Tritium speciation in environmental matrices by isotopic exchange

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Background

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

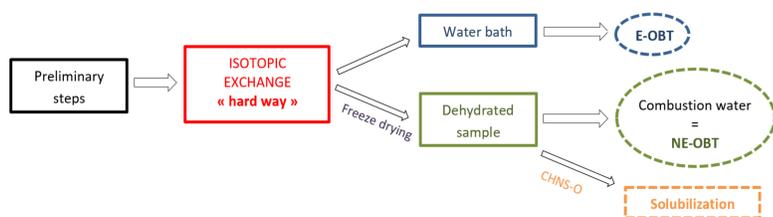**NE-OBT**   **E-OBT**   **BT (Buried Tritium)**
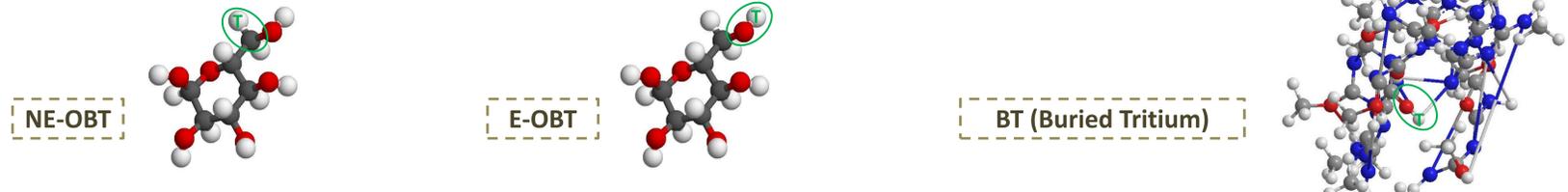
OBJECTIVE : The main goal is to improve the global understanding of tritium exchange mechanisms in environmental matrices, to validate the E-OBT and NE-OBT information and to develop the knowledge about tritium migration processes in the environment.

Experimental approach
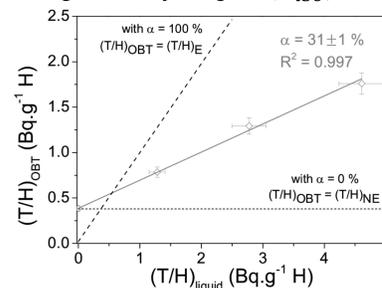
Isotopic exchange « hard way »

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].

Preliminary steps → ISOTOPIC EXCHANGE « hard way » → Water bath → E-OBT
Freeze drying → Dehydrated sample → Combustion water = NE-OBT
CHNS-O → Solubilization

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].

with α = 100 % $(T/H)_{OBT} = (T/H)_E$
α = 31 ± 1 %
$R^2 = 0.997$
with α = 0 % $(T/H)_{OBT} = (T/H)_{NE}$

x-axis: $(T/H)_{liquid}$ (Bq.g^{-1} H) y-axis: $(T/H)_{OBT}$ (Bq.g^{-1} H)

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

$$\left(\frac{T}{H}\right)_{NE-OBT} = \frac{\left[\left(\frac{T}{H}\right)_{OBT} - \alpha \times \left(\frac{T}{H}\right)_{liq.}\right]}{1-\alpha}$$
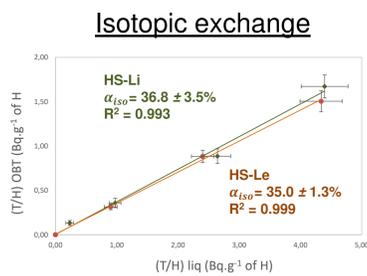
→ The (α_{iso}) parameter determination highlights the BT form in a matrix by confrontation with the ($\alpha_{theoretical}$) parameter obtained from molecular models of the matrix constituents.
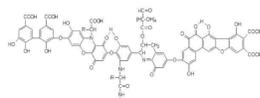
Results and discussion

1. Humic substances :

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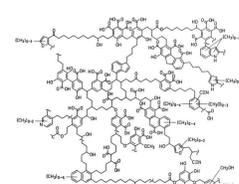
Isotopic exchange

HS-Li α_{iso} = 36.8 ± 3.5% $R^2 = 0.993$
HS-Le α_{iso} = 35.0 ± 1.3% $R^2 = 0.999$

x-axis: (T/H) liq (Bq.g^{-1} of H) y-axis: (T/H) OBT (Bq.g^{-1} of H)

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 %

HS functional groups characterizations and contributions

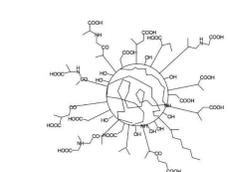|	Method	HS-Li	HS-Le
$\alpha_{total\ acidity}$	Ba(OH)$_2$ method	14.3 ± 2.0 %	14.5 ± 1.3 %
$\alpha_{carboxyl}$	Ca(OAc)$_2$ method	0.14 ± 0.07 %	0.56 ± 0.03 %
$\alpha_{total\ OH}$	ISO14900:2017 method	15 ± 7 %	15 ± 6 %
α_{depro}	Calculated	15 ± 11 %	16 ± 7 %

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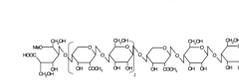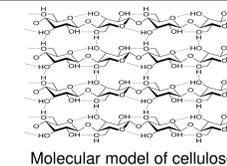
2. *Myriophyllum Spicatum* (La Loire, France) and wheat carbohydrates (OBT WG) :

	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})	✔	≠	✔	≠
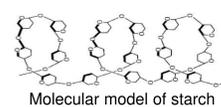
Molecular model of starch
Molecular model of cellulose

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

Conclusions:
- 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 %

Conclusion: 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.

References

[1] LNHB, Mini Table de Radionucléides 2015, EDP Sciences, Les Ulis, 2015.
[2] IRSN, 2017, Actualisation des connaissances acquises sur le tritium dans l'environnement. IRSN/PRP-ENV/SERIS 2017-00004
[3] ASN, 2010, Livre Blanc du Tritium.
[4] Baglan, N., et al. (2010). Métrologie du tritium dans différentes matrices: cas du tritium organiquement lié (TOL). Radioprotection, 45(3), 369-390 .
[5] Péron, O., et al. (2018). Towards speciation of organically bound tritium and deuterium: Quantification of non-exchangeable forms in carbohydrate molecules. Chemosphere 196 120-128.
[6] Pansu, M., & Gautheyrou, J. (2007). Handbook of soil analysis: mineralogical, organic and inorganic methods. Springer Science & Business Media.