SAND2007-2888C

Radium in Groundwater Aquifers in the United States and Middle East:

Occurrence, Treatment and Implications for Inland Desalination.

Malcolm Siegel, Ph.D. M.P.H., Richard Kottenstette,
Sandia National Laboratories, Albuquerque, NM 87185.

Avner Vengosh, Ph.D.,
Duke University, Durham, NC 27708

April 30, 2007

Albuquerque, NM

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Acknowledgements

- Ward Hunter and Pinehill Water Utility staff
- Deb Misra (NNEPA)
- Kathleen Holt, Rose Preston, Malynda Aragon, Randy Everett, William Holub Jr
- Heather Himmelberger (NMT)
- Arsenic Water Technology Partnership (SNL, AwwaRF, WERC)

Sandia National Laboratories

Outline

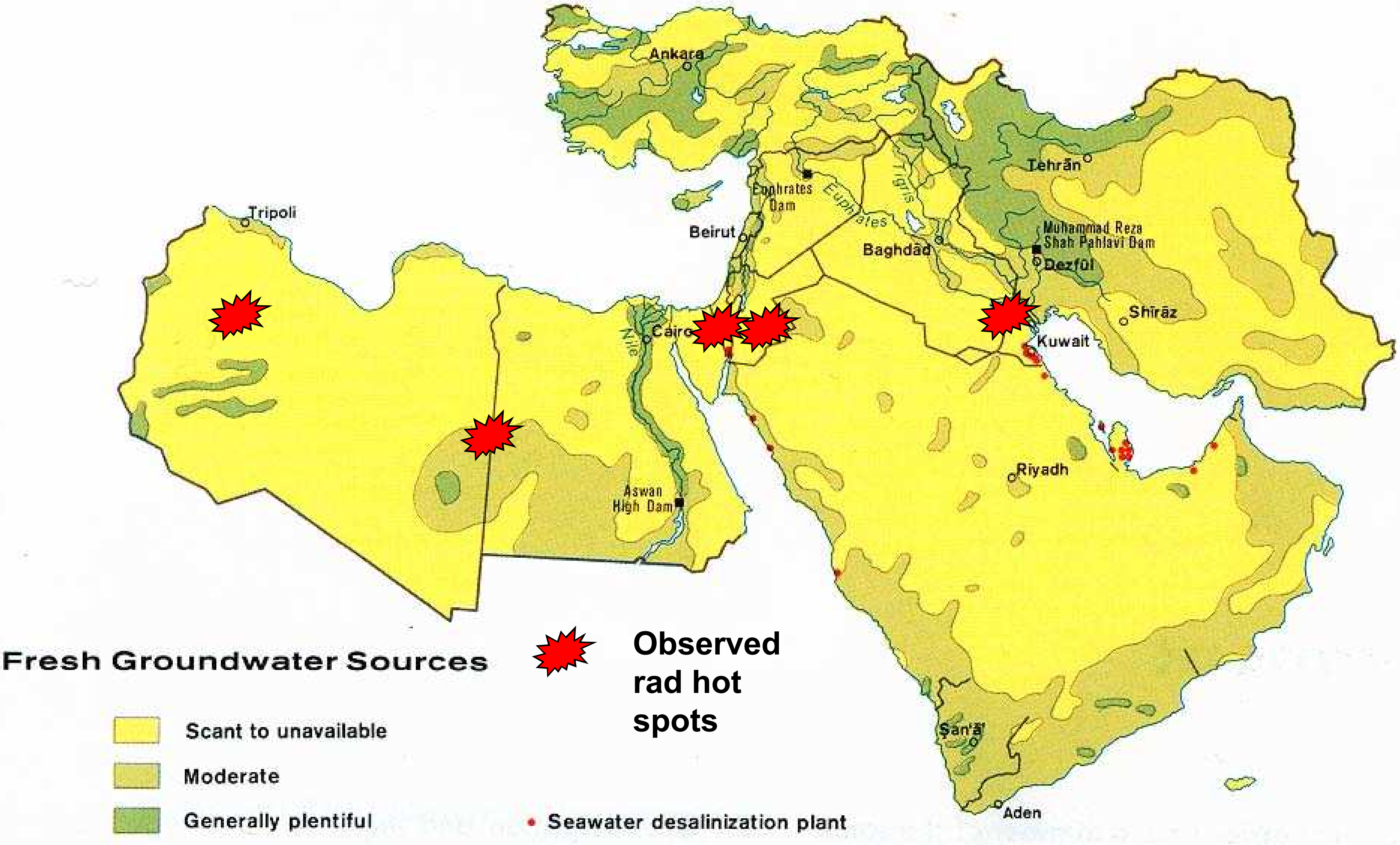
- Present overview of occurrence of radium in fossil and brackish water aquifers in Middle East and Southwest USA
- Describe potential implications for exploitation of brackish water aquifers as drinking water sources
  - Treatment processes and production of TENORM
- Describe results of studies of source identification and treatment of radium
  - Studies of Ra isotopes in Negev Desert, Israel
  - Pilot tests of radium removal on Navajo Reservation

Health Effects and Radium

- **Biochemically similar to Ba and Ca; concentrates in bone when ingested.**
- **Increased risk of bone sarcomas, head carcinomas.**
- **Effects of oral ingestion demonstrated by studies of a large cohort of women who painted radium watch dials at beginning of century.**
- **Increased incidence of leukemia not observed but expected.**
- **Current regulation for drinking water: $^{226}Ra + ^{228}Ra = 5$ pCi/L**

Unfortunate Occurrences of Radium in Fossil and Brackish Waters in Middle East and USA

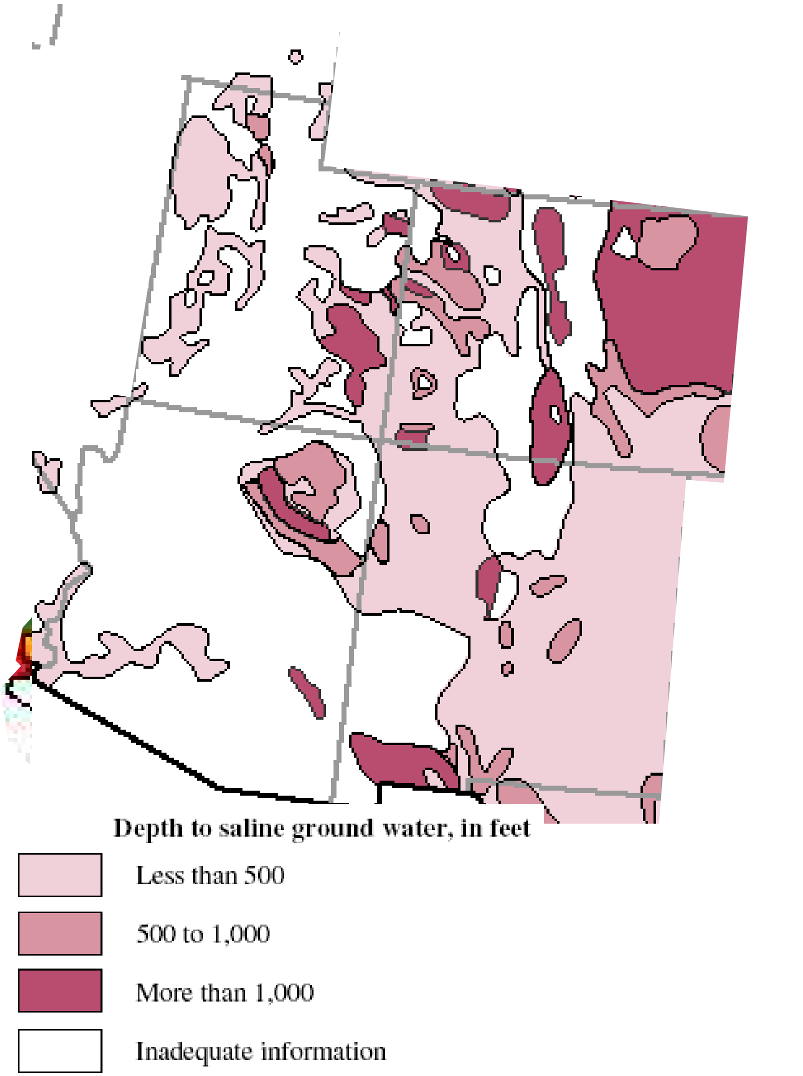
Fossil groundwater is the last natural water resource in the Middle East



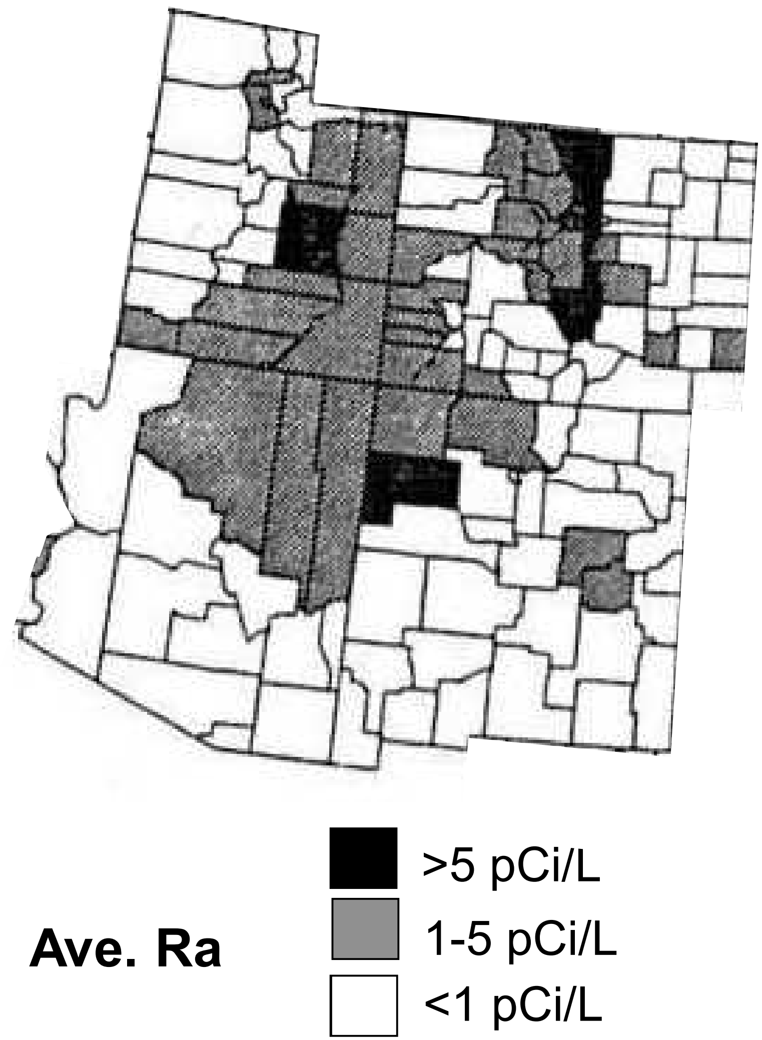
Resource Potential of Brackish Groundwater for New Mexico

- ¾ of groundwater in New Mexico is saline and requires treatment
- Potential saline groundwater resource is 15 billion acre-ft.
- Most suitable for development:
  - Albuquerque Basin (slightly saline, 1-3K mg/L))
  - San Juan, Roswell Basins and Capitan Limestone (moderately saline: 3-10K mg/L))
  - Jornada del Muerto and Estancia Basins (highly saline: 10-35K mg/L))
  - Tularosa Basin (brine: > 35K mg/L))

Brackish water and radium in the Southwest USA



Large Potential resource



Ra in groundwater

Radium is high in brackish waters

- Radium levels high in saline waters or reduced water due to low sorption by rock matrix
  - Source of radium is decay of uranium and thorium
  - High salt content of saline waters competes with radium for sorption sites on clays
  - Lack of sorbent Fe and Mn oxides in reduced water
  - Many studies in Australia, Canada, US
  - Confirmed by studies in Israel
- Radium occurs as cation and is relatively insoluble (as sulfate and carbonate) but ^{226}Ra can be solubilized by alpha-recoil leading to high concentration in fresh water.

Ra content of brackish water could affect viability of desalination

- Economic impact
  - Affect use of brine in fish farms (Israel)
    - Ra bioaccumulation (50 L/kg) may prevent use of brine
  - Reduce economic value of salts
    - Will radioactive component reduce value?
- Regulatory headaches
  - Concentration of radionuclides will create TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials).

Definition of TENORM

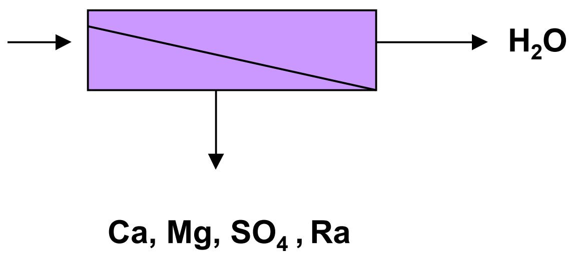
- Technologically enhanced naturally occurring radioactive materials
  - any naturally occurring radioactive materials not subject to regulation under the Atomic Energy Act
  - whose radionuclide concentrations or potential for human exposure have been increased above levels encountered in the natural state by human activities.

Radium can be concentrated by nanofiltration or reverse osmosis

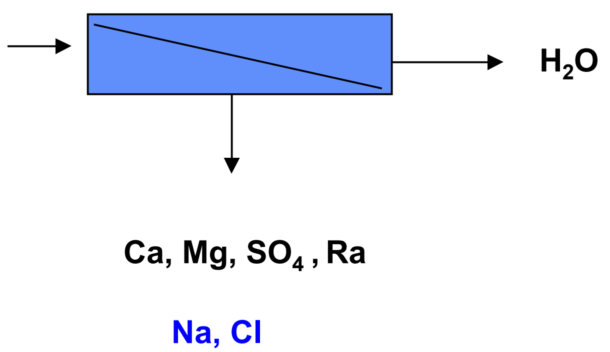
•NF removes 75 to 85 percent of radium from drinking water

•RO remove 85 to 98 percent of radium from drinking water

NF softening



RO treatment



Sandia National Laboratories

Radionuclides will be enhanced in the RO concentrate

Recovery	Raw water at MCL	50%	75%	88%
Concentration factor	0	2	4	~ 8
Conc Volume (Mgal/day)	0	5	2.5	1.2
Ra 226 and 228 (pCi/L)	5	10	20	40
Uranium (ug/L)	30	60	120	240

(assume 10MGD feed- raw water at MCL)

Sandia National Laboratories

TENORM waste regulations are complex

- **Discharge of RO concentrate directly to a surface water is governed by federal and state regulations**
  - Decision is based on appropriate and accessible receiving water
  - National Pollutant Discharge Elimination System permit required
- **Discharge of RO Concentrate to a Waste Water Treatment Plant (WWTP)**
  - The WWTP can refuse waste and must conform to NPDES permit
  - Subject to Technically Based Local Limits
  - May need permit or contract
- **Underground Injection Control regulations define ^{226}Ra and ^{228}Ra concentration >60 pCi/L as radioactive waste and must be disposed of in Class I wells.**

http://www.epa.gov/radiation/tenorm/drinking_water.htm

Examples of TENORM from Water treatment

Treatment Technology	Contaminant Removed	Removal Efficiency	Wastes Produced	Waste Concentrations
Cation exchange	Radium	85-97%	Rinse & backwash water	8 to 94 pCi/L 50 to 3,500 pCi/L
Reverse osmosis	Radium	90+%	Reject water	7 to 43 pCi/L-Ra
Selective sorbents	Radium	90+%	Selective sorbents (radium selective and activated alumina	up to 3.6 pCi/g-Ra
Iron removal -Oxidation -Greensand	Radium	0-70%	Solids & supernatant from filtration backwash Green sand media	12 to 1,980 pCi/L-Ra 28 to 250 pCi/g-Ra

Data from : A Regulators' Guide to the Management of Radioactive Residuals from Drinking Water Technologies [EPA 816-R-04-005]

Sandia National Laboratories

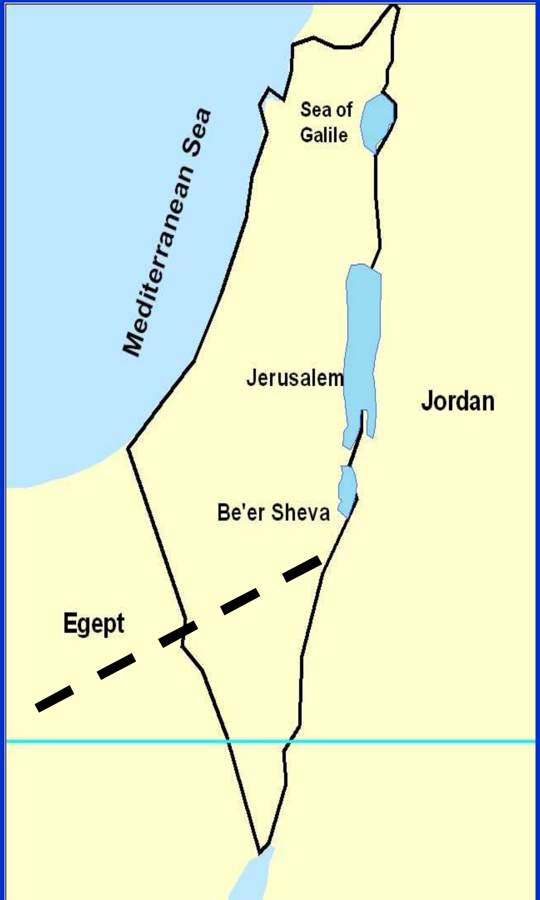
Better to Avoid Radium in Disposal Brines

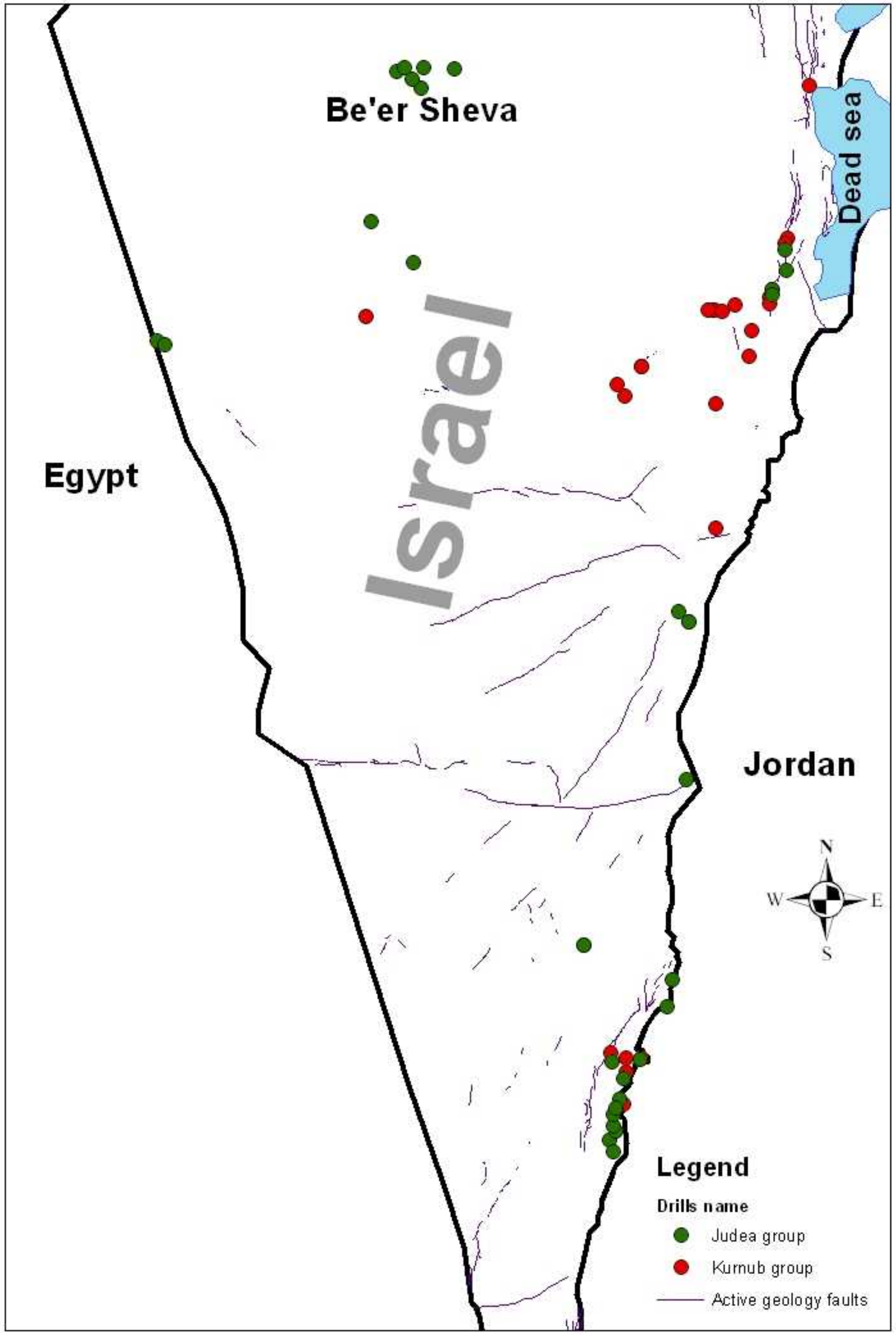
- Option 1: Avoid aquifers with high radium content
  - Is radium coming from an point source (ore deposit) or non-point source (uniform property of aquifer)?
  - Use of radium isotopes to determine source
    - Example Negev Desert in Israel
- Option 2: Selectively remove radium from salts
  - Adsorptive media or coagulation/filtration
    - Example - Pine Hill pilot study

Option 1:
Avoiding aquifers with high radium contents

Radium isotopes in the Negev

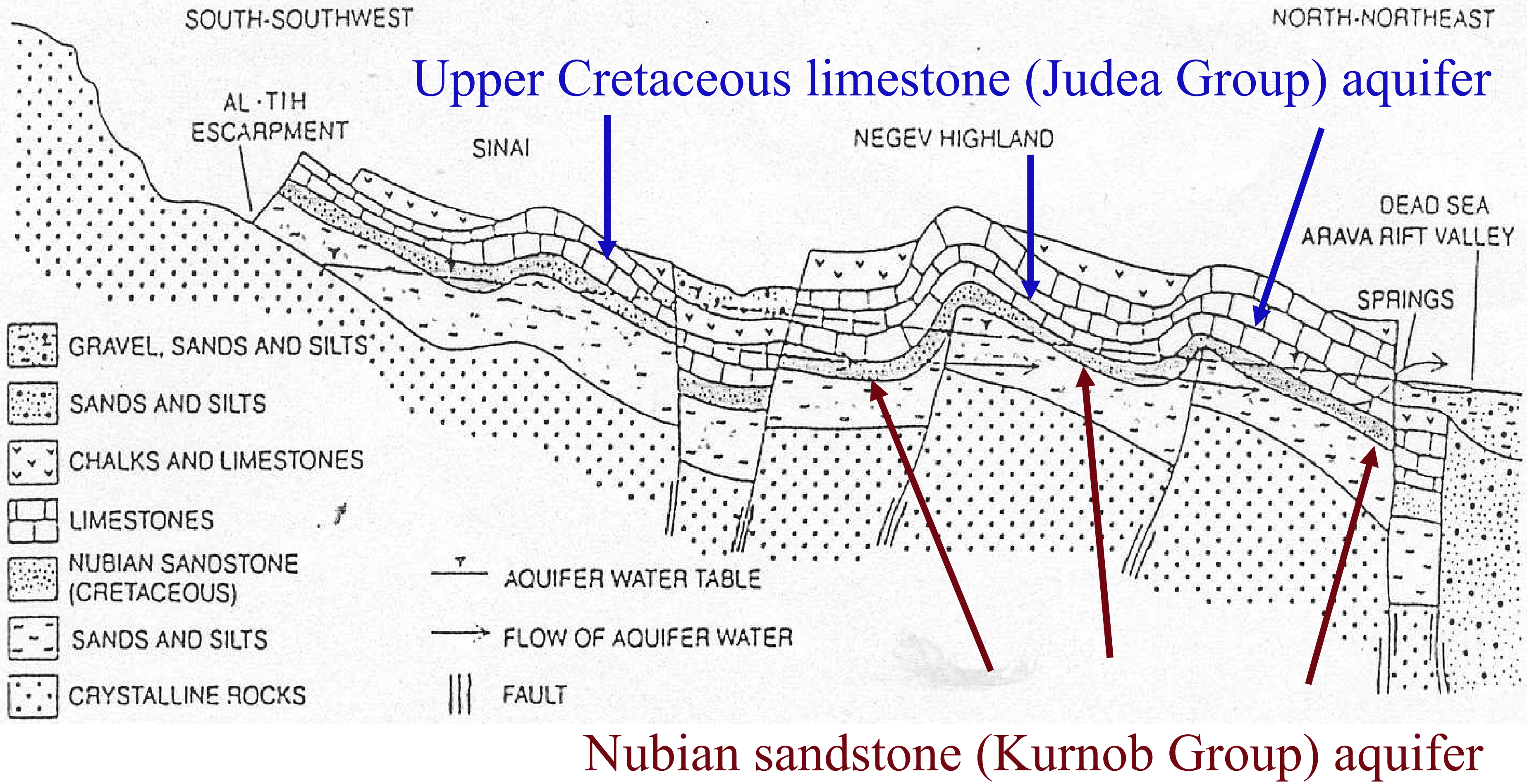
Radium in Groundwater from the Negev and Arava Valley, Israel



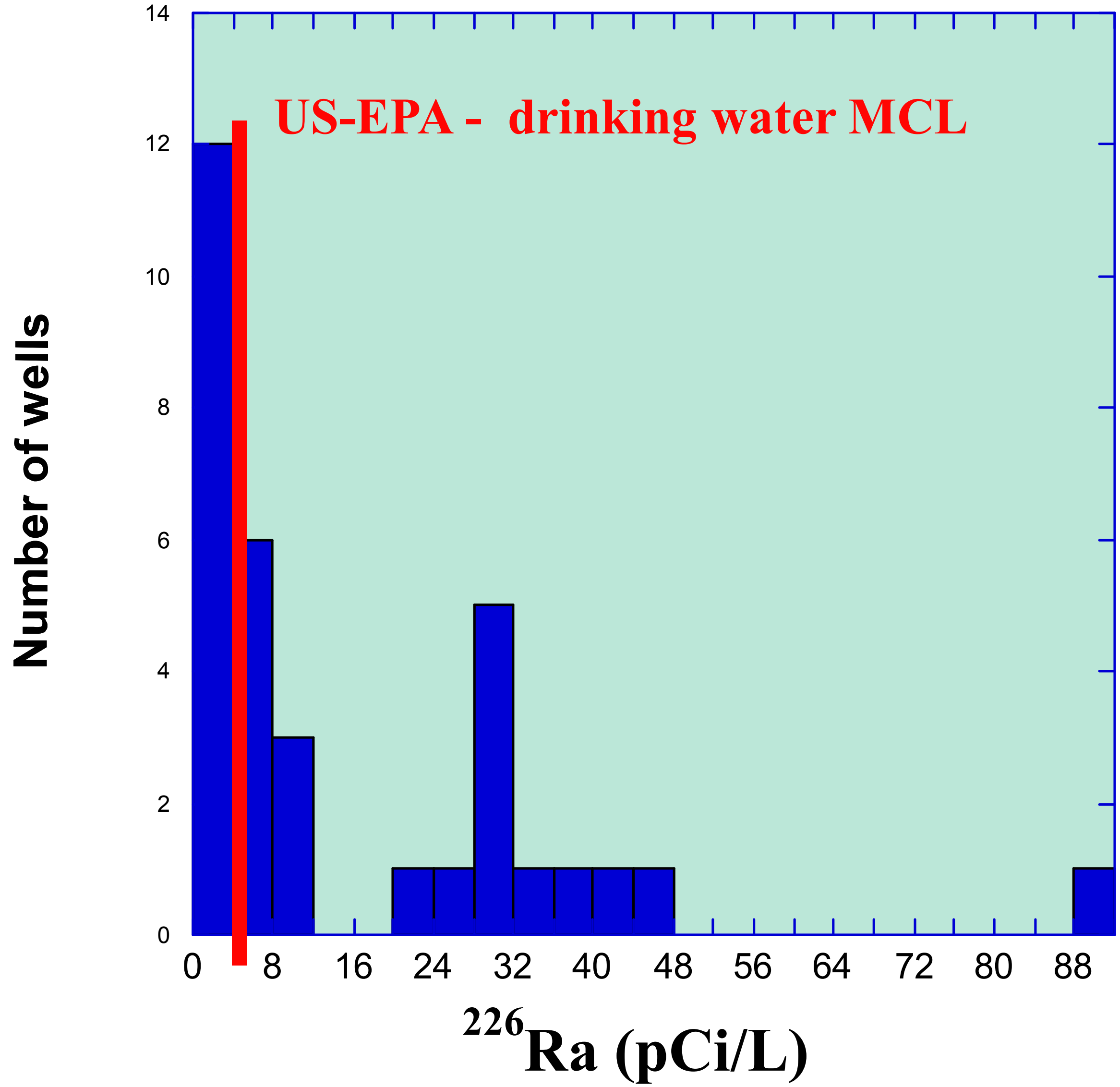


Hydrogeological cross-section

Sinai Peninsula to Negev



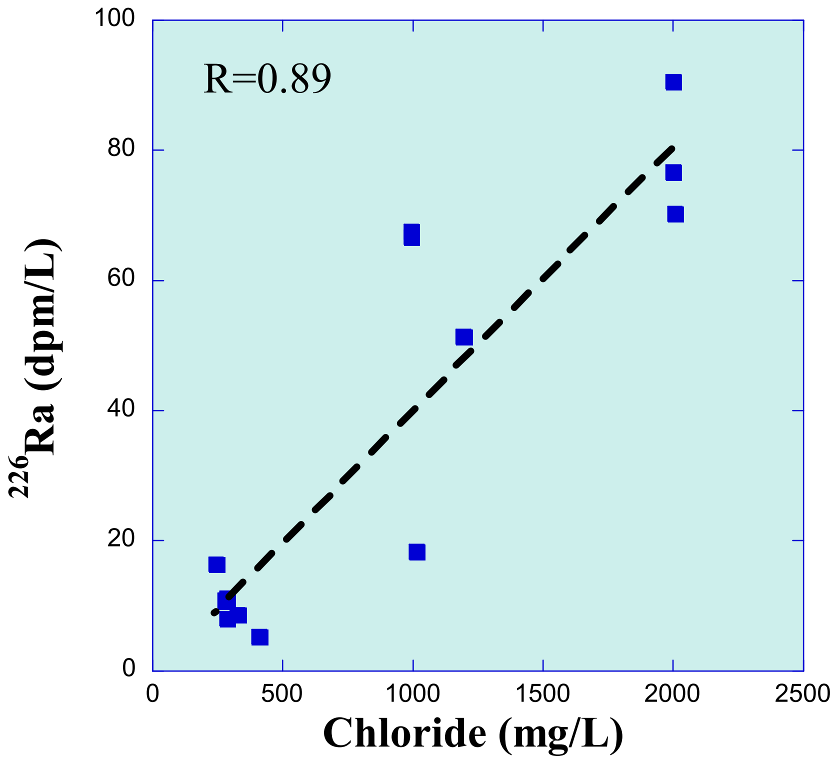
Radium activities in groundwater from the Judea Group carbonate aquifer



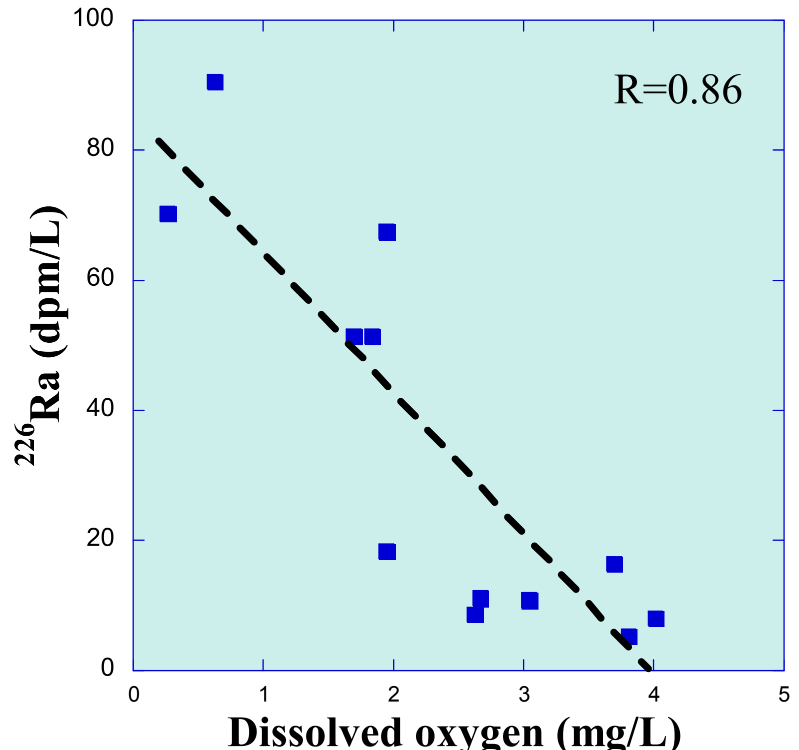
Sandia National Laboratories

Geochemical effects illustrated in Judea Group aquifer

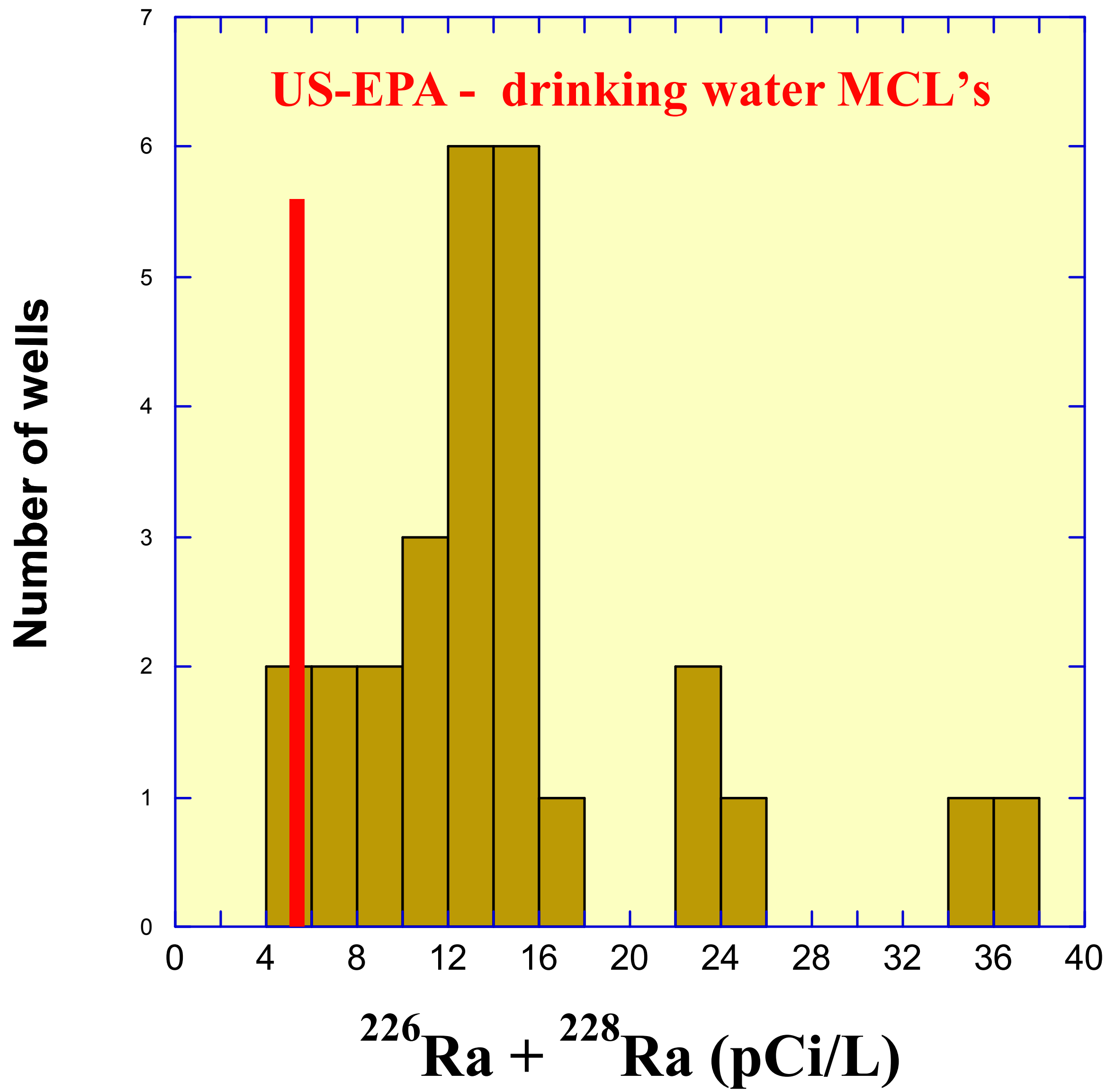
Salinity effect



Redox effect



Radium activities in groundwater from the Nubian Sandstone aquifer

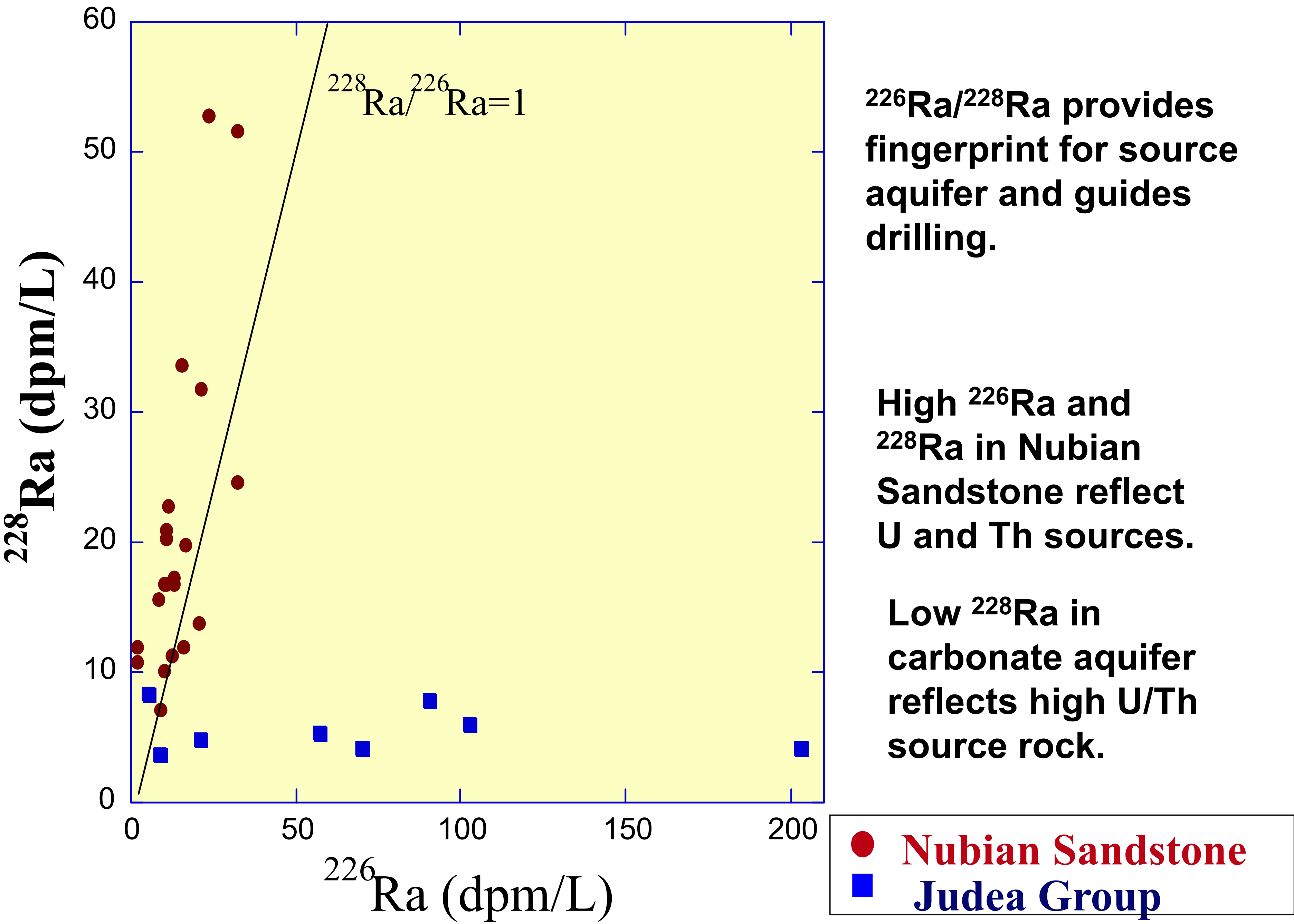


Sandia National Laboratories

Use of radium isotopes to determine source

- Ra-226: fifth member of U-238 series
  - (α-decay ; $t_{1/2}$ = 1622y)
  - Distribution dominated by transport of soluble uranium parent
  - Concentration highest near enriched (reduced) uranium deposits.
- Ra-228: second member of Th-232 series
  - β–decay ; $t_{1/2}$ = 5.7y)
  - Distribution controlled by insoluble Th parent
  - Dominates in absence of secondary U enrichment
- Ra-223 and Ra-224 also used in this study

Sandia National Laboratories

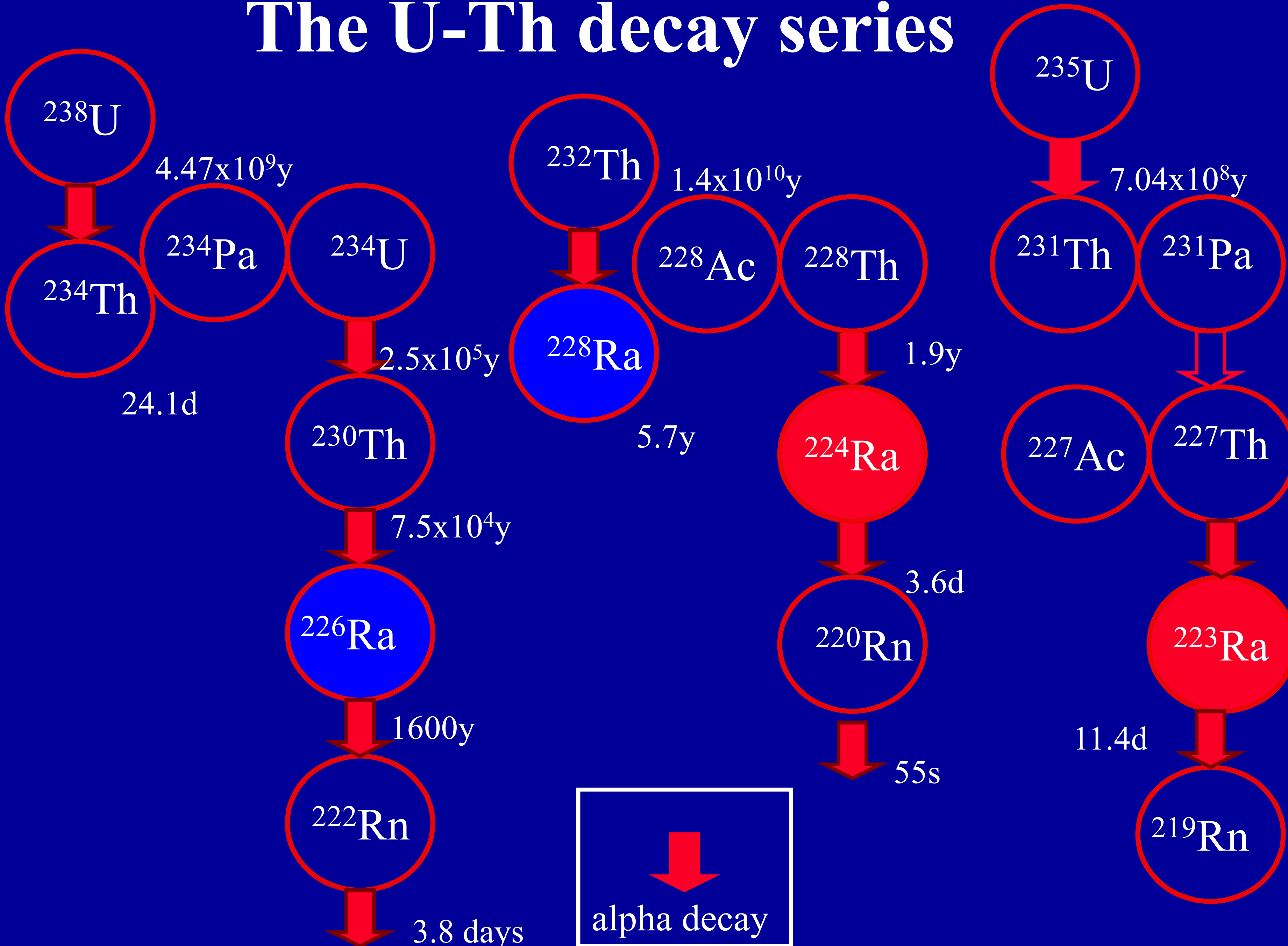


$^{226}Ra/^{228}Ra$ provides fingerprint for source aquifer and guides drilling.

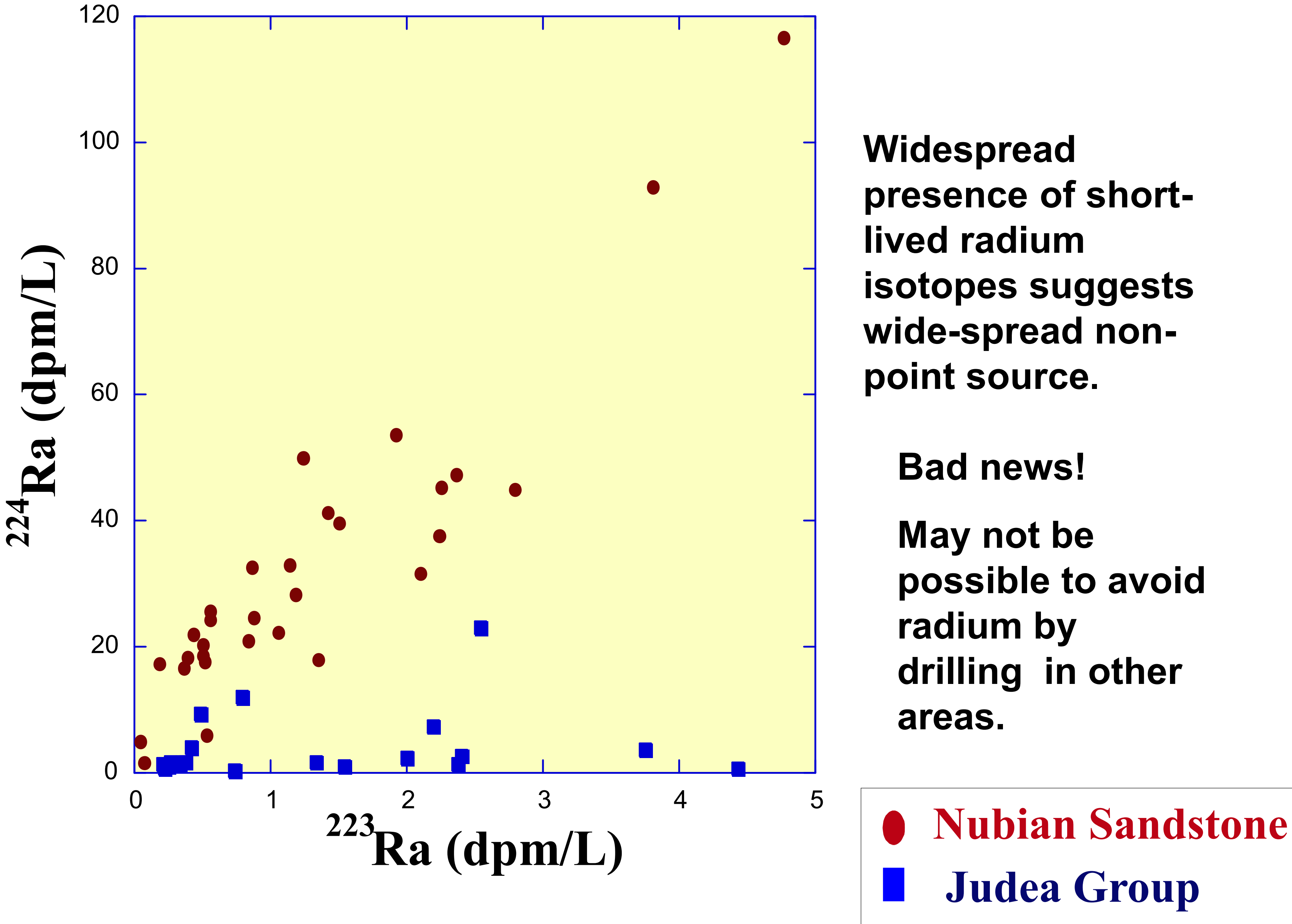
High ^{226}Ra and ^{228}Ra in Nubian Sandstone reflect U and Th sources.

Low ^{228}Ra in carbonate aquifer reflects high U/Th source rock.

The U-Th decay series



Short-lived ^{224}Ra and ^{223}Ra



Widespread presence of short-lived radium isotopes suggests wide-spread non-point source.

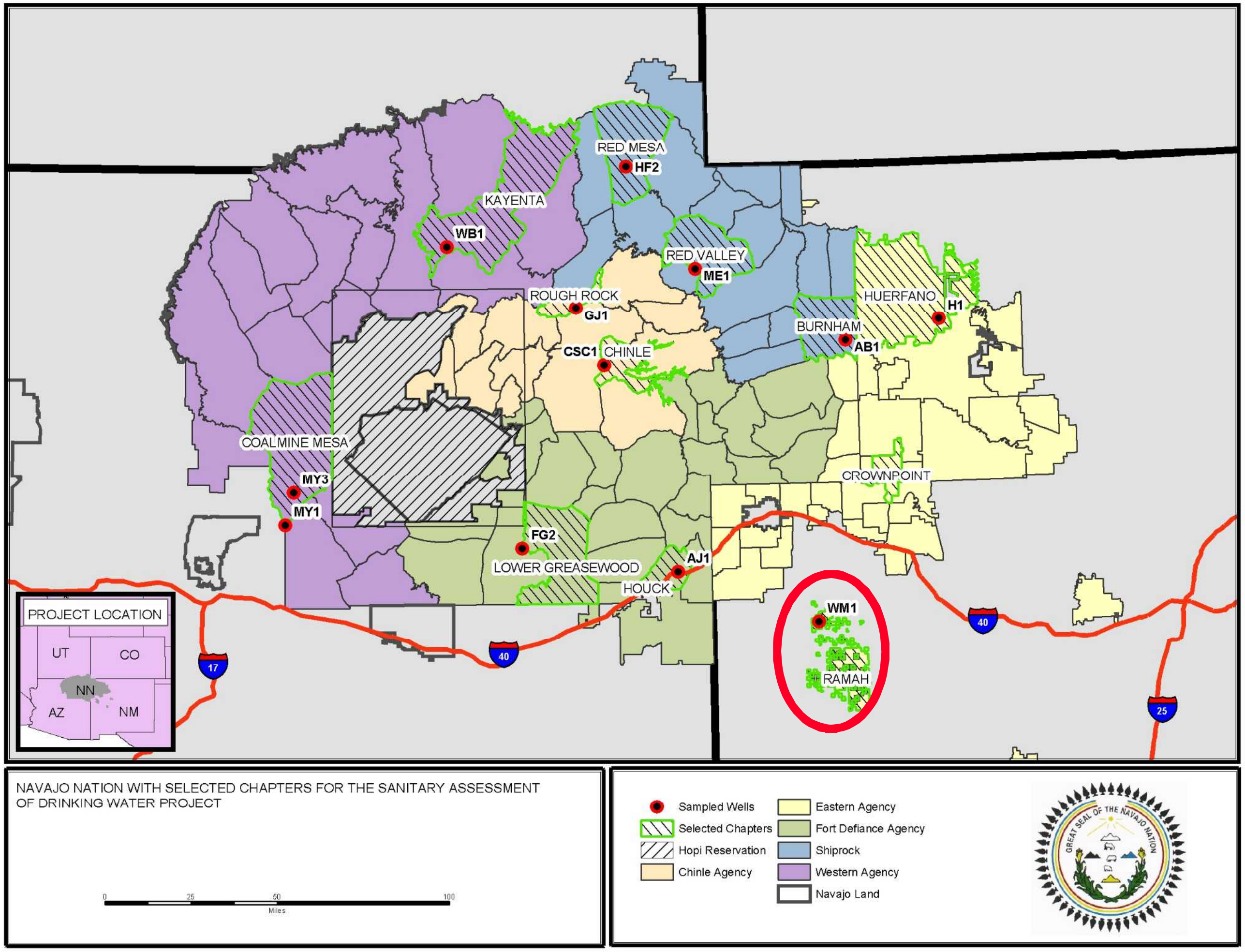
Bad news!

May not be possible to avoid radium by drilling in other areas.

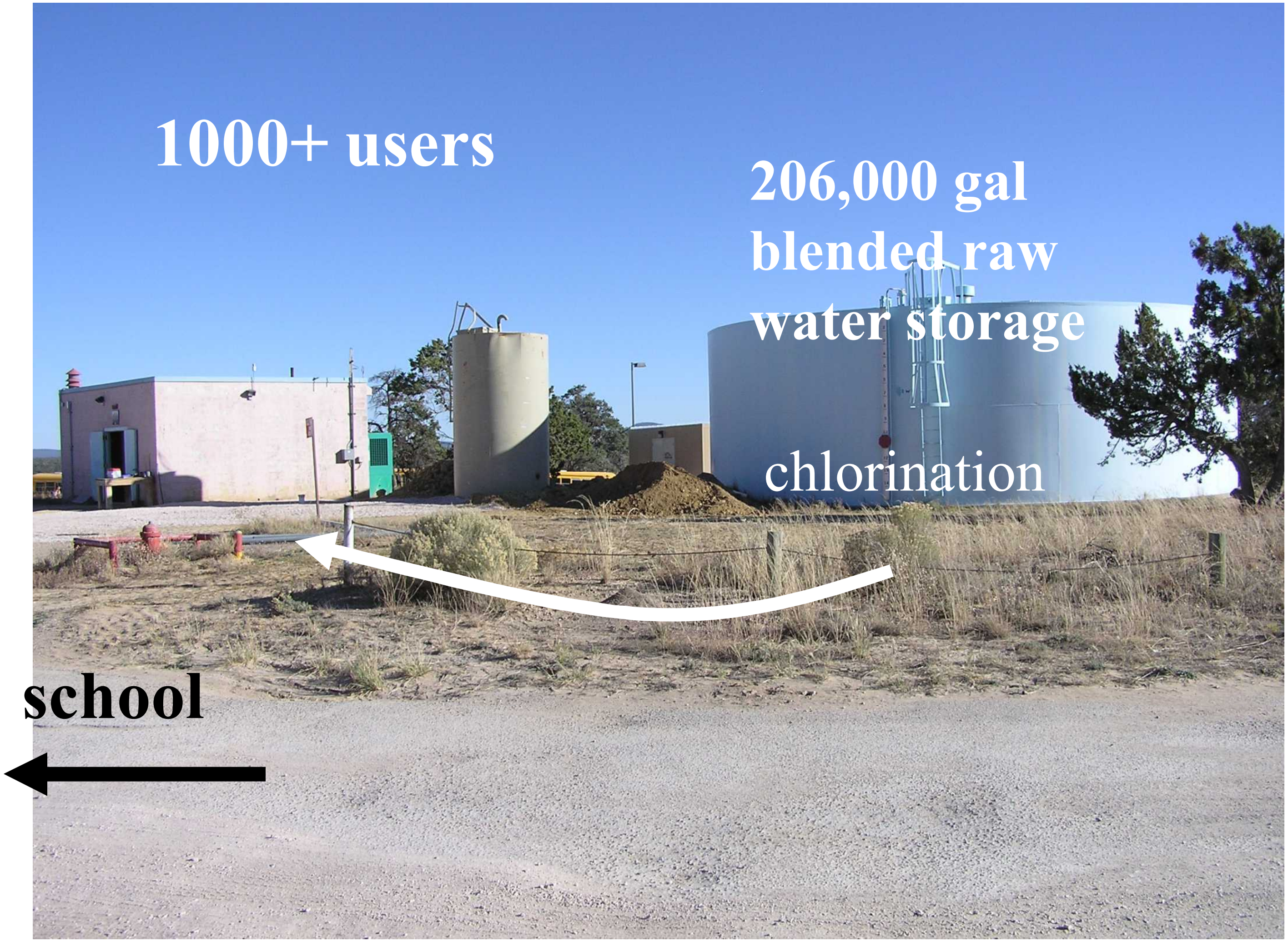
Option 2:
Selective removal of radium

Pilot test of radium removal technologies at Pine Hill School

Radium treatment on Navajo Nation



Pine Hill Water Treatment Plant



Pine Hill Water Quality

	Well #2	Standard
As (ppb)- about 85% as As(III)	30 (69)	10
Fe (ppm)	1.5	0.3
pH	7.8	NA
Gross alpha (^{230}Th pCi/L)	44.2 (103)	15
Gross beta (^{90}Sr pCi/L)	23.5	4 rem
Ra-226 (pCi/L)	12.0 (95)	Total = 5
Ra-228 (pCi/L)	2.3	
U (ppb)	2.9	30
SO_4^{2-} (ppm)	302	250
Hardness as $CaCO_3$ ppm	146	NA

Red values exceed standards; (max) values shown

Sandia National Laboratories

Pilot Treatment Shed and Storage Tank Supplied by Pine Hill School Facilities

Radium treatment technologies

- Selective adsorption test by Sandia Labs
  - Purolite resins
- Oxidation/filtration
  - Calgon Carbon GSR media
- Reverse osmosis
  - Siemens RO system
    - Short-term test showed Ra removal but longer test needed to evaluate cost and performance (i.e. fouling, scaling)
    - RO requires higher level of operator training than currently available at site.

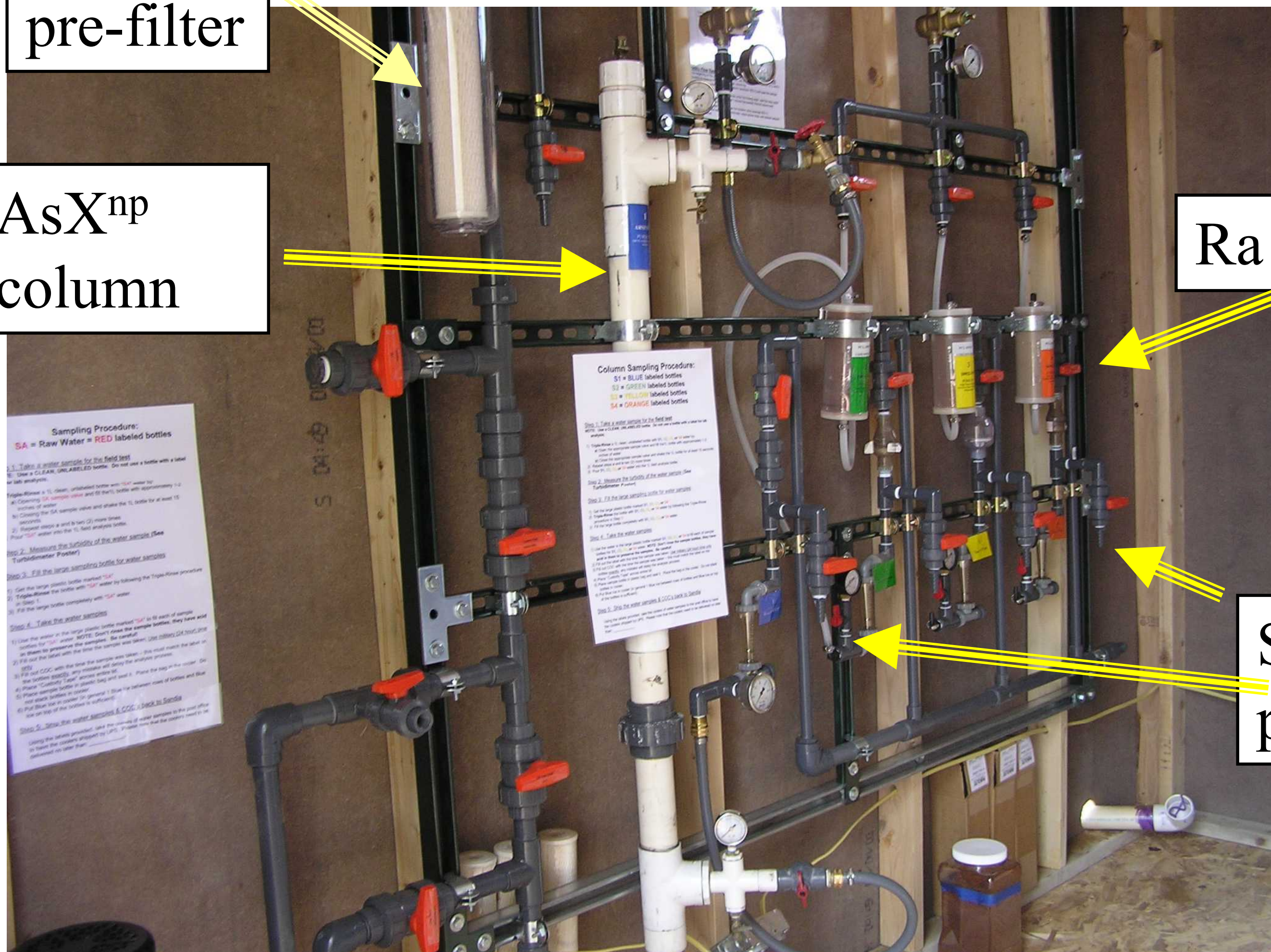
SNL Adsorptive media skid

5- µm pre-filter

AsX^{np} column

Ra columns

Sample ports



Sandia National Laboratories

Low cost semi-quantitative Radium Analysis (RPSD)

3M Empore Radium Rad Disk

1L sample, 2M HNO3

1L ^{226}Ra standard

Correct for % recovery and elapsed time

Count samples for 100 minutes in GPC

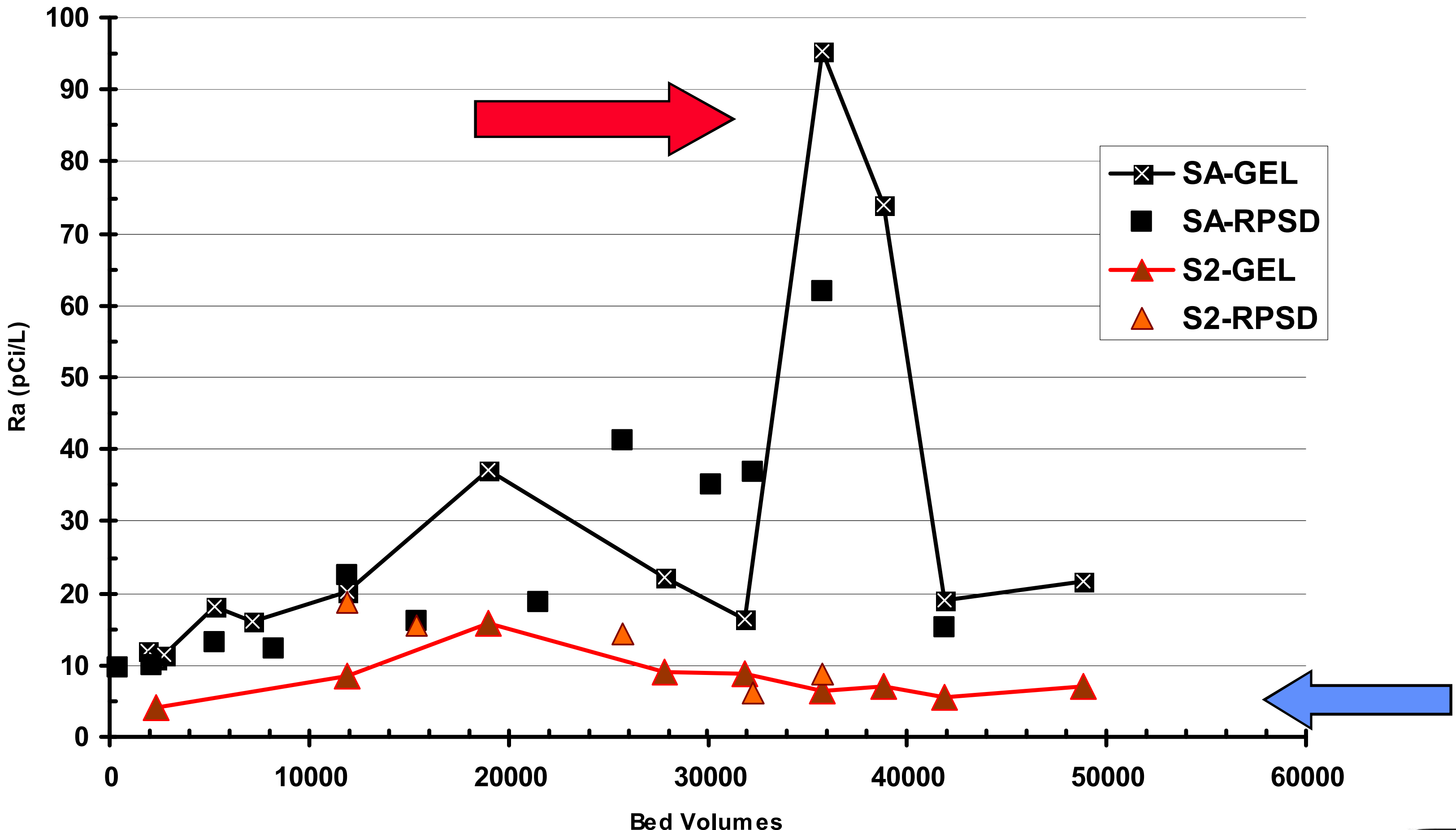
Place filter on planchet and dry in oven

Results compared to EPA lab (GEL)

Sandia National Laboratories

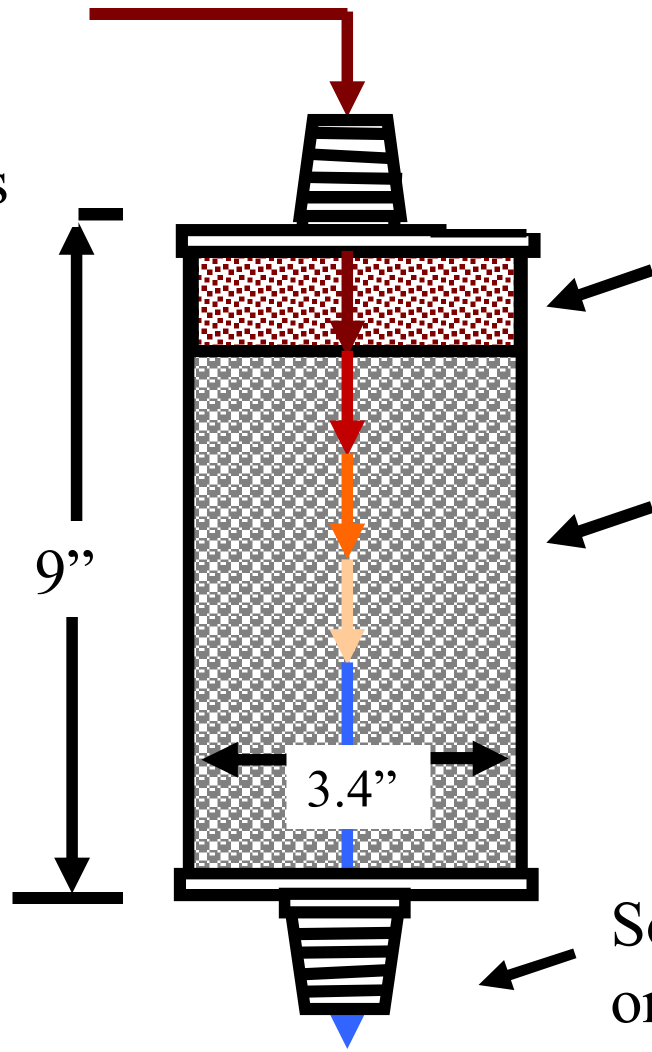
Results: IX resin failed to remove Ra to below MCL

Ra-226 removal with D9916-Ra high-capacity single-use resin



Sandia National Laboratories

High Fe content of water may have interfered with Ra removal

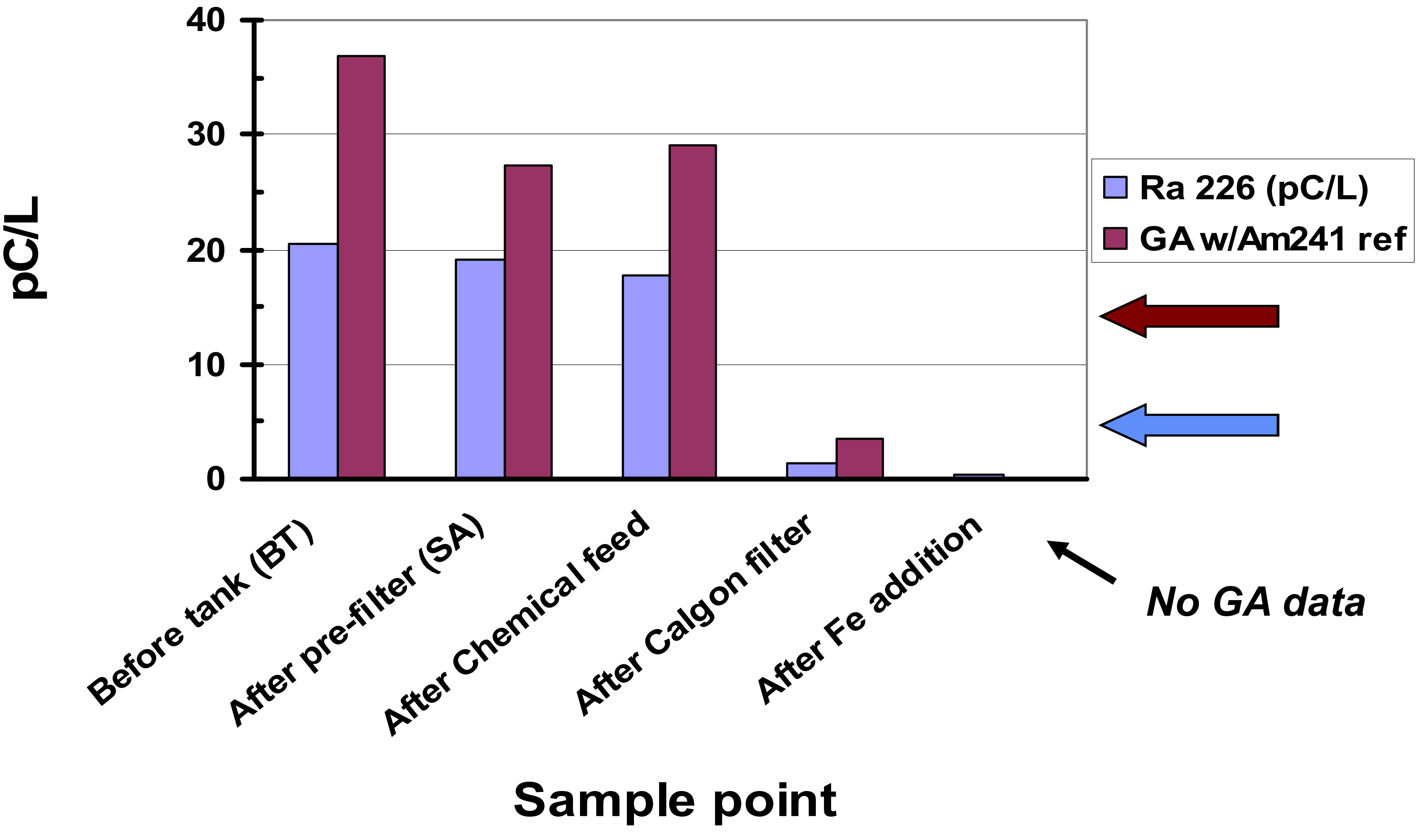


Radium columns

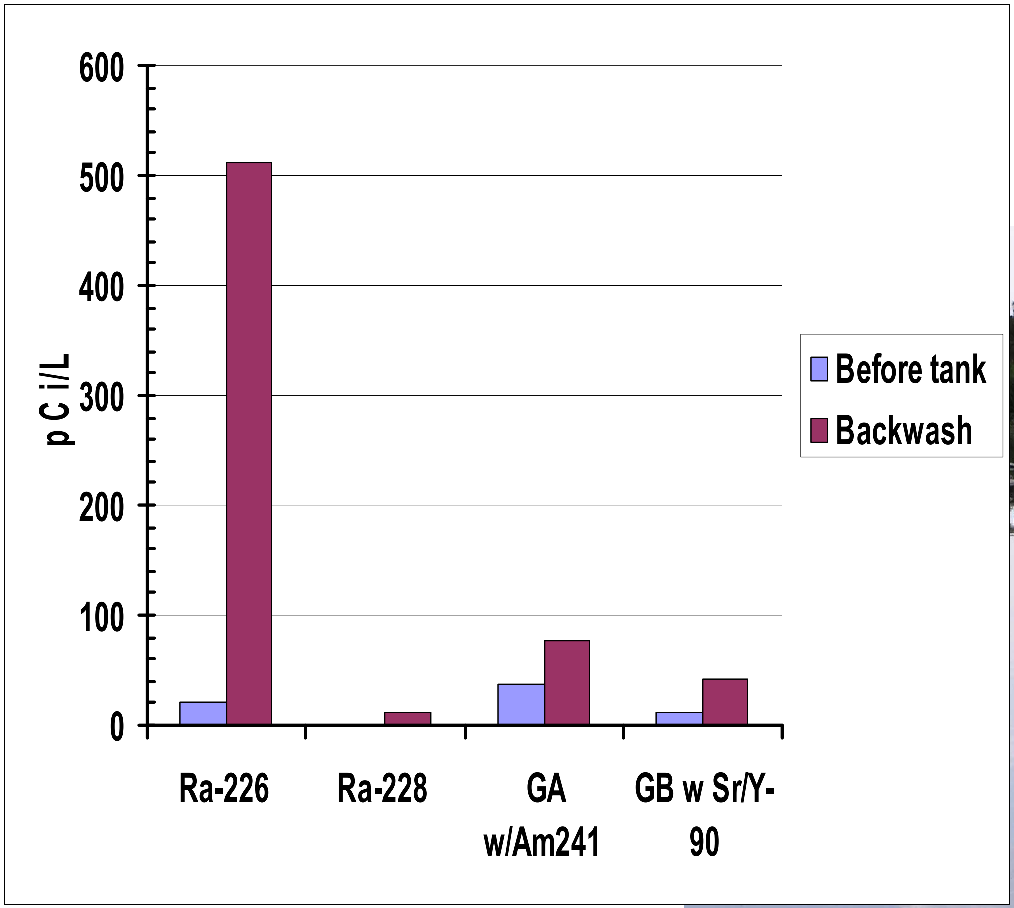
Calgon Carbon Pilot System

Oxidation/filtration system

Removal of radionuclides by Calgon Oxidation Filtration Process



Backwash analysis:



Pine Hill Sewage Lagoon

Tribal concerns about disposal

Conclusions: Assume there is no problem?

It is recommended that the solid wastes produced by membrane techniques (i.e. spent membranes and pre-filters) could be discharged into communal dumps. The other wastes produced by membrane techniques are not accumulated in fixed matrices. The concentrate containing radionuclides, is constantly drained into the sewer as the unit operates.

The concentrations of radionuclides in concentrate are, however, low and do not create a waste problem.

Finnish Radiation and Nuclear Safety Authority*:*

- **STUK-A169 Helsinki 2000.**

Summary: Radium occurrence and treatment

- Radium occurs in fossil groundwater and brackish aquifers.
  - Radium isotopic techniques using 4 isotopes show promise for identification of radium free-aquifers.
- Current RO treatment technologies can remove radium in brine but may not be appropriate for small systems in Southwest due to required training and poor recovery.
- Test of Ra-specific IX resins in presence of high Fe content not successful.
- Oxidation/Coagulation test for Ra removal successful in dilute water – high radium in backwash
  - limited for brackish water – removal of other salts?
- Other technologies should be evaluated
  - Selective electrodialysis

Sandia National Laboratories

TENORM waste regulations are emerging

- Discharge of solid residuals is governed by solid waste regulations (reluctance by some landfills); no free liquids allowed
- Underground Injection Control regulations define ^{226}Ra and ^{228}Ra concentration >60 pCi/L as radioactive waste and must be disposed of in Class I wells.
  - If uranium is present, NRC regulations will also apply
  - Proposed changes to groundwater regulations in New Mexico would lower uranium discharge limit to drinking water standard (30 μg/L) from 5 mg/L.

Will attempts to permit disposal of brines with high radium be difficult?