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Using groundwater age data to understand Nitrate contamination in a coastal aquifer

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Nitrate contamination in groundwater from over-application of fertilizers and wastewater sources is a significant and growing threat to water quality in major aquifers around the world. Nitrate concentrations in groundwater underlying the agriculturally intensive Arborea plain in Sardinia (Italy) commonly exceed the World Health Organization's threshold of 50 mg/L (N as NO_3). The area was designated as a "Nitrate Vulnerable Zone" (NVZ) in 2006 following introduction of the EU Nitrates Directive. The NVZ designation requires applying agricultural action programme measures aimed at reducing the transfer of nitrogen from soils to surface and groundwater. Despite these efforts, nitrate concentrations in the area have remained constant, probably due to the time lag of nutrient transport from source areas to receptor wells. Environmental tracers are potentially powerful tools for studying NO_3contamination because of their ability to reliably characterize recharge sources, flow paths, and residence times. Samples from 13 wells within the shallow Sandy Hydrological Unit (SHU) and 2 deeper wells exploiting the underlying Alluvial Hydrological Unit (AHU) were collected for major and trace element chemistry, stable isotopes of water (^{2}H and ^{18}O), sulfur hexafluoride (SF_6), tritium (^{3}H), dissolved noble gases (He, Ne, Ar, Kr, and Xe), and helium isotopes (^{3}He and ^{4}He). Most wells display a trend of increasing apparent age with depth, while a correlation between apparent age and horizontal position in the study area is not well-defined. The greater dependence of age on depth than on horizontal distance down-gradient suggests that direct recharge and local irrigation water are the dominant sources of recharge to the SHU. Wells within the AHU are untritiated and contain high terrigenic ^{4}He concentrations that exceed the atmospheric He component by 200-500%, while samples from wells in the SHU are mostly tritiated and contain little terrigenic ^{4}He. This suggests that AHU waters are substantially older than those in the SHU. Recharge temperatures for samples from the SHU are equal to local ground temperatures (18-20˚C), whereas recharge temperatures for the two AHU samples are much cooler (12-14˚C), indicating a clearly different recharge source. The greater age and different recharge source of groundwater in the AHU compared to the overlying SHU suggest that the former may not be recharged locally, and the hydraulic connection between the two aquifers may be limited. A general trend of decreasing NO_3 concentrations with increasing apparent age was observed. A possible explanation for this trend is that NO_3 is chemically degraded along flow paths by denitrification. Denitrification produces N_2 gas, and most samples do contain significant excess N_2 (>20% of atmospheric component), verifying that denitrification is indeed widely occurring. In summary, age and dissolved gas results provide valuable information regarding groundwater flow paths, sources of recharge in the Arborea area that could be valuable for managing the nitrate problem and advancing the understanding of solute transport processes in NO_3 contaminated groundwater.

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