Variability of ^{13}C-^{14}C in soil CO_2: Impact on ^{14}C groundwater ages

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The ^{14}C age correction models for groundwater use generally an input function that depends on the carbon isotopic composition (^{13}C and ^{14}C) of the soil CO_2. However, in most cases the activity ($A^{14}C$) of atmospheric CO_2 is directly used as input function without considering processes occurring in soil and leading to significant isotopic changes between the composition of atmospheric CO_2 and of soil CO_2 [1][2]. We present here the role of these processes as well as the associated isotopic changes and their impact on the calculation of the age of groundwater. Our approach is based on the use of experimental data from two sites (Fontainebleau sands and Astian sands, France) and its interpretation by a distributed model [3].

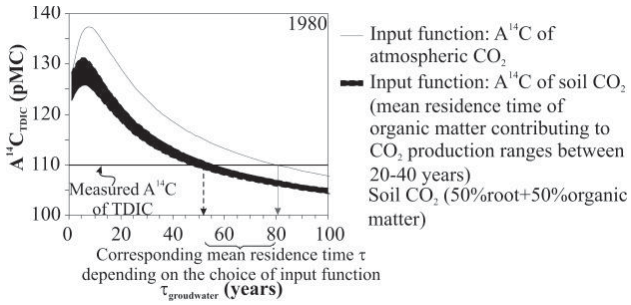

Figure 1: Calculated mean ages of groundwater with respect to different input function; case of a theoretical sampling in 1980.

Since 1950, the evolution of the $A^{14}C$ in soil CO_2 reflects the competition between the fluxes of root derived-CO_2 and organic matter derived-CO_2 due to the residence times of organic matter in the soil. We demonstrate that a mean ^{14}C groundwater age based purely on the ^{14}C atmospheric data may lead to significant biases [2]. For example, a measured $A^{14}C$ of 110 pMC in 1980 corresponds to a mean age of 50±5 or 80±2 y depending on the choice of the input function (Fig. 1). Moreover, the analytical $\delta^{13}C$ of soil CO_2 showed large seasonal variations. Therefore, for dating modern groundwater, a systematic sampling of soil CO_2 has to be integrated into numerical simulations to define ^{13}C-^{14}C content at the water table [4].

[1] Fontes (1992) *Radiocarbon After Four Decades*, 242-261; [2] Gillon et al. (2009), *Geochim. Cosmochim. Acta* **73**, 6488-6501; [3] Gillon et al., *geoderma*, in revision; [4] Gillon (2008), Ph. D. Thesis, Paris Sud XI Univ., France.

What we do and don't know about microbial mercury methylation

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More than 40 years after the discovery of the Hg methylation process in sediments, we still don't know why some bacteria are capable of methylmercury (MeHg) production and others are not. This paper will present an overview of our understanding of those processes, taken from the recent literature and ongoing research in our groups.

The intimate and complex relationship between mercury and sulfur is a dominant feature of mercury's biogeochemical cycle. However, while sulfate- and iron-reducing bacteria (SRB and FeRB, respectively) are implicated in MeHg production, only a subset of these organisms have the ability to produce MeHg. Other than the observation that most methylators have membership in the *Deltaproteobacteria* , there is no obvious physiological or genetic trait that is common. Recent data suggesting net MeHg production in novel environments, like surface ocean waters, suggest that the diversity of Hg-methylators may be broader than we realize. However, to date, and with modern analytical methods, Hg methylation has only been demonstrated within the *Deltaproteobacteria*.

The earliest work on Hg methylation mechanisms focused on intra-cellular methylases. Methylcobalamine was identified as the proximate methyl transfer group in one *Desulfovibrio*, but the proposed pathway is also present in many non-methylating SRB and FeRB. The sulfate-reducing apparatus in SRB does not appear to play a direct role in methylation, although the sulfide and other reduced sulfur compounds produced by SRB have dramatic effects on Hg bioavailability to cells

Stable isotope fractionation suggests that some portion of the Hg methylation pathway is enzymatic, but whether that portion is uptake, methylation or even export is unknown. Cell-free protein extracts of methylators exhibit low levels of methylation not seen in extracts of non-methylators. Denaturation of proteins eliminates the activity detected confirming the apparent enzymatic nature of the catalyst. Importantly, Hg-methylators release MeHg from cells very rapidly, and perhaps as a part of a larger organic complex. SRB (and FeRB) also demethylate MeHg, sometimes very rapidly. These organisms do not contain the *mer* operon and the mechanism of demethylation remains a mystery.

More recently, Hg transport has emerged as a potentially distinguishing characteristic of some Hg-methylators. Certain Hg-thiol complexes are highly bioavailable to methylators Nanoparticulate HgS, bound up in organic colloids, is also bioavailable to Hg methylators. However, the uptake mechanism(s) for both remain uncertain. Progress on understanding MeHg production in the environment depends on a fuller understanding of Hg methylation pathways in bacteria. The recent completion of full genome sequences for a number of Hg-methylating SRB may help solve this mystery through phylogenetic comparisons and genetic approaches.