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Revisiting excess air in groundwater with a new hydroclimate tracer

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Excess air in groundwater (commonly represented by dissolved neon supersaturation, ΔNe) affects solubility-based noble gas temperature reconstructions and other dissolved gas tracers in groundwater hydrology (e.g., CFCs and SF_6 as residence time tracers). Over the past several decades, various models have been developed and refined to represent the formation of excess air from entrapped air bubbles and quantitatively account for its impact on dissolved gas observations. Excess air may serve as an indicator of past hydroclimatic conditions and may be linked to patterns of precipitation and recharge, which can drive water table fluctuations that entrap unsaturated zone air. However, interpreting excess air as a hydroclimate indicator remains challenging, with open questions regarding the mechanisms of air entrapment and subsequent dissolution, and how key hydrogeologic and climate parameters (e.g., the mean water table depth and the amplitude of seasonal water table fluctuations) may influence the amount of air entrapment and its partial dissolution.

Recent analytical advances have enabled simultaneous determination of the amount of excess air (ΔNe) and the water table depth (from high-precision Kr and Xe isotope measurements) that characterize the conditions of groundwater recharge. This water table depth tracer is based on the nearly linear increase of Kr and Xe isotopic ratios with depth in the unsaturated zone due to gravitational settling. We hypothesize that deeper water table depths occur under more arid conditions with smaller and less frequent water table fluctuations from areal recharge, resulting in less excess air. We find evidence for this relationship between water table depth and excess air at three semi-arid field sites in the western U.S., while one arid Mojave Desert site suggests that extreme precipitation regimes and/or rapid streamflow infiltration may diverge from this pattern. Using a sample with anomalously high excess air, we also demonstrate unambiguously that excess air originates from gravitationally fractionated unsaturated zone air at the water table. These results represent an important advance in understanding the climatic influences on excess air formation and interpreting excess air as a paleoclimate tracer.