A novel method to quantify exchangeable hydrogen fraction in organic matter

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Background

Key to accurate isotopic value is to constrain the exchangeable hydrogen fraction (f_x) represented by the non-carbon bound H, (i.e. N-, COO-, O-, and S-bound H).

Theoretical considerations suggests f_x values: cellulose (30%), proteins (25%), lignin (9%)

Here we used a novel sample manipulation based on ^1H-^2H exchange experiments and quantified through proton based liquid-state nuclear magnetic resonance (^1H-NMR) spectroscopy.

At the same time we carried out exchange experiments with dual water vapor isotope and Isotope Ratio Mass Spectrometry (IRMS) – most recent procedure according to Soto et al. (2017).

Materials and methods

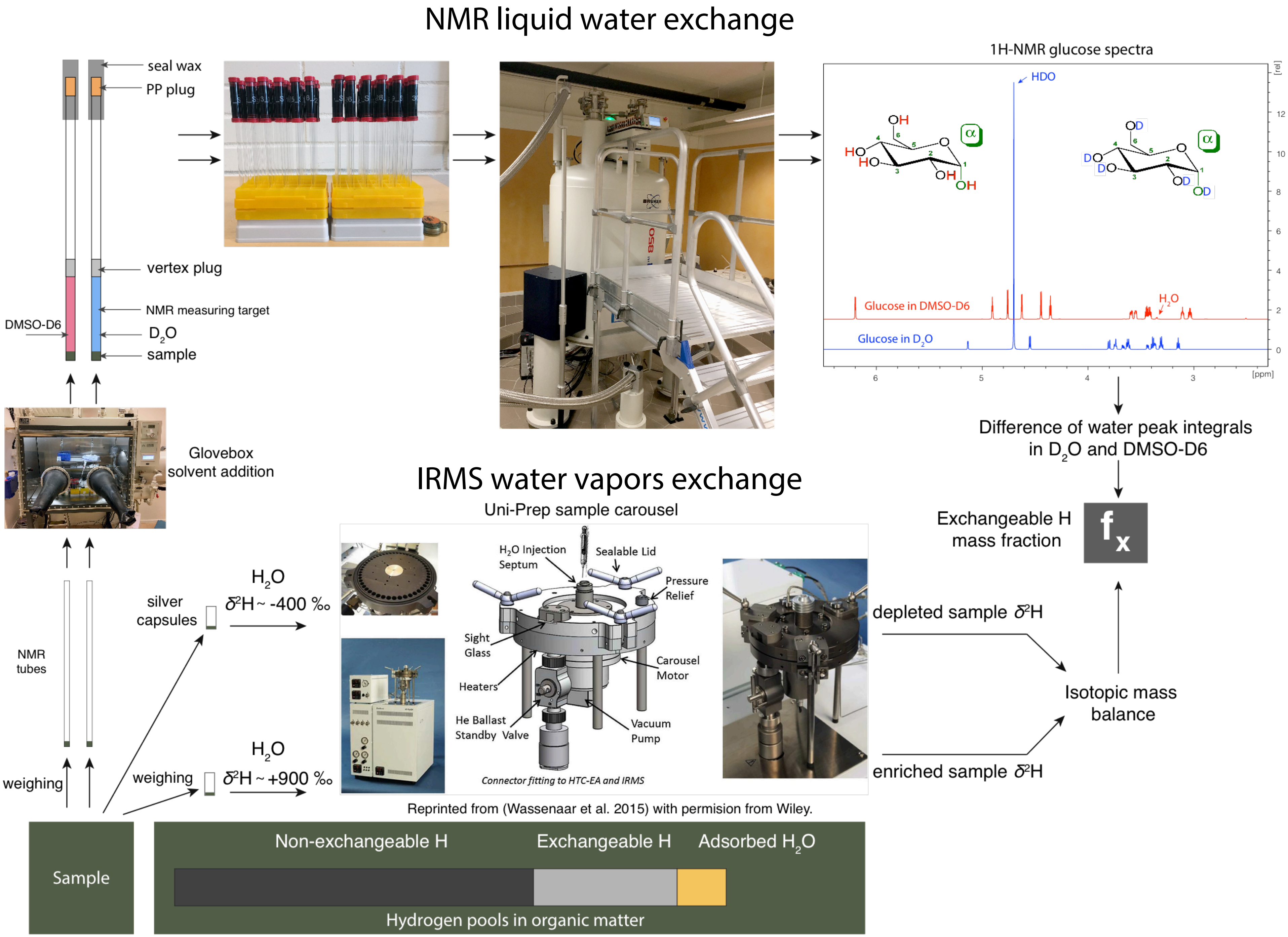
We tested a wide range of organic matter types such as: cellulose, keratin(USGS reference materials KHS, CBS), pine wood(USGS54) and needles, birch wood and leaves, green algae (cultured and natural), dissolved organic matter (Suwanee NOM reference), demineralized soils and sediments, zooplankton and fish (trout, perch arctic char) and polyethylene powder as a reference with no f_x .

Glucose was used as external standard and proof of proton exchange.

Known volumes of DMSO-D6 and deuterium oxide (D_2O) were added to known amounts of powdered material, were kept at room temperature and measured between 1 and 7 days.

Water peak integrals of 1-H NMR spectra generated as a result of proton exchange (D_2O treatment) and corrected for background water (DMSO-D6 treatment) were used to calculate the amount of hydrogen (H) produced.

Glucose peak integrals from the 1-H NMR spectra were used as external standard.



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Results

The f_x (relative to total H) was on average across 21 materials analyzed 21.4 ±5.1% SD measured through NMR and 2.5 ± 0.45% SD, measured based on IRMS, respectively.

Polyethylene showed no f_x as expected with both methods.

Measured glucose f_x was 41.4 % and close to the theoretical value of 41.7 % based on NMR, while IRMS based determination showed no exchangeability.

The error in NMR determined f_x was estimated at 2%.

Conclusions

- The higher NMR-f_x and lower IRMS-f_x using water steam equilibrations and following extensive drying procedure, suggests a differential accessibility of exchangeable H in organic materials between methods − that can depend on temperature and state of water exchange procedure.
- The labile H in glucose cannot be accessed with water vapors exchange due to crystalline structure, which becomes available at dissolution as determined with NMR.
- We propose that ^{1}H NMR method of quantifying f_x is an independent and novel approach that can contribute to a better understanding of H exchangeability in a wider range of organic materials.