frac{T}{H}\right)_{NE-OBT} = \frac{\left[\left(\frac{T}{H}\right)_{OBT} - \alpha \times \left(\frac{T}{H}\right)_{liq.}\right]}{1-\alpha}$$


Chemosphere 196 (2018) 120–128
Contents lists available at ScienceDirect
Chemosphere
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Towards speciation of organically bound tritium and deuterium: Quantification of non-exchangeable forms in carbohydrate molecules

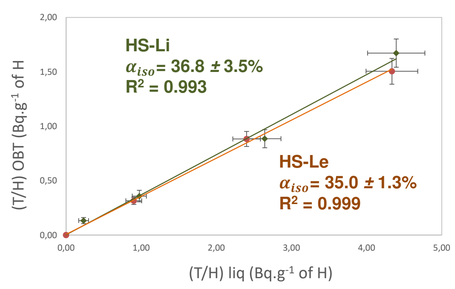
→ The (α_{iso}) parameter determination highlights the BT form in a matrix by confrontation with the $(\alpha_{theoretical})$ parameter obtained from molecular models of the matrix constituents.

Results and discussion

1. Humic substances :

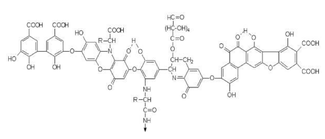
Humic substances (HS) are part of the soil organic matter. Their molecular structures complexity favors the presence of BT [6].

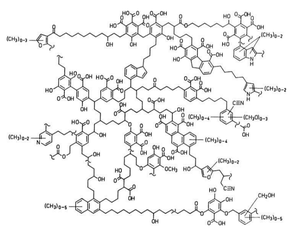
Isotopic exchange

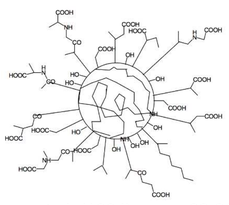


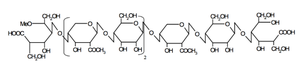
HS functional groups characterizations and contributions

	Method	HS-Li	HS-Le
$\alpha_{total\ acidity}$	$Ba(OH)_2$ method	14.3 ± 2.0 %	14.5 ± 1.3 %
$\alpha_{carboxyl}$	$Ca(OAc)_2$ method	0.14 ± 0.07 %	0.56 ± 0.03 %
$\alpha_{total\ OH}$	ISO14900:2017 method	15 ± 7 %	15 ± 6 %
α_{depro}	**Calculated**	**15 ± 11 %**	**16 ± 7 %**


Stevenson (1982), α_{th} = 42 %


Schulten and Schnitzer (1993), α_{th} = 13-16 %

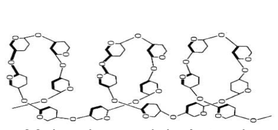

Andreux et al. (1994), α_{th} = 22-30 %

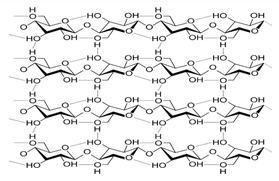

Richard (2002), α_{th} = 19 %

<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.

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)	*Myriophyllum Spicatum* (La Loire, France)
(α_{th})	30 %	30 %	31.6 %	30 %
(α_{iso})	31 ± 1 %	21 ± 1 % and 13 ± 1 %	31.1 ± 1.0 %	26.4 ± 0.5 %
(α_{th}) vs (α_{iso})	✔	≠	✔	≠


Molecular model of starch


Molecular model of cellulose

* Wheat carbohydrates :
- 85 % of starch (α_{th} = 30 %)
- 15 % of maltose (α_{th} = 36.4 %)

<u>Conclusions</u>:
- Exchangeable capacity model based on major constituent is validated for cereals matrices type.
- 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)	*Myriophyllum Spicatum* (La Loire, France)
NE-OBT (Bq.L^{-1}) « soft way »	30.3 ± 2.6	-	24.3 ± 2.1	26.5 ± 2.3
NE-OBT (Bq.L^{-1}) « hard way »	33.1 ± 2.6	-	32.7 ± 2.5	33.7 ± 3.1
NE-OBT deviation	**8.5 ± 1.0 %**	-	**25.8 ± 2.9 %**	**21.3 ± 2.7 %**

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

Perspectives

- ❑ <u>Analytical concerns</u>: Apple and simple carbohydrates (OBT WG)
- ❑ <u>Speciation concerns</u>: Evolution of the (α_{iso}) parameter depending on the degree of crystallinity of cellulose and environmental matrices applications.

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