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Subsurface dynamics of reactive and inert gases in the context of noble gases as environmental tracers in groundwater hydrology

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Applications of inert gases in groundwater hydrology require a profound understanding of underlying biogeochemical processes. Some of these processes are, however, not well understood and therefore require further investigation. This is the first study simultaneously investigating soil air and groundwater in the context of noble gas tracer applications, accounting for seasonal effects in different climate regions. The sampled data confirm a general reliability of common assumptions proposed in the literature. In particular, a solubility-controlled description of excess air formation and of groundwater degassing can be confirmed. This study identifies certain effects which need to be taken into account to reliably evaluate noble gas patterns. First, long-term samplings suggest a permanent temperature-driven equilibration of shallow groundwater with entrapped air bubbles, even some years after recharge. Second, minor groundwater degassing is found to challenge existing excess air model approaches, depending on the amount and the fractionation of excess air. Third, soil air composition data of this study imply a potential bias of noble gas temperatures by up to about 2°C due to microbial oxygen depletion and a reduced sum value of O_2+CO_2. This effect causes systematically lower noble gas temperatures in tropical groundwater samples and in shallow mid-latitude groundwater samples after strong recharge during the warm season. However, a general bias of noble gas temperatures in mid-latitudes is probably prevented by a predominant recharge during the cold season, accompanied by nearly atmospheric noble gas mixing ratios in the soil air. Findings of this study provide a remarkable contribution to the reliability of noble gas tracer applications in hydrology, in particular with regard to paleoclimate reconstructions and an understanding of subsurface gas dynamics.