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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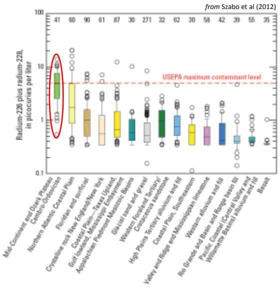
U.S. Geological Survey
National Water Quality Assessment (NAWQA) Project

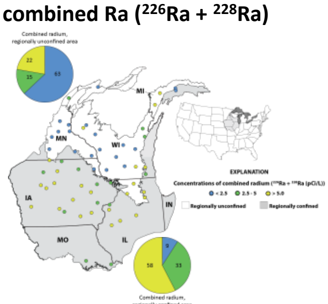
Background

- *MCL = ^{226}Ra + ^{228}Ra = 5 pCi/L*
- *Szabo et al., (2012) compiled available NAWQA data from public- and domestic-supply wells and shallow monitoring wells*
- *^{224}Ra not routinely sampled by NAWQA prior to 2013*



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

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



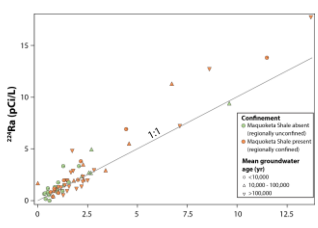
Mean Groundwater Age

- *^{14}C indicates young water in regionally unconfined area and water ≥ 30,000 yrs. in the regionally confined area*

- *^{4}He indicates residence times > 100,000 yrs in regionally confined area*
- *GW ages correspond to flow system*

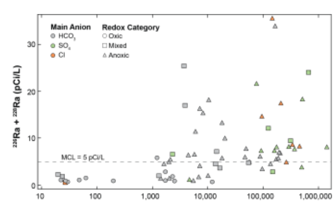
^{224}Ra and ^{228}Ra occur in a 1:1 ratio

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



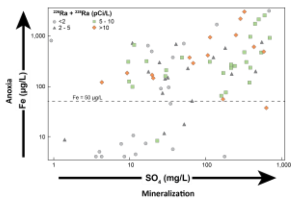
Redox conditions and water types evolve with GW age

- *Mean ages ranged from 19 to > 1Myr*
- *Youngest samples were from the regionally unconfined area*
- *Redox conditions and water types evolve with increasing GW age*



Combined Ra (^{226}Ra + ^{228}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*



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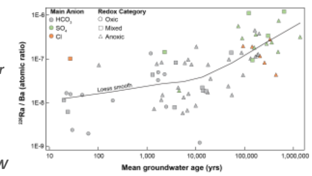
^{226}Ra:Ba ratios illustrate change in ^{226}Ra sorption under differing redox conditions

- *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}Ra is sorbed on Fe-hydroxide coatings under "oxic" conditions and becomes mobilized under reducing conditions and accumulates in solution with increasing GW age*



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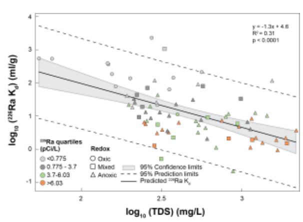
^{226}Ra K_d illustrate change in ^{226}Ra sorption with increasing mineralization

- *Highest K_d values in low TDS, oxic samples with low Ra*
- *Lowest K_d values in mineralized, anoxic samples with high Ra*
- *^{226}Ra is mobilized into solution with anoxia and increasing mineralization due to decreasing sorption capacity*



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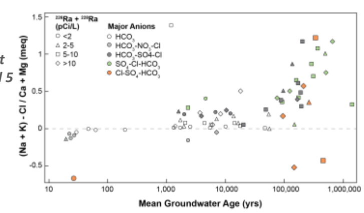
Exchange processes do not reduce ^{226}Ra concentrations

- *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*



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Evaluating Results in a Human-Health Context

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

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

WHO, 2011, Table 9.2

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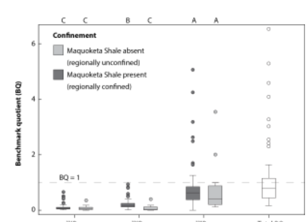
Human-health Context

- *^{228}Ra only Ra isotope with BQ > 1*
- *^{228}Ra BQ values from regionally unconfined area approached or exceeded unity*
- *Risk from ^{224}Ra is greatest where ^{228}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*



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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*
- *^{224}Ra and ^{226}Ra contribute to total exposure*
- *GW age is a surrogate for causative factors*

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