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Mass independent fractionation of mercury isotopes.

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Mass-independent fractionation (MIF) of isotopes in geochemical processes was first observed in the early 1980's for oxygen and later for sulfur [1]. Recently mercury (Hg) was added to this shortlist when isotopic anomalies were observed for Hg's two odd isotopes, ^{199}Hg and ^{201}Hg in biological tissues [2-5]. The five remaining even isotopes of Hg display mass dependent fractionation (MDF) in all of these studies. Experimental work identified net photoreduction of Hg species by fulvic acids under quasi-environmental conditions as a plausible mechanism for inducing MIF [3]. At the atomic level, these MIF observations appear to be the result of the so called nuclear spin effect.

The observation of isotopic anomalies due to MIF has a much longer history in the chemical physics community. Already in 1935, Mrozowski demonstrated the feasibility of inducing isotopic anomalies in mercury vapor by nuclear spin selective excitation [6]. The nuclear spin effect (also known as magnetic isotope effect) may take place when Hg isotopes with natural isotopic abundances are excited into a radical state by bio- or photo-chemical means [7, 8]. Since the life-time of isotope radicals with nuclear spin (^{199}Hg, ^{201}Hg) may differ from the life-time of isotope radicals without nuclear spin (the even ^{196}Hg, ^{198}Hg, ^{200}Hg, ^{202}Hg, and ^{204}Hg), a means exists to separate even from odd isotopes in reaction products and reactants. A second mechanism capable of inducing MIF in Hg isotopes has been suggested to be the nuclear field shift (also known as nuclear volume fractionation)[9], yet no field studies have confirmed this.

In this contribution MIF for Hg will be reviewed. New data on MIF in tropical and Arctic food chains will be presented and highlights i) how odd-isotope anomalies

depend on latitude in the Alaskan Arctic, and ii) that besides aquatic photochemistry, natural biochemical reactions in marine bird species also induce MIF.

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