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Tritium speciation in environmental matrices by isotopic exchange

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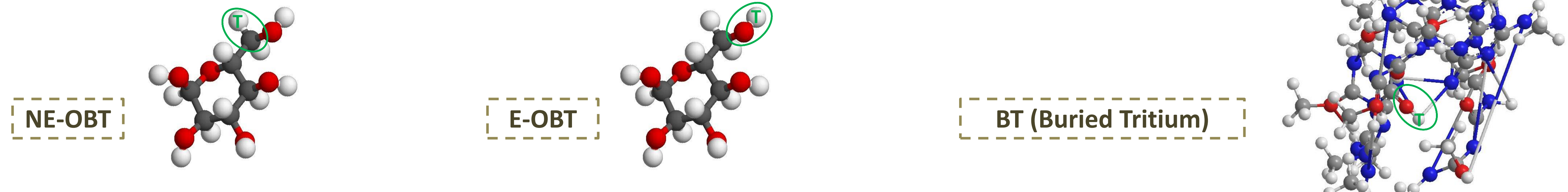
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Background

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.

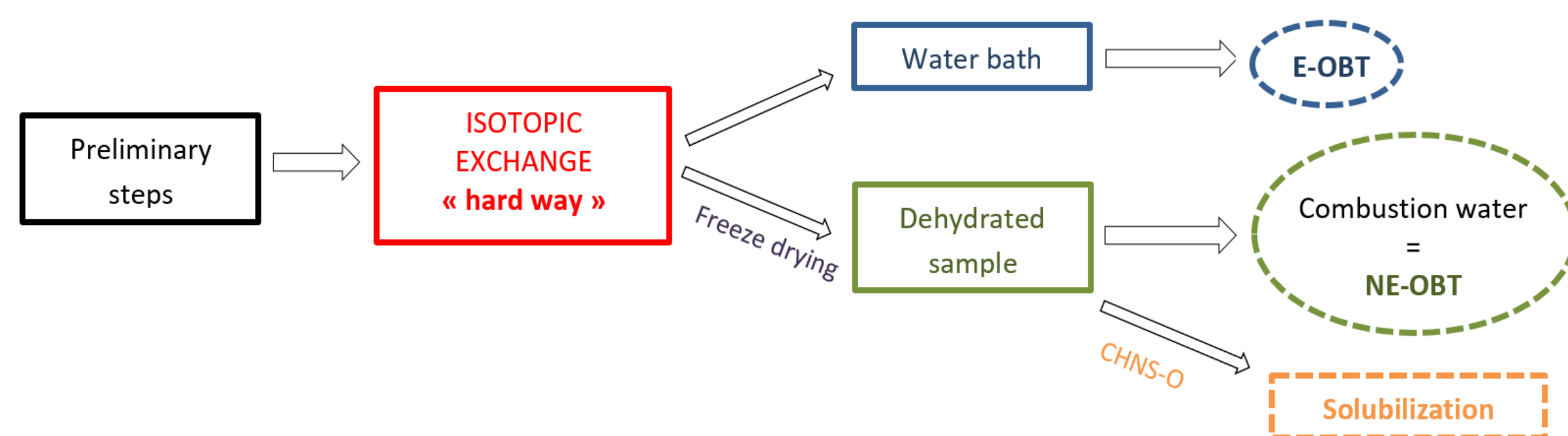


OBJECTIVE : The main goal is to improve the global understanding of tritium exchange mechanisms in environmental matrices, to validate the E-OBT and NE-OBT information and to develop the knowledge about tritium migration processes in the environment.

Experimental approach

Isotopic exchange « hard way »

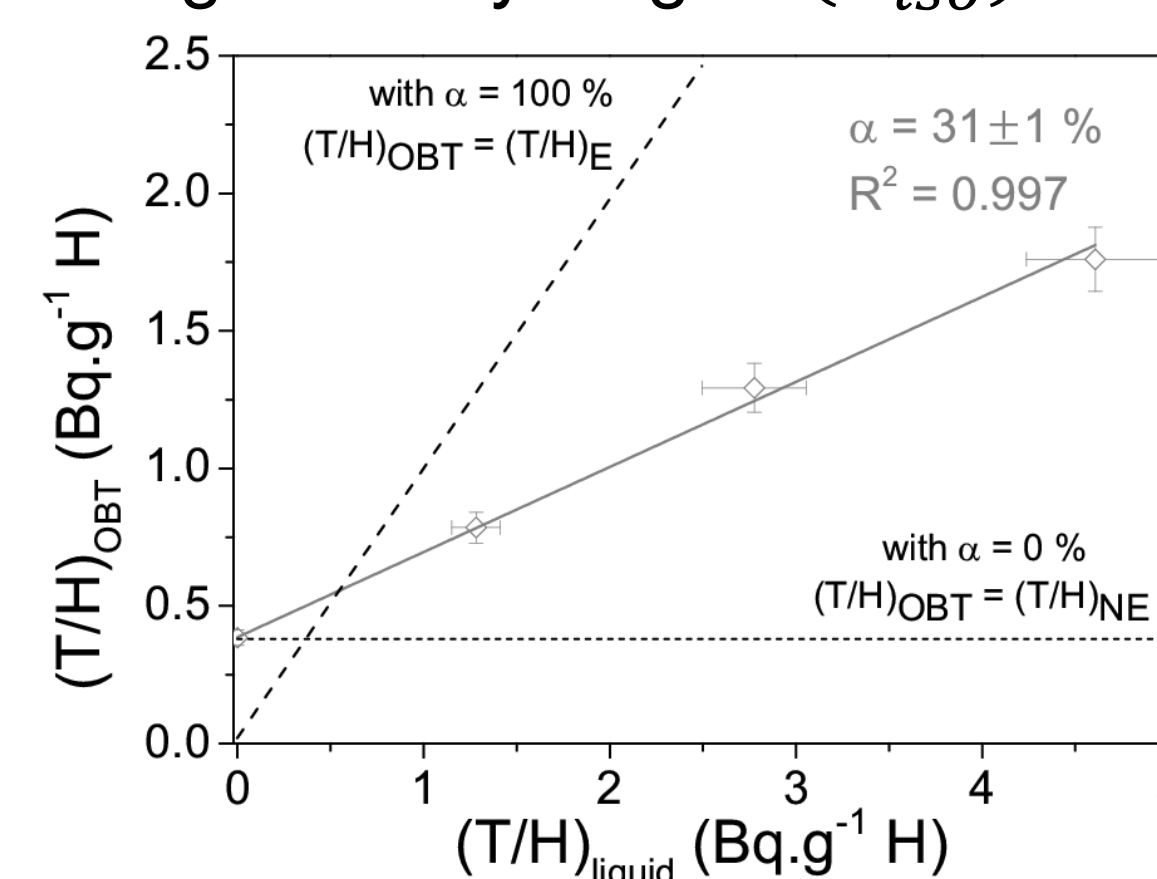
In a tritium free water bath, tritium atoms in the exchangeable position are exchanged with the hydrogen atoms of the bath : E-OBT fraction is removed from the sample. E-OBT is measured in the exchange bath and NE-OBT remaining in the sample after combustion [4].



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].



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

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

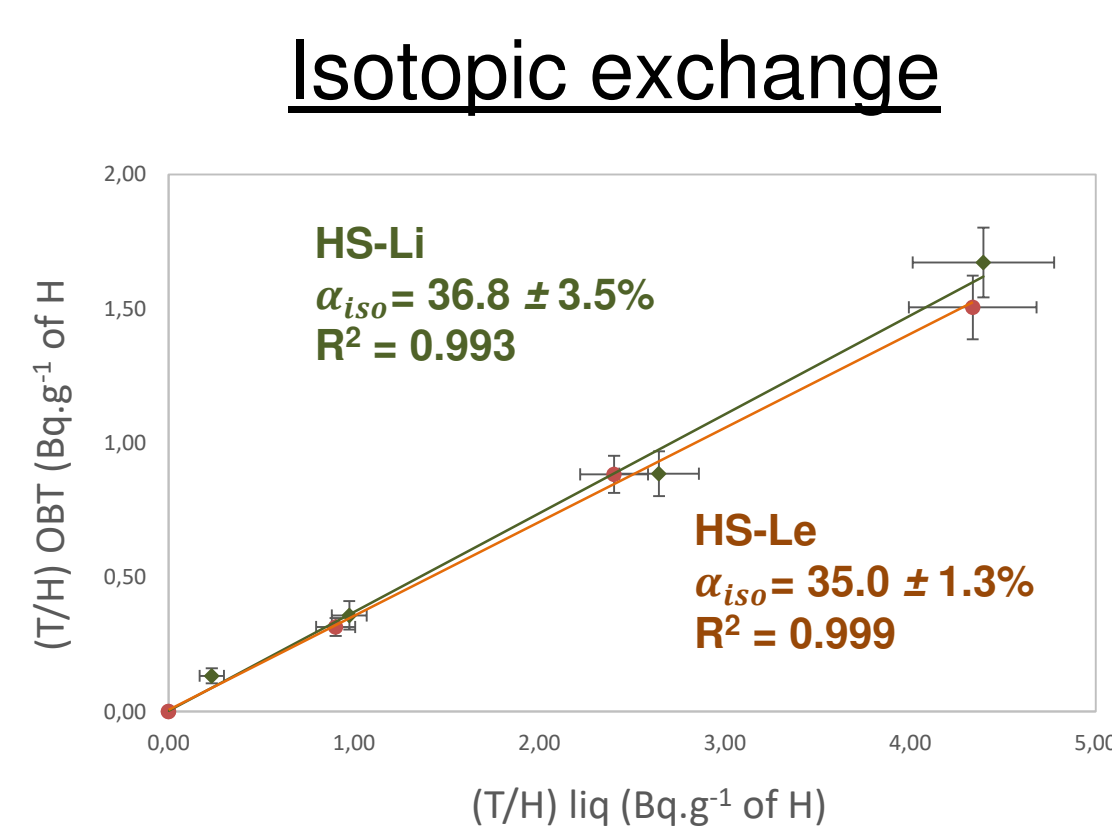


→ The (α_{iso}) parameter determination highlights the BT form in a matrix by confrontation with the ($\alpha_{theoretical}$) parameter obtained from molecular models of the matrix constituents.

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].



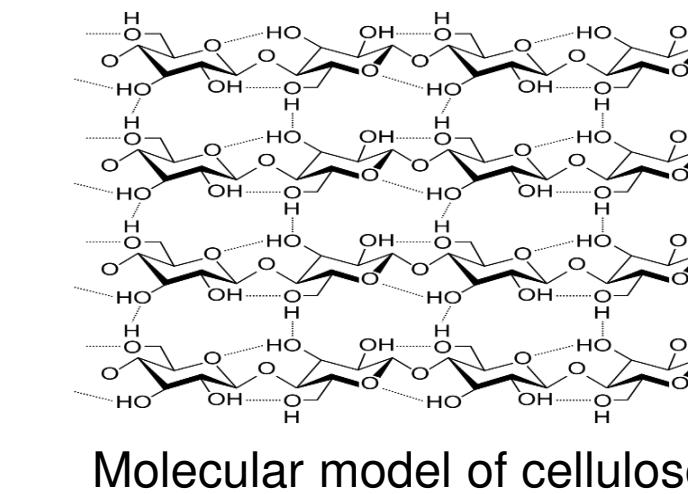
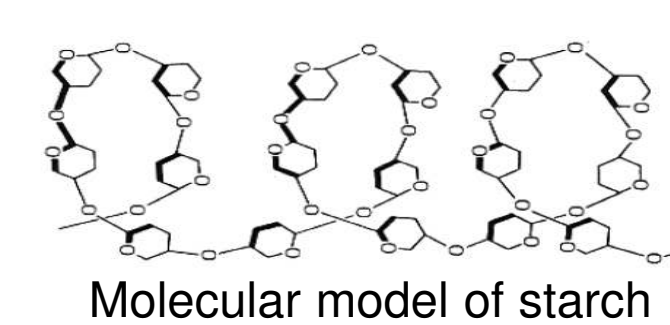
HS functional groups characterizations and contributions

	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 microcrystalline 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})	✓	≠	✓	≠



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

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 microcrystalline 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 led by « hard way » isotopic exchange is verified according to the solubility properties of the studied matrix.

Perspectives

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

References

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