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Multi-element isotope fractionation concepts to characterize the biodegradation of hydrocarbons – from enzymes to the environment

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Multi-element compound-specific isotope fractionation (ME-CSIA) has become a state-of-the-art approach for identifying biotransformation reactions. In the last decade, several studies focused on the combined analysis of carbon and hydrogen stable isotopes upon biodegradation of hydrocarbons due to its widespread environmental occurrence as contaminants, often in high concentrations. Most known initial transformation reactions of hydrocarbons have been isotopically characterized in laboratory experiments using model cultures. The data suggest that several of these reactions – especially those occurring under anoxic conditions – can be identified by ME-CSIA, although a number of constraints have been realized which may lead to wrong ME-CSIA data interpretations in field studies. Generally, the applicability of ME-CSIA regarding hydrocarbon biodegradation needs to be corroborated in future field studies.

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Current Opinion in Biotechnology 2016, 41:90–98

This review comes from a themed issue on Analytical Biotechnology

Edited by Hans-Hermann Richnow and Tillmann Lueders

<http://dx.doi.org/10.1016/j.copbio.2016.04.027>

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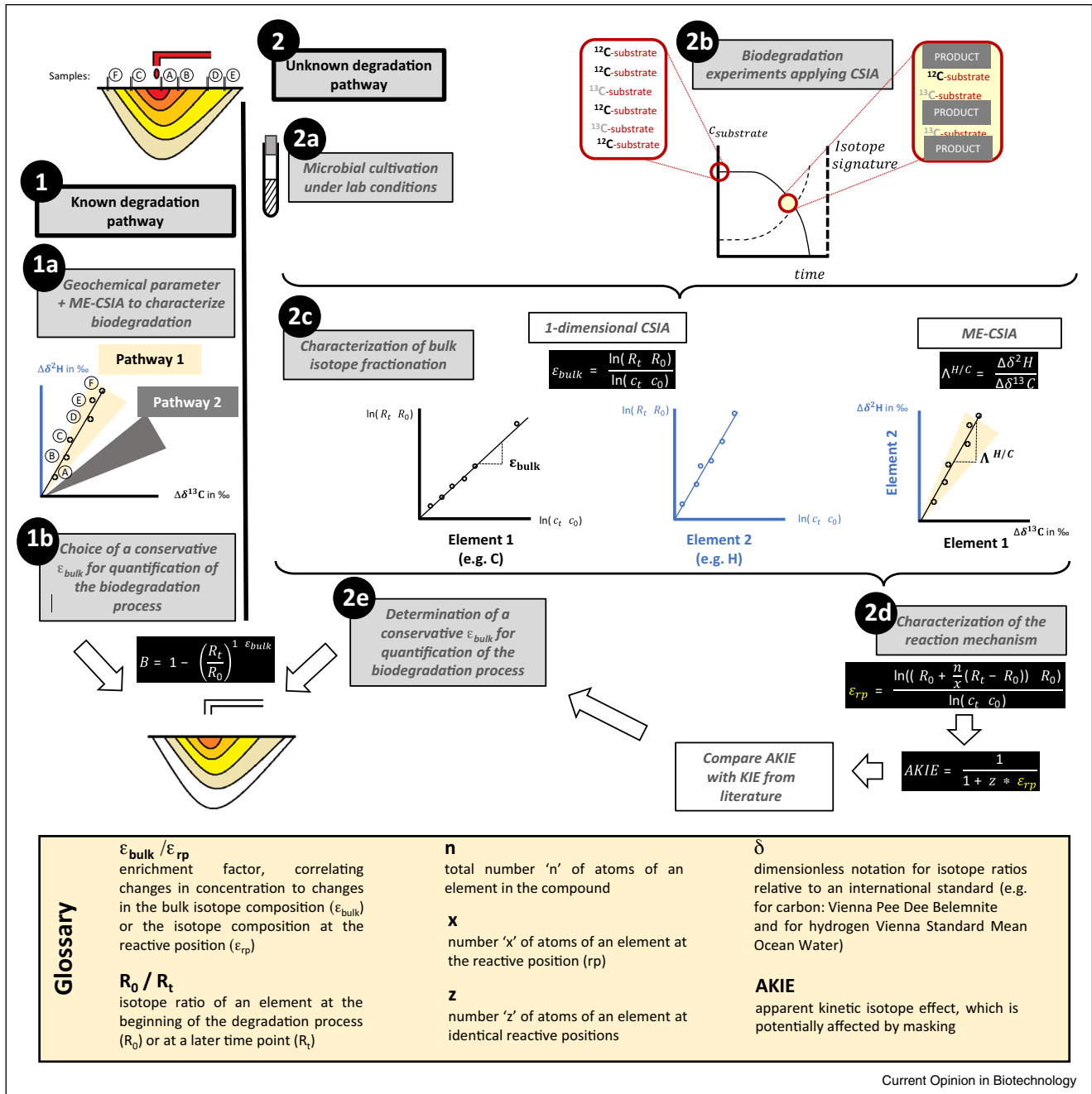
Introduction

Saturated and aromatic hydrocarbons are major constituents of crude oils and fossil fuels and are thus released in huge amounts into the biosphere by both natural seepage of subsurface reservoirs and anthropogenic activities, causing environmental problems due to their toxicity. Several biodegradation studies were dealing with (volatile) hydrocarbons from mineral oil as those can be readily extracted from water and eventually analyzed for stable hydrogen and carbon isotopes by established GC-IRMS techniques [1]. In the last decade, compound-specific stable isotope analysis (CSIA) has become a standard method for source

apportionment and monitoring of natural attenuation processes at contaminated sites [2] as the method basically allows determining biodegradation of various pollutants qualitatively and quantitatively [3]. The principles of CSIA are illustrated in Figure 1. With regard to biological transformations, CSIA is based on slightly different reaction rates of isotopologues in the rate-limiting steps of enzymatic reactions due to energetic constraints. As the lighter isotopologue reacts usually faster, the product of the reactions becomes isotopically lighter and the residual substrate pool becomes isotopically heavier in the course of the reaction, a process termed kinetic isotope fractionation. The magnitude of isotope fractionation for a distinct reaction mechanism can vary considerably depending on, for example, the mass of the involved isotope or the type of biochemical reaction [4**]. Enrichment factors (ϵ_{bulk}) applied in field studies are usually determined from laboratory model cultures with known transformation pathways. Elucidating hydrocarbon biodegradation in the field based on single enrichment factors is not that straightforward as CSIA for one element can be considerably influenced by rate-limiting processes before the isotope-sensitive reaction [4**,5,6*]. In contrast, multi-element compound-specific stable isotope analysis (ME-CSIA) is not sensitive against masking of isotope effects if rate-limiting processes occurring before the bond cleavage (commitment to catalysis) do not cause significant isotope fractionation [4**,6*,7]. ME-CSIA was first introduced as a concept for detecting specific biodegradation pathways in groundwater plumes using carbon and hydrogen isotopes of MTBE as model substrate [8,9]. ME-CSIA for hydrocarbons relies on lambda (λ) values expressing the slope of changing hydrogen and carbon isotope signatures in the course of hydrocarbon transformation reactions ($\delta^2\text{H}/\delta^{13}\text{C}$; see Figure 1). The combined analysis of other isotopes, for example, $\delta^{15}\text{N}/\delta^{13}\text{C}$ [10] or $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ [11] has been recently also applied to characterize reactions upon substituted organics or micropollutants [12]; hence, ME-CSIA has become the state-of-the-art approach to identify distinct environmental transformation reactions but its relevance has to be thoroughly investigated.

A couple of different microbial-mediated enzymatic reactions governing the first irreversible step in the initial transformation of hydrocarbons ('activation reactions') are principally susceptible for ME-CSIA (see Table 1). Under aerobic conditions, monooxygenases or dioxygenases

Figure 1



Application of (ME-)CSIA for assessing biodegradation at contaminated sites. (1) CSIA can be directly applied when the microbial activation step(s) of a pollutant are known and were isotopically characterized before in laboratory. A conservative choice of an isotope enrichment factor from prior laboratory investigations should be chosen to quantify biodegradation. (2) When biodegradation of a pollutant was not isotopically characterized, enrichment cultures from environmental samples are established at laboratory scale (2a) and used for biodegradation experiments applying CSIA (2b). The enrichment of stable isotopes of an element depends on the enzymatic reaction mechanism and is reflected by the enrichment factor ϵ (bulk). Combining isotope enrichments for different elements leads to Λ values which are in opposite to ϵ values independent of rate-limiting steps before the enzymatic transformation and thus can give direct insight into the mechanism (2c). When a reaction mechanism with n atoms of an element in the molecule and x atoms at the reactive sites is known or can be assumed, the isotope enrichment factor for the reactive position ϵ (rp) can be calculated and be used to determine the apparent kinetic isotope effect (AKIE) considering z indistinguishable reactive positions. The kinetic isotope effect (KIE) helps to describe the transition state during a reaction. Hence the comparison of a KIE for an abiotic reaction (e.g. H abstraction) and the AKIE (influenced by other parameters due to the more complex environment) can give a hint for the reaction mechanism (2d). Several biodegradation experiments, for example, carried out with different microorganisms/enrichment cultures and under various redox conditions lead to several isotope enrichment factors. The most conservative ϵ (bulk) for a pathway should be chosen when quantifying biodegradation (2e). The theoretical background and its importance for application at field sites is profoundly presented elsewhere [4**].

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