Carbon and hydrogen isotope effects in contaminant volatilization and phase partitioning – Implications for contaminant attenuation studies

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The standard practice in contaminant attenuation studies utilizing CSIA (compound-specific isotope analysis) is to attribute the observed isotope effects to degradative processes. Published data on isotope effects upon phase partitioning, volatilization etc. have suggested that these processes result with minor isotope fractionation and therefore they should not interfere with the isotopic signatures of degradation. Experimental results will be shown to demonstrate that pathways involving vapor phase transfer (experimental models were set for simulation of phase partitioning, passive volatilization and dynamic vapor extraction) are likely to result with measurable changes of isotope ratios in contaminants such as MTBE and benzene remaining in the aqueous or NAPL matrix. For processes involving unidirectional mass flux (e.g., vapor phase extraction), isotope fractionation can be described in terms of Rayleigh model, with cumulative isotope effects that increase with progressive mass removal. The enrichment factors of the studied non-degradative processes are lower than those resulting from most biotic or abiotic degradation processes. On the other hand, enrichment factors characteristic of a number of degrading organisms (e.g., some of the published carbon isotope enrichment factors of aerobic MTBE degraders) are low and similar in magnitude to those resulting from volatilization. The practical significance of the non-degradative interferences varies depending on the site context. The key elements are the type of contaminant and the degradation process (defining the magnitude of isotope fractionation attributable to *in situ* degradation) and the relative significance of mass attenuation by degradative vs. non-degradative pathways. Evaluation of *in situ* biodegradation for weakly fractionating compounds, in particular those with few sampling points and those utilizing only one isotope species (as opposed to 2-D CSIA) should take into account the potential for isotope effects caused by non-degradative attenuation. Adjustments to "traditional" protocols of CSIA data evaluation will be proposed to account for the isotope effects resulting from non-degradative processes.

Climate variability in the Mojave Desert over the past 43 ka

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Noble gas concentrations and oxygen isotopes in groundwaters from the western Mojave Desert, California contain a ~43 ka paleoclimate record denoting that mean annual temperatures in the late Pleistocene, during the period from ~43 ka BP to 12 ka BP, were 4.2 ± 0.8 ° C cooler than from ~10 ka to the present day. Groundwaters recharged during the period from 43 ka to 12 ka BP also contain higher concentrations of excess-air (entrained air bubbles), enrichments in ^{18}O. Interpreted ages from the dissolved inorganic ^{14}C in the groundwaters were used to constrain the records.

Higher concentrations of excess-Ne (a proxy for 'excess-air') prior to 12 ka BP suggest more vigorous aquifer recharge, while enriched $^{18}O/^{16}O$ ratios may indicate greater rainfall or more intense precipitation events during this period. Combined, these parameters provide evidence that the Mojave climate during the late Pleistocene was more humid than present-day arid conditions.

Taken together, the noble gas, oxygen isotope, and excess-air based paleoclimate archives proffer evidence that the Mojave desert of southern California was both cooler and wetter prior to the Last Glacial Maximum. More humid conditions may have resulted from an enhanced hydrological cycle throughout the southwestern United States, which is consistent with chemical, biological and geological evidence of extensive late Pleistocene pluvial lakes and lacustrine phase during this period.