Radium mobility and the age of groundwater in public-drinking-water supplies from the Cambrian-Ordovician aquifer system, north central USA

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Background

- MCL = \(226^{\text{Ra}} + 228^{\text{Ra}} = 5 \text{ pCi/L}\)
- Szabo et al., (2012) compiled available NAWQA data from public- and domestic-supply wells and shallow monitoring wells
- \(228^{\text{Ra}}\) not routinely sampled by NAWQA prior to 2013

Sampling locations & combined Ra \((226^{\text{Ra}} + 228^{\text{Ra}})\)

- Aquifer-wide, systematic assessment of \(224^{\text{Ra}}, 226^{\text{Ra}}\) and \(228^{\text{Ra}}\) in public-drinking-water supplies
- 60 PSW's selected using a stratified, randomized sampling design
- Samples collected prior to any treatment

\(224^{\text{Ra}}\) and \(228^{\text{Ra}}\) occur in a 1:1 ratio

- Progeny in the same decay series
- \(224^{\text{Ra}}\) adds alpha-particle activity to drinking-water supplies at concentrations similar to beta-particle activity from \(228^{\text{Ra}}\)
- \(224^{\text{Ra}}\) can be used to identify areas where \(224^{\text{Ra}}\) should be measured and where GAA measurements should be made within 72 hrs of sample collection

Mean Groundwater Age

- \(^{14}\text{C}\) indicates young water in regionally unconfined area and water \(\geq 30,000\) yrs. in the regionally confined area
- \(^{4}\text{He}\) indicates residence times \(> 100,000\) yrs in regionally confined area
- GW ages correspond to flow system

Redox conditions and water types evolve with GW age

- Mean ages ranged from 19 to \(> 1\)Myr
- Youngest samples were from the regionally unconfined area
- Redox conditions and water types evolve with increasing GW age
Combined Ra ($^{226}\text{Ra} + ^{228}\text{Ra}$) increases with anoxia and mineralization

- Under oxic conditions, Ra sorbs to Fe-hydroxide coatings
- Under reducing conditions, Fe-hydroxide coatings dissolve:
  1. Releasing Ra into solution
  2. Decreasing the number of available sorption sites
  3. Increasing the amount of other cations (mineralization) that will compete with Ra for sorption sites

$^{226}\text{Ra}:\text{Ba}$ ratios illustrate change in $^{226}\text{Ra}$ sorption under differing redox conditions

- Ba is a close chemical analog to Ra
- Ba concentrations do not differ across the aquifer system
- Ratios are lowest for "oxic" and highest for "anoxic" samples
- $^{226}\text{Ra}$ is sorbed on Fe-hydroxide coatings under "oxic" conditions and becomes mobilized under reducing conditions and accumulates in solution with increasing GW age

$^{226}\text{Ra}$ $K_d$ illustrate change in $^{226}\text{Ra}$ sorption with increasing mineralization

- Highest $K_d$ values in low TDS, oxic samples with low Ra
- Lowest $K_d$ values in mineralized, anoxic samples with high Ra
- $^{228}\text{Ra}$ is mobilized into solution with anoxia and increasing mineralization due to decreasing sorption capacity

Exchange processes do not reduce $^{226}\text{Ra}$ concentrations

- If cation exchange was a dominant process, these ratios would exceed 5
- As a minor process, Ra is not efficiently removed
- Carbonate rocks do not provide abundant exchange capacity

Evaluating Results in a Human-Health Context

Benchmark Quotient = \frac{\text{Environmental Concentration}}{\text{Human-health Benchmark}}

- Ra MCL is based on the combined concentrations of $^{226}\text{Ra} + ^{228}\text{Ra}$
- The health risk from $^{226}\text{Ra}$ is less than that from an equal amount of $^{228}\text{Ra}$
- $^{224}\text{Ra}$ does not have a MCL
- WHO guidance values were used in lieu of MCLs to calculate Benchmark Quotients for the three Ra isotopes.

Human-health Context

- $^{226}\text{Ra}$ only Ra isotope with BQ > 1
- $^{226}\text{Ra}$ BQ values from regionally unconfined area approached or exceeded unity
- Risk from $^{226}\text{Ra}$ is greatest where $^{226}\text{Ra}$ is greatest
- Indicates importance of monitoring all 3 Ra isotopes in upgradient areas as well as downgradient where the Ra MCL is more frequently exceeded

WHO, 2011, Table 9.2
Conclusions

- Geochemical conditions mobilize Ra into solution
- Under "oxic" conditions Ra sorbs to Fe-hydroxide coatings
- Under "anoxic" conditions Ra is mobilized into solution
- Decreased sorption capacity maintains Ra in solution
- Geochemical processes such as co-precipitation and cation exchange are ineffective
- $^{228}$Ra occurs at concentrations greater than its WHO guidance value
- $^{226}$Ra and $^{228}$Ra contribute to total exposure
- GW age is a surrogate for causative factors

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Questions?

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