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Carbon and mercury stable isotope fractionation during aqueous photodemethylation of CH_3Hg.

LUISA M MALBERTI[1], CHRISTELLE LAGANE[1], DAVID POINT[1] AND JEROEN E SONKE[2]

[1]Géosciences Environnement Toulouse, CNRS/IRD/Université Paul Sabatier Toulouse III
[2]CNRS/Université de Toulouse

Presenting Author: lmalberti1996@gmail.com

The photodemethylation of monomethylmercury (CH_3Hg) is one of the most important natural processes for the decomposition of CH_3Hg and is therefore key to understanding its natural cycle. The isotopic composition of a compound carries information about the sources and pathways of transformation of that compound. Natural degradation and formation processes often leave specific and characteristic isotopic fingerprints. The fractionation of the stable isotopes of Hg during photodemethylation of CH_3Hg has been studied [1][2]. Among the results, a particular mass independent fractionation (MIF) was observed for the odd isotopes of Hg [1]. However, to date, no studies have been conducted from the perspective of the carbon (C) isotopes of the methyl group (-CH_3) of CH_3Hg. If we want to use $\delta^{13}C_{CH3Hg}$ to understand the origin of the C source in CH_3Hg, then we must consider the fractionation of C isotopes during the degradation of CH_3Hg. In the present work we present the results of different photodegradation experiments where, in addition to the Hg isotopes and the degradation kinetics, the fractionation of C isotopes of the CH_3Hg methyl group was analyzed using the compound specific isotope analysis (CSIA) technique: purge and trap – gas chromatography – combustion – isotope ratio mass spectrometry (PT -GC-C-IRMS) [3]. Our results show MIF consistent with the 2007 Bergquist and Blum study, and a relatively minor enrichment of heavy C isotopes in the residual CH_3Hg during photodemethylation. Changes on the $\delta^{13}C$ values of ~2.3‰ in real seawater experiments were observed. While for the experiments in water MQ the change on $\delta^{13}C$ values ranged from 7 up to 11‰.

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[2] Zhang and H. Hsu-Kim, 2010, doi: doi:10.1038/ngeo892.
[3] Queipo-Abad, et.al., 2020, doi: 10.1016/j.chroma.2019.460821.