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Highlights

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How much bio is in there?

Can stable isotopes be used to determine the bio-based content of products?

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Resource supply and environmental aspects are considered to be of increasing importance to industrial production. Products like building blocks, intermediates, materials and chemicals based on renewable resources can contribute to both economically and ecologically efficient solutions. Therefore, it is of interest to determine and communicate information on the *content of biomass resources* of an individual product. Currently, the bio-based content of products is usually determined on the basis of the quantification of ^{14}C carbon (radiocarbon dating). This is based on the radio-active decay of ^{14}C, which can be used to estimate the age of organic materials up to roughly 60,000 years. Radiocarbon dating for estimating the bio-based content is based on the near absence of ^{14}C in fossil-based materials such as oil and gas, whereas bio-based materials contain modern concentrations of ^{14}C. These methods focus on carbon, and consequently only determine the bio-based *carbon* content, thereby neglecting the fact that bio-based products also contain large quantities of other elements, like oxygen, nitrogen and hydrogen. Consequently, measured bio-based carbon content can deviate significantly (higher as well as lower) from the actual biomass content (table 1).

Stable isotope approach

Previous studies have hinted towards the potential application of stable isotope analysis as an additional means to determine the bio-based content of materials and products. This relies on the observation that the stable isotope composition of some bio-based materials and products is on average different from that of their fossil-based analogues. For example, the carbon isotope ratio ($\delta^{13}C$) reported for bio-ethanol from maize has delta values between -13 and -11 ‰, whereas synthetic ethanol has delta values varying between -32 and -25 ‰. Although no stable isotope based methods have been used for determination of the bio-based content of products so far, the potential to use stable isotope analysis for this purpose attracted the attention of standardisation committee CEN/TC 411 and was evaluated in detail in the framework of the KBBPPS project[1].

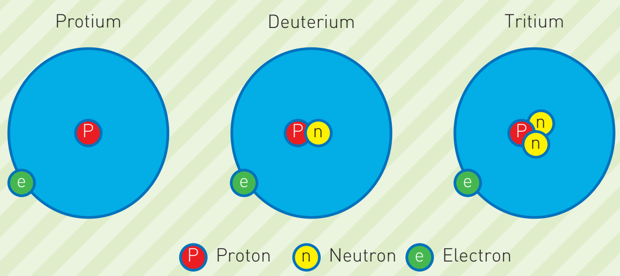
Stable isotopes

Isotopes have the same number of protons and electrons but have different numbers of neutrons. Therefore, isotopes of the same element have the same atomic number but different masses. Hydrogen for example has three isotopes, two of which are stable and one which is unstable (radio-active) (figure 1). To determine the bio-based content the focus is on the stable isotopes of carbon, hydrogen, nitrogen and oxygen, which together with sulphur make up the bulk of organic material. Fortunately all these elements have at least two stable isotopes and this allows to determine their respective ratios in a material or product. The stable isotope composition is often expressed as a ratio of the heavier isotope to the lighter which is then expressed relative to the ratio in some defined reference material with known isotope composition. The isotope ratios are quoted as delta (δ) values and reported in units of per mill (‰). If a sample has more of the heavier isotope than the reference material it is considered enriched (positive δ-value). If the sample has less of the heavier isotope compared to the reference material it is depleted and has a negative δ-value.

Table 1: Examples of differences in bio-based carbon content and biomass content of specific products.

	Bio-based carbon content (%)	Biomass content (%)
Plastic composite: 70 % PE / 30 % cellulose	18	30
'Plant based' PET	20	31
PVC based on bioethylene	100	43
Cellulose triacetate (oil based acetic acid)	50	55
Coating (with bio-based resin)	76	15

Figure 1: Isotopes of hydrogen: protium (^1H), deuterium (^2H) and tritium (^3H).



Stable isotope composition

The stable isotope composition of organic materials and compounds on Earth is variable and depends on the initial composition of source materials/compounds as well as different fractionation processes that takes place during formation. For example, the stable hydrogen and oxygen composition of plants and algae, as well as the compounds produced by these organisms, is related to the isotopic composition of source water as well as fractionation that occurs during evaporation and biosynthesis. The isotopic composition of the source water is again related to the isotopic composition of local precipitation, which follows a global pattern of successive depletion from the equator to the poles (illustrated in figure 2). For carbon and nitrogen similar type of processes cause a considerable variation in the $\delta^{13}C$ and $\delta^{15}N$ composition of organisms and compounds hereof. Transformation of biogenic matter to organic matter in sediments (e. g. coal or crude oil) involves further isotope fractionation. This means that the isotopic composition of a particular material or product depends on the source, type, and geographical origin of the (biomass) feedstock, and the applied processing technologies.

Requirements

To successfully apply stable isotopes for determining the bio-based content of materials and products, the following requirements should be met:

1. The average isotopic composition of the bio-based fraction should be different from the average isotopic composition of the fossil-based fraction.
2. The isotopic composition of the bio-based and the fossil-based fraction should be known with sufficient precision and the range of variation in both fractions should be limited.
3. The range of variation in the isotopic composition of the bio-based fraction should not overlap with that of the fossil-based fraction.

To determine whether, and up to what extent these requirements can be met in practice, an inventory was made of the natural range of variation of the stable isotope composition of various major groups of organisms such as plants and algae, including their main constituents like carbohydrates, lipids and proteins.

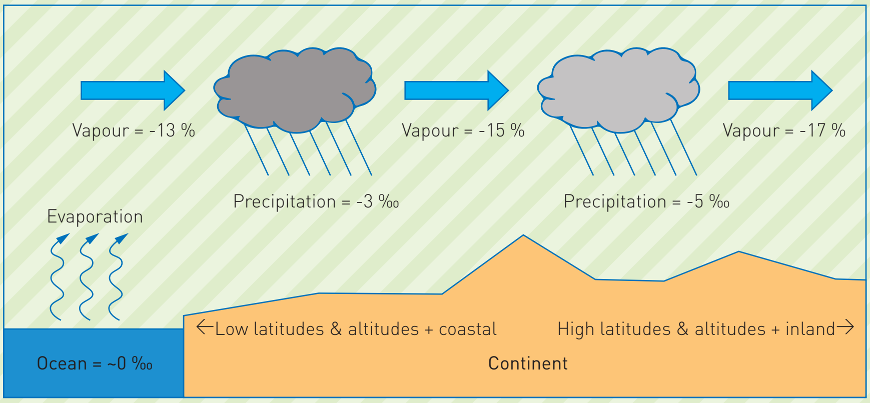


Figure 2: Simplified example of the effect of successive rain-out which causes a successive depletion of $\delta^{18}O$ values in precipitation (and consequently in biomass of plants taking up this water) from the equator to higher latitudes and inland.

Figure 3: Indicative ranges of $\delta^{2}H$ values in different materials and compound classes (bio-based and fossil-based). The ranges in grey boxes are indicative world-wide estimates, ranges in solid black lines are indicative ranges based on limited data sets with limited geographical coverage, and ranges in dotted black lines are incomplete ranges based on limited data sets and assumptions.

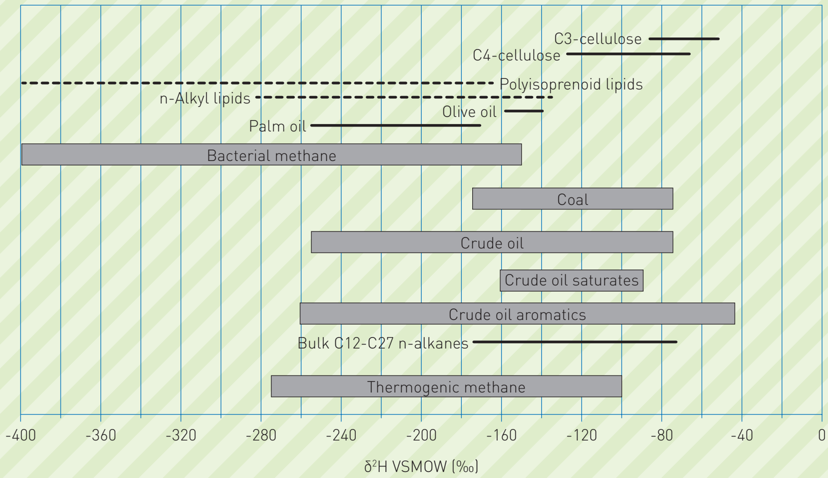
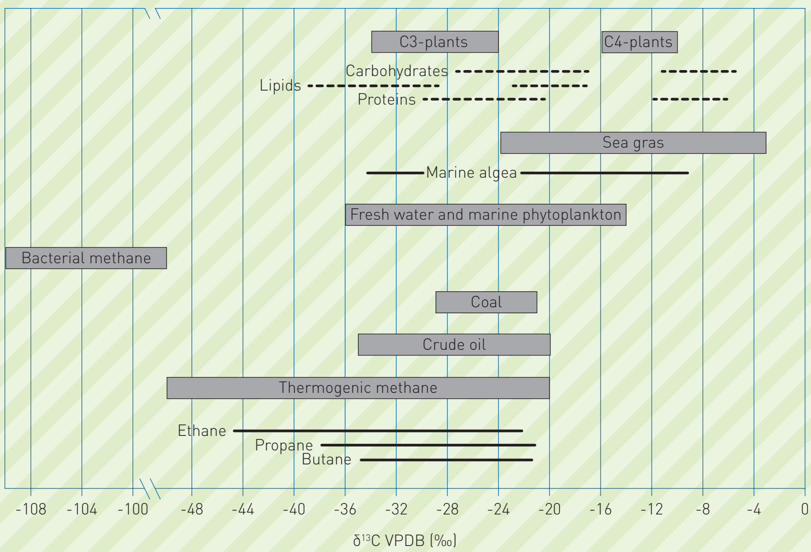


Figure 4: Indicative ranges of $\delta^{13}C$ values in different materials and compound classes (bio-based as well as fossil-based). Ranges in grey boxes are generally accepted ranges (C3- and C4-plants) or indicative world-wide estimates, ranges in solid black lines are indicative ranges based on limited data set with limited geographical coverage or on a data set with limited geographical coverage, ranges in dotted black lines are incomplete ranges based on the generally accepted values for C3- and C4-plants and assumptions.



In addition, fossil residues of living matter such as crude oil, natural gas and coals were also taken into account. As an example, a summary of the stable isotope ratio ranges of $\delta^{2}H$ and $\delta^{13}C$ values for these material and compound classes are shown in figure 3 and 4, respectively. In general it was found that the range of variation of the isotopic composition of living matter and its major constituents shows a considerable overlap with the range of variation observed in materials of fossil origin such as coal and oil (e. g. figure 3 and 4). Only C4-plants, especially their carbohydrates and proteins, are less depleted with regard to their $\delta^{13}C$ composition than raw materials of fossil origin (figure 4). The photosynthetic pathway of C4-plants (e. g. maize, sugar cane) differs from that of the common C3-plants (e. g. sugar beet, potato, grain).

Conclusions

Based on an extensive literature overview of the $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ values of bio-based as well as fossil-based and fossil energy-based materials and compounds, it is shown that stable isotope ratios of these elements are in general not suitable for determining the bio-based content of products[1]. This is due to the large range of variation observed in the isotopic composition of these materials and compounds, leading to large uncertainties in the estimate of the bio-based content. Moreover, information about the isotopic composition of many relevant materials and compounds is currently lacking. The stable isotope approach could therefore only be feasible in specific cases provided that manufacturers would manage to tightly control the isotopic composition of their raw materials. In addition more data about the isotopic composition of materials and compounds should come available.

[1] This research was carried out within the KBBPPS project ("Knowledge Based Bio-based Products' Pre-Standardization", see also www.kbbpps.eu) and has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No. 312060.

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