NEW JERSEY STATEWIDE AND NATIONAL OCCURRENCES IN GROUND WATER OF URANIUM, RADIUM, AND ARSENIC AND IMPLICATIONS FOR MONITORING

Zoltan Szabo
zszabo@usgs.gov

RADIONUCLIDE HEALTH EFFECTS

Ionizing Radiation Damage = Long-term cancer risk
Tissue Retention Controls Dose (Time = Dose, Linear)

About 1 in 20,000 risk
Carcinogens
Class "A" = Humans
Linear dose, No threshold

Uranium
Bone cancer (50%)
Kidney toxicity (50%)

Radium
Bone Cancer (228>226>224)
Sinus Cancer (226)
Bone fracturing (224, 226)

Radon
Lung cancer (>80%)
Stomach cancer (<20%)

MCLs

Radium-226 and radium-228 combined	5 pCi/L
Gross alpha-particle activity (including radium-226 but excluding uranium and radon	15 pCi/L
Gross beta-particle activity	4 millirems per year
Uranium	30ug/L

Arsenic Health Effects

Carcinogen: Lung, Bladder, Skin
Rates: 11-72 excess per 10,000
Chen et al (1992), Taiwan study
Bangladash: large cancer cluster

Circulatory disease: Hypertension
Adverse Reproductive Outcomes
Neuro-cognitive development effects in children, fetuses
Respiratory and Immune System?

These lifetime risk levels are high enough that those at risk could fill NFL Stadiums on a given Sunday
MCL = 10 ug/L

OBJECTIVES

1. Where do U, Ra, As occur? Do they co-occur?
2. Are there geological, hydrological, or geochemical features at various scales that are indicators of occurrence?
3. Are field parameters or gross measurements (gross alpha) helpful?
4. Incorporate improvements in technology in monitoring to gain under-standing of occutrrence

USGS
science for a changing world

TRACE ELEMENTS -- CONSIDER

1. THE SOURCES

Are there SPECIFIC geological features that might indicate certain materials are likely the source? Associated with potable water?

2. GEOCHEMISTRY

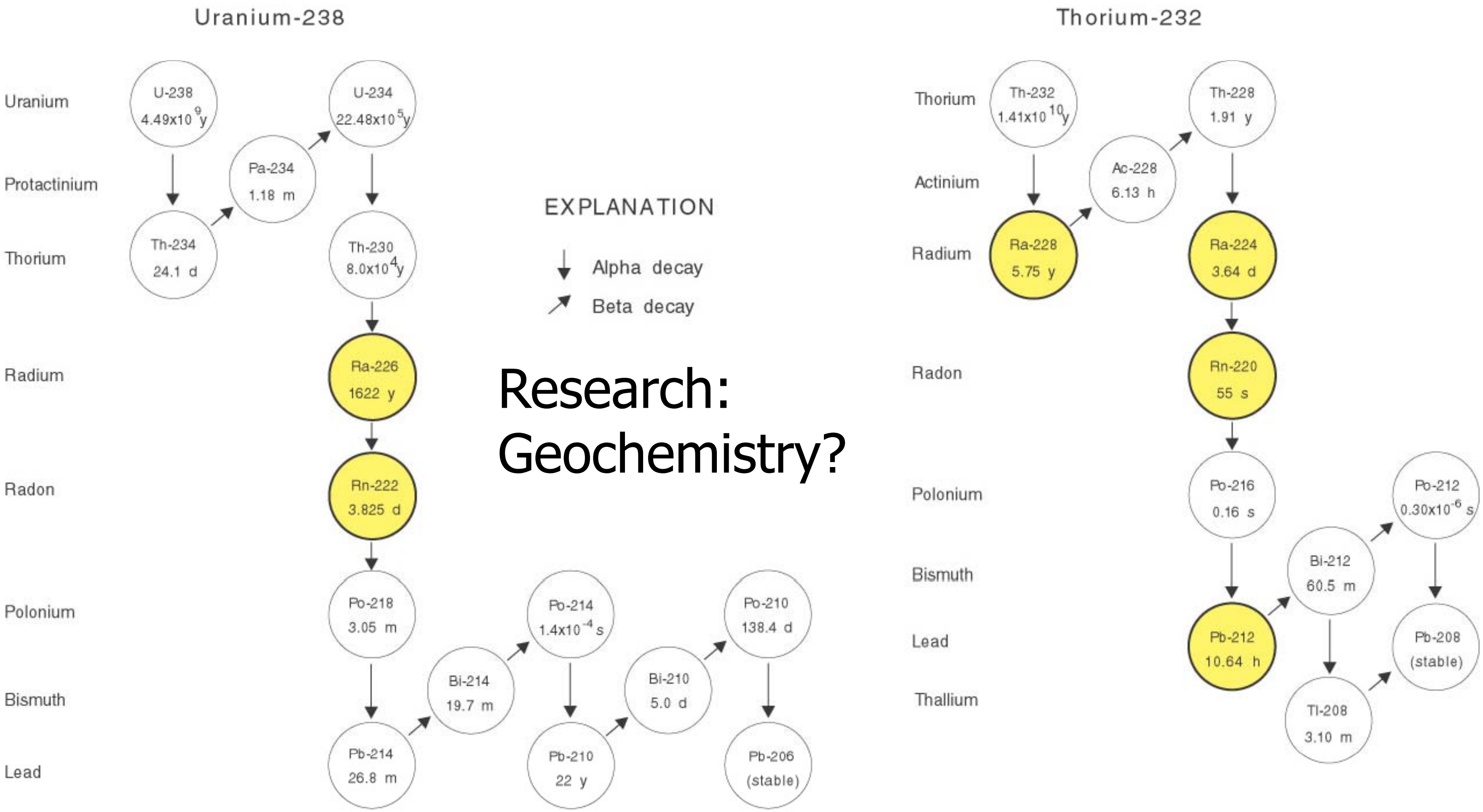
Solubility extremely variable

3. HYDROLOGY

Controls solution residence time, geochemical evolution, mineralization

USGS
science for a changing world

U = Long half lived parent

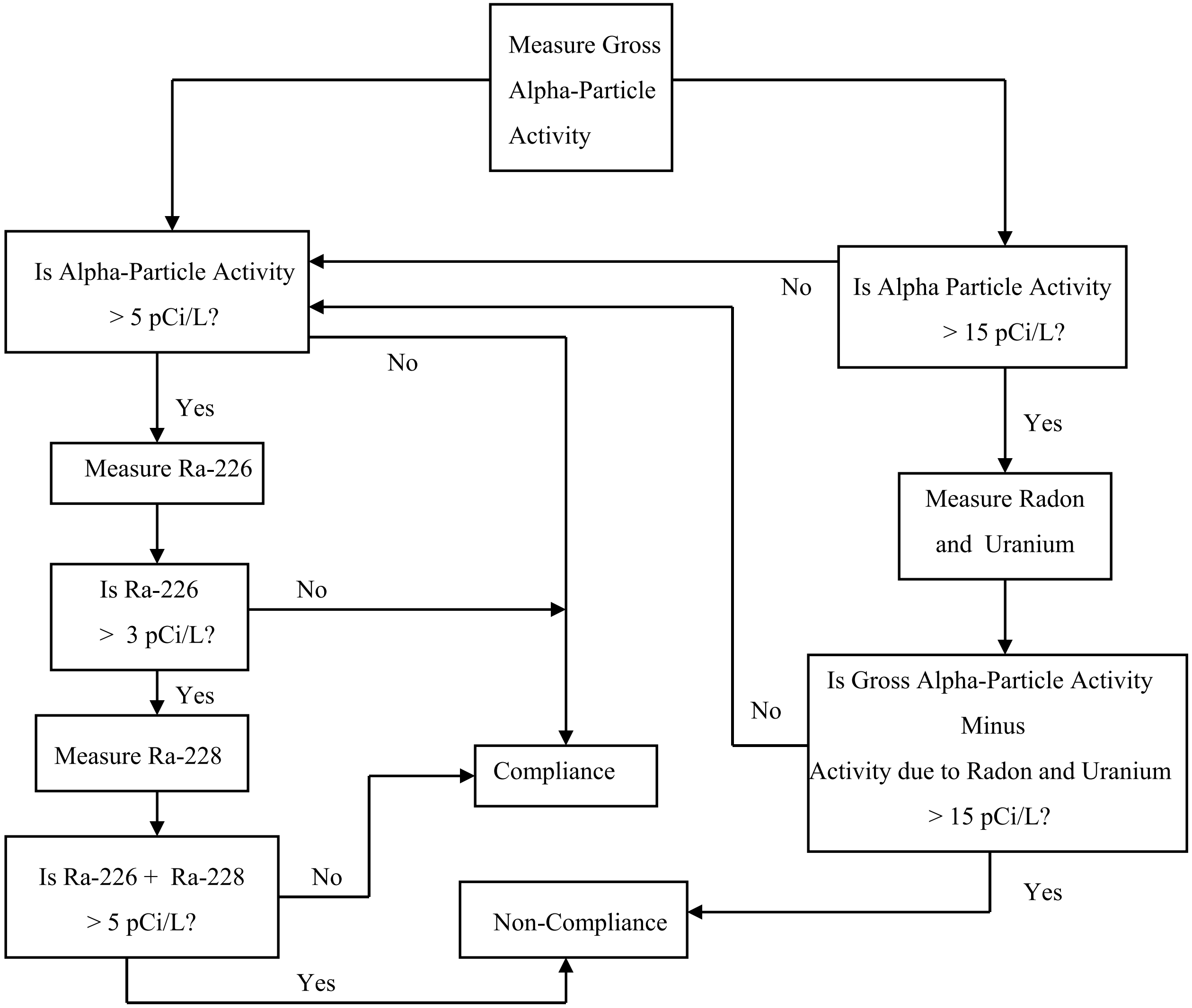


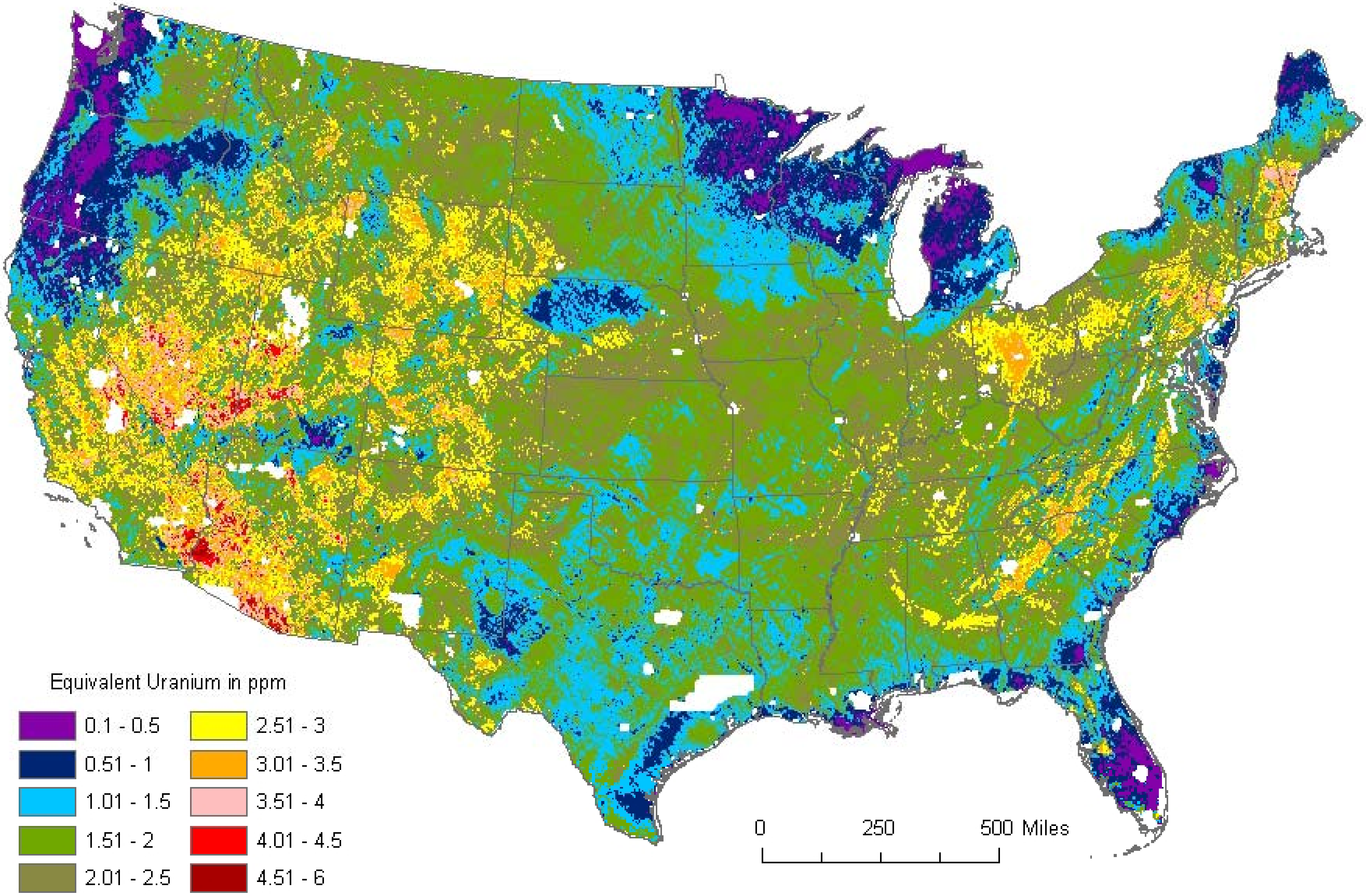
Research: Geochemistry?

Figure 1. Diagram showing uranium-238 and thorium-232 radioactive decay series. (Radionuclides of interest in this study are shaded). [Times shown are half-lives: y, years; d, days; h, hours; m, minutes; s, seconds] (From Hall and others, 1985)

Gross alpha = many individual isotope contributions!

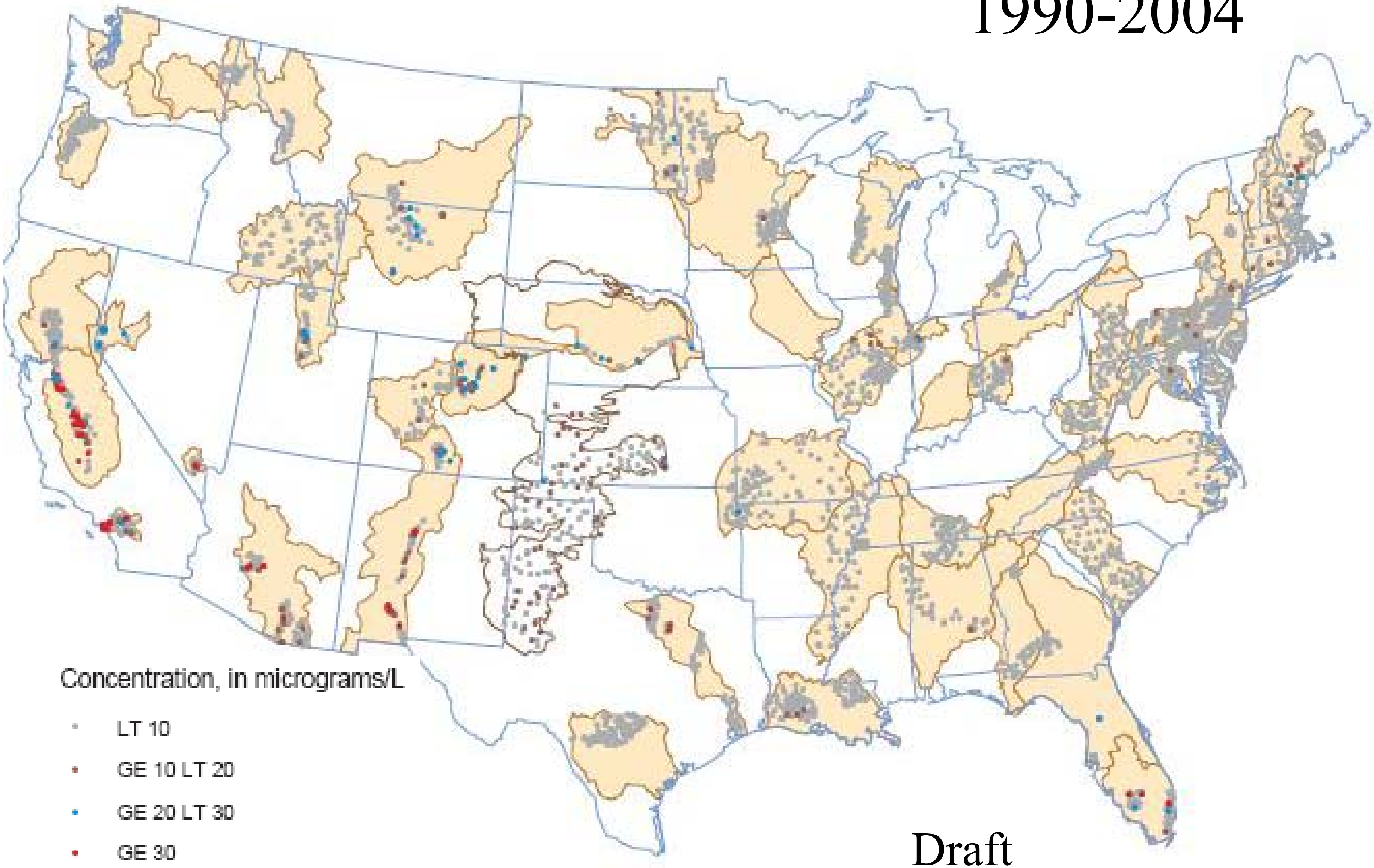
USEPA Radionuclide Monitoring till 2000 – since 2000, at least one measurement of each is required





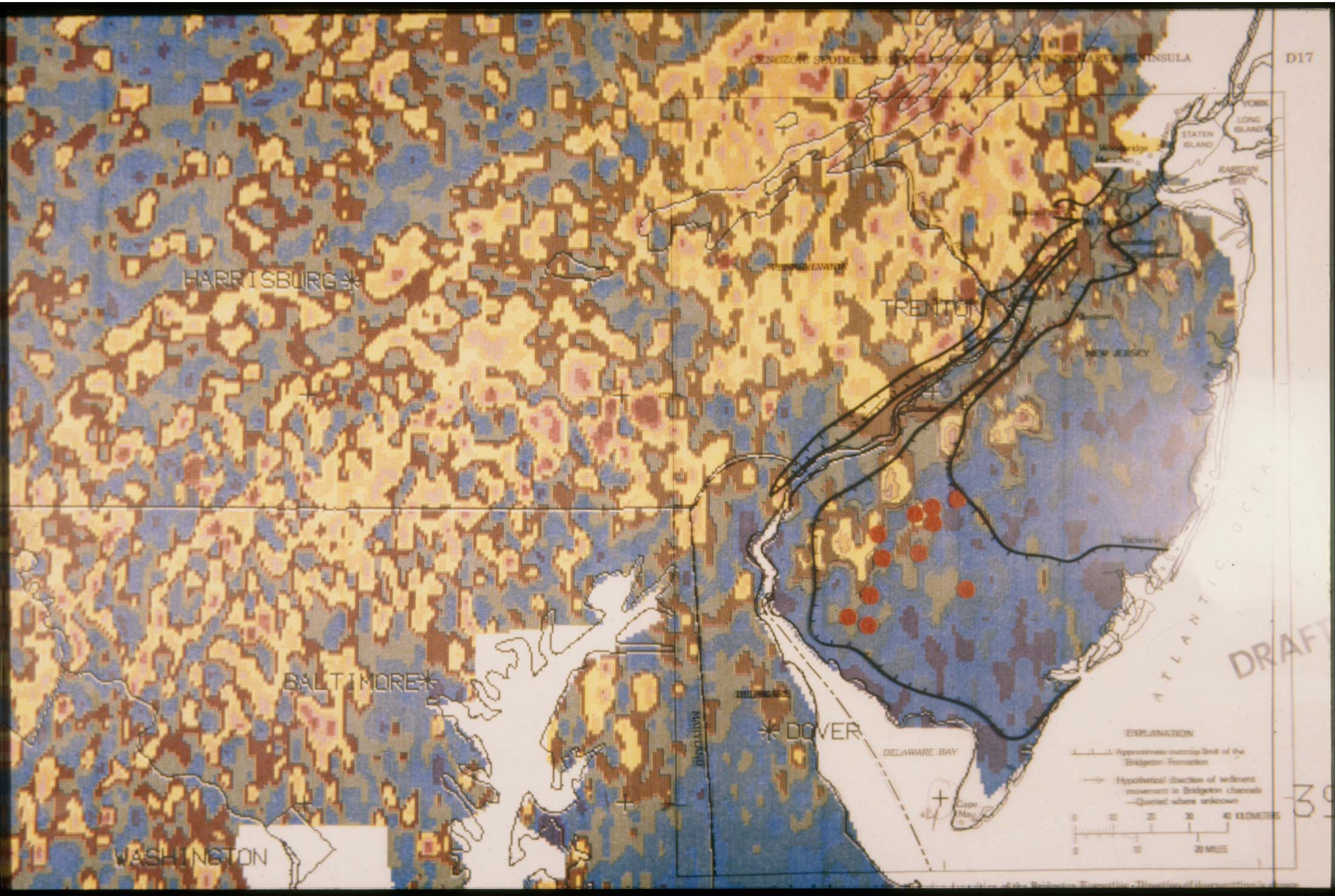
Areao-radiometry map of surficial gamma radiation; NURE program;

U in Wells sampled by NAWQA 1990-2004

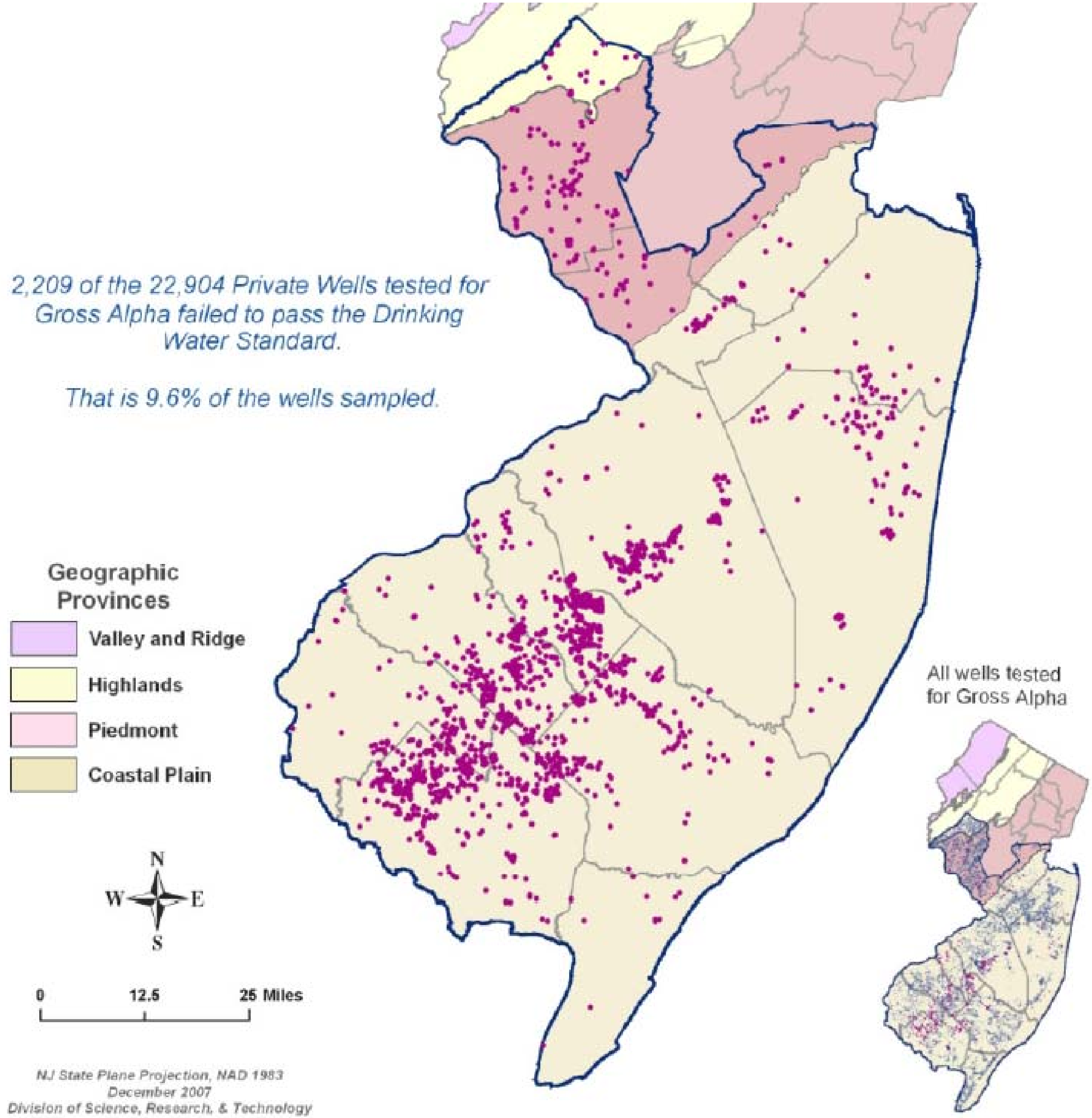


Draft

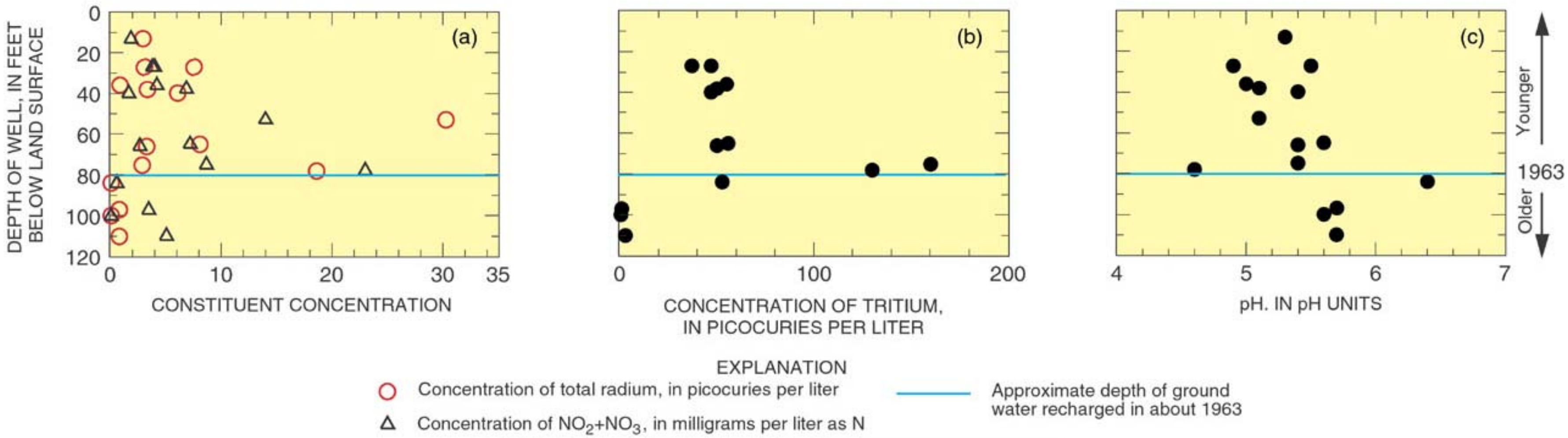
Supply wells with high gross alpha in low radioactivity Coastal Plain

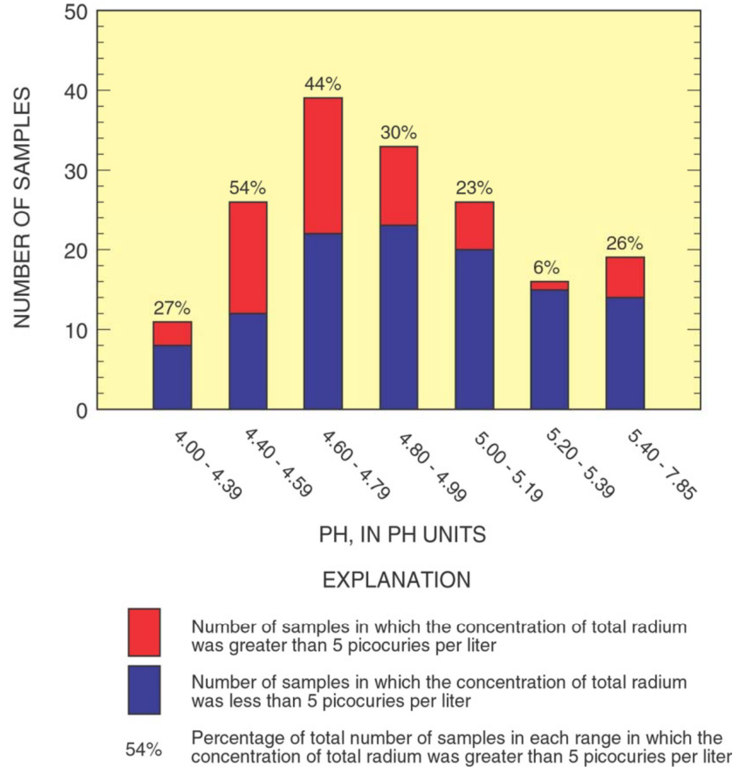


NJ Private Well Testing Results for Gross Alpha



*www.state.nj.us/dep/**pwta***





Szabo and dePaul, 1998

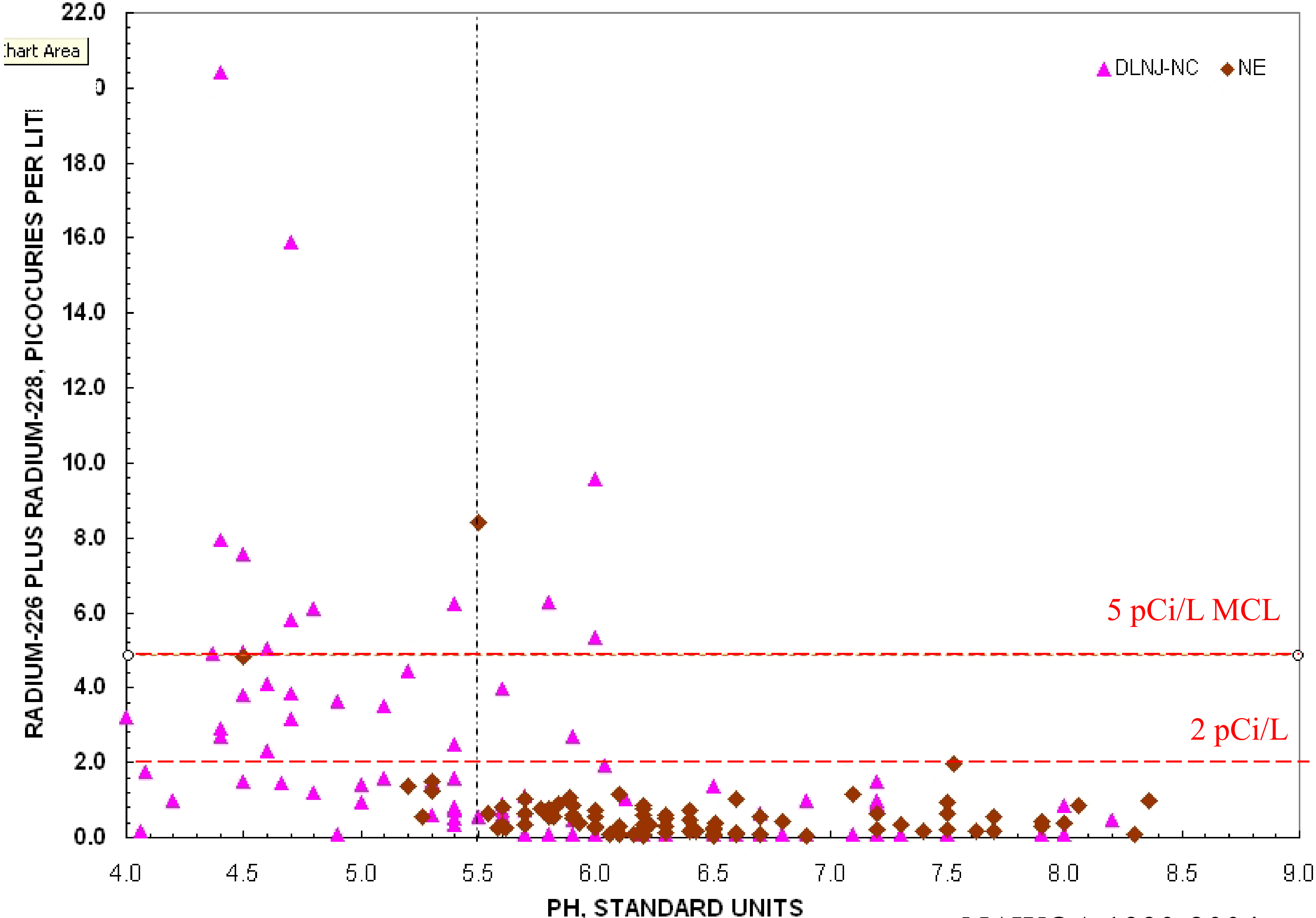
Hypothetical Chemical Reactions by which Hydrogen Ions in Water Increase Radium Mobility

➢ **Ion-exchange, desorption reactions:**

$$2H^{+} + Ra_{x} \Rightarrow Ra^{+2} + 2H_{x}$$

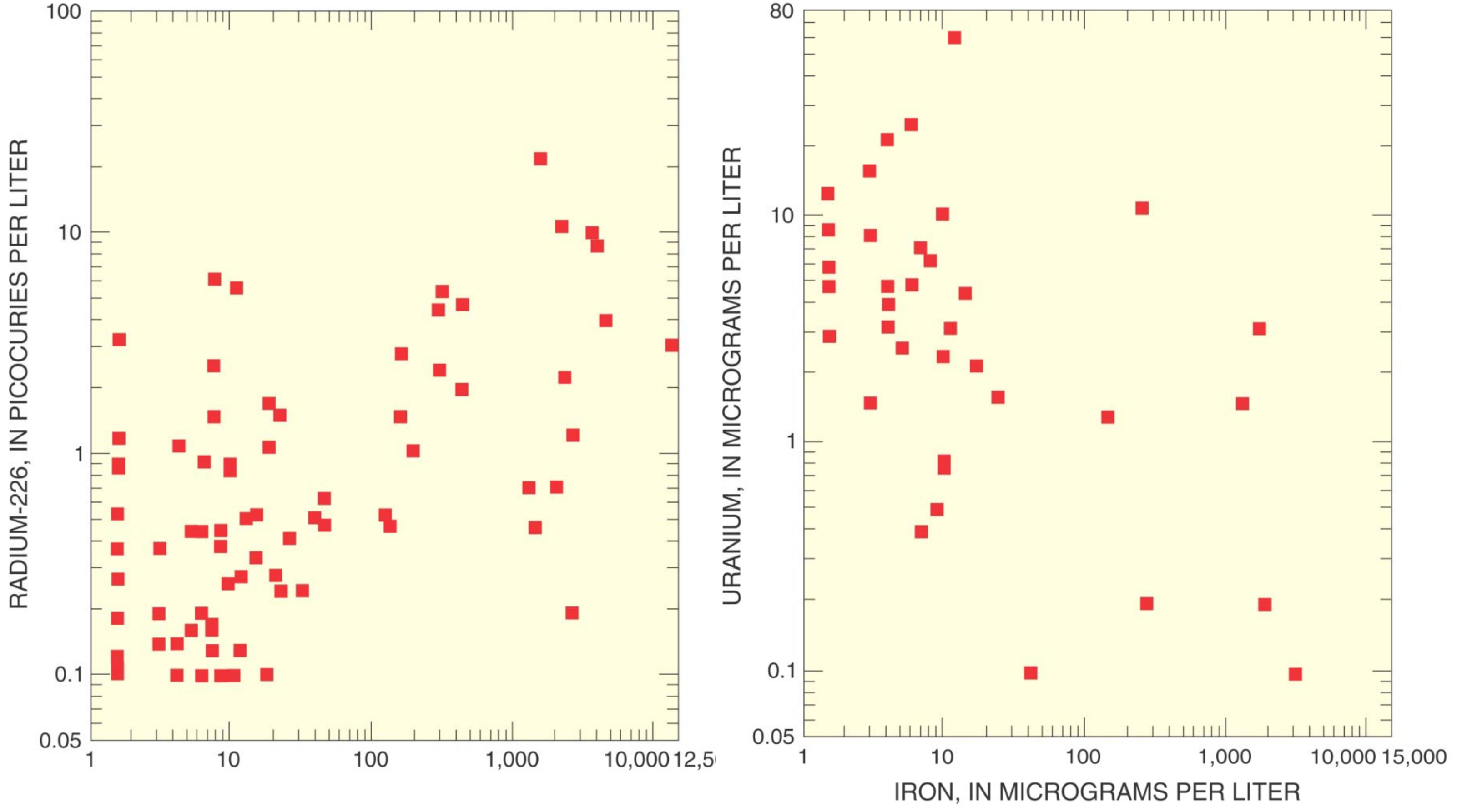
- Ra is preferentially removed from solid.
- Hydrogen ion is a master variable that exerts significant control over these reactions, preferentially removes Ra from solids even more so than high concentrations of other cations
- Geochemistry is critical controlling variable.

Radium is most likely to be in solution in acidic waters



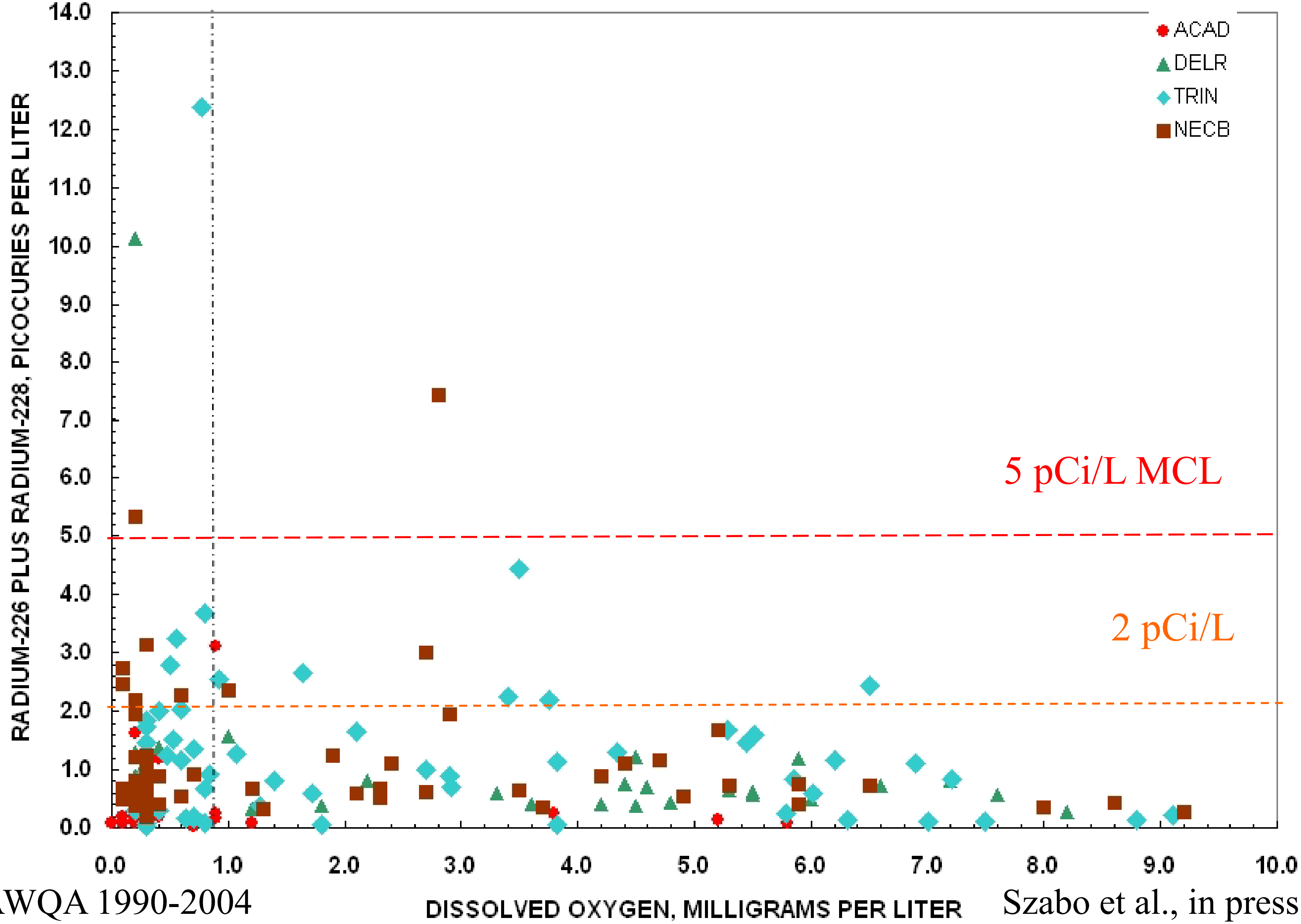
NAWQA 1990-2004;
Szabo et al., in press

U and Ra have opposing trends based on geochemistry (pH, DO, or iron) in U rich aquifers (North NJ)



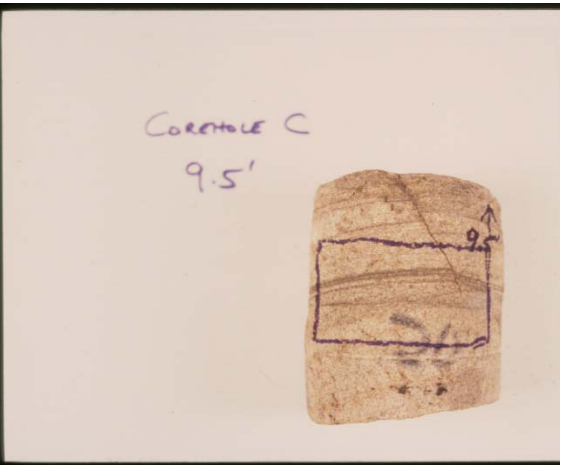
Szabo et al., 1991

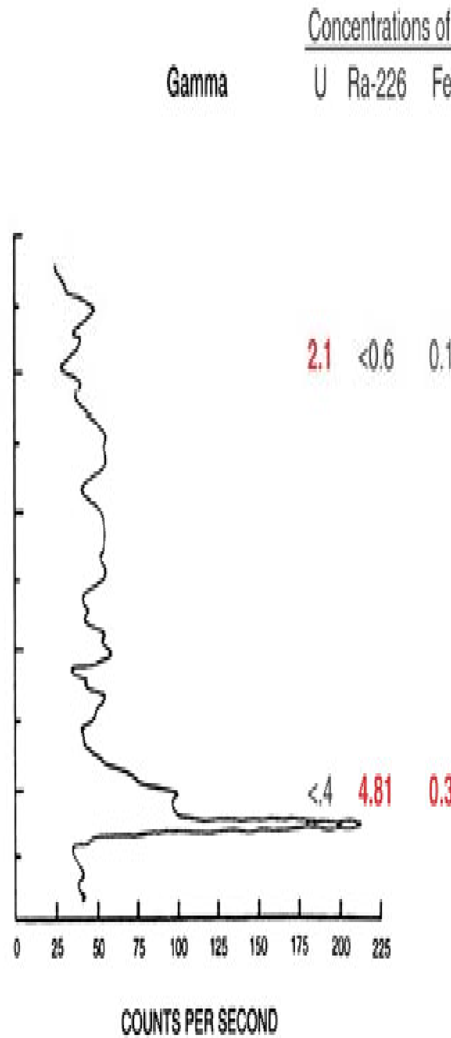
Ra concentration is generally greatest in wells in suboxic water (DO < 1 mg/L)

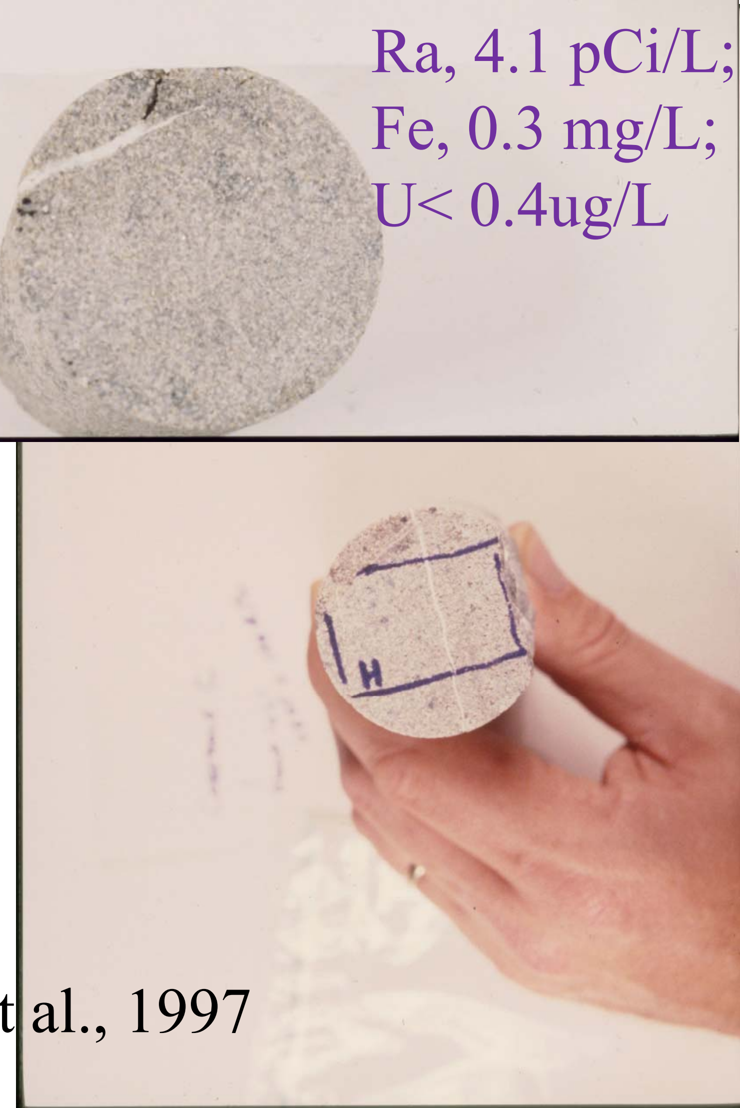


NAWQA 1990-2004

Szabo et al., in press





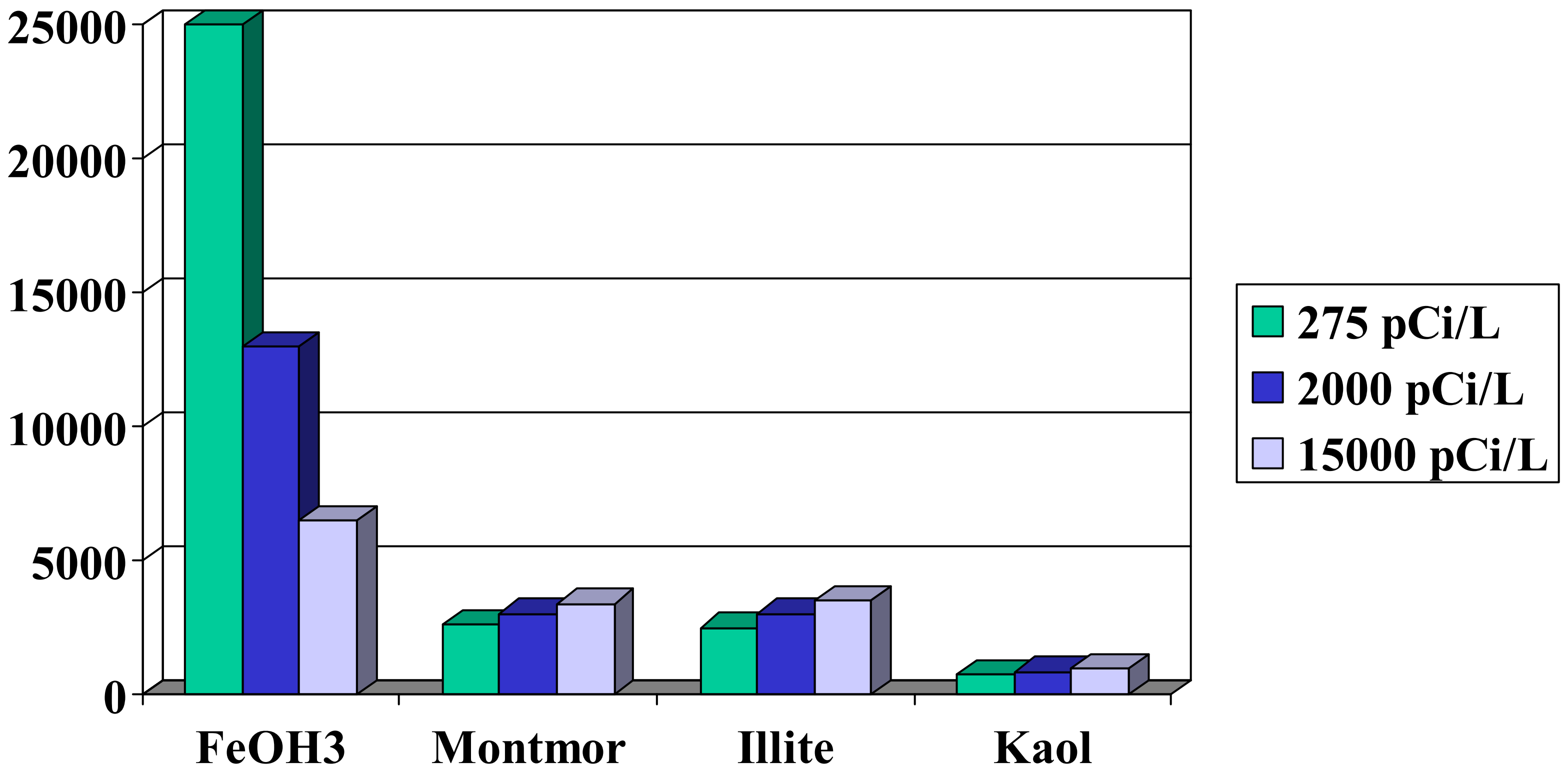


SUBOXIC
Ra, 4.1 pCi/L;
Fe, 0.3 mg/L;
U< 0.4ug/L

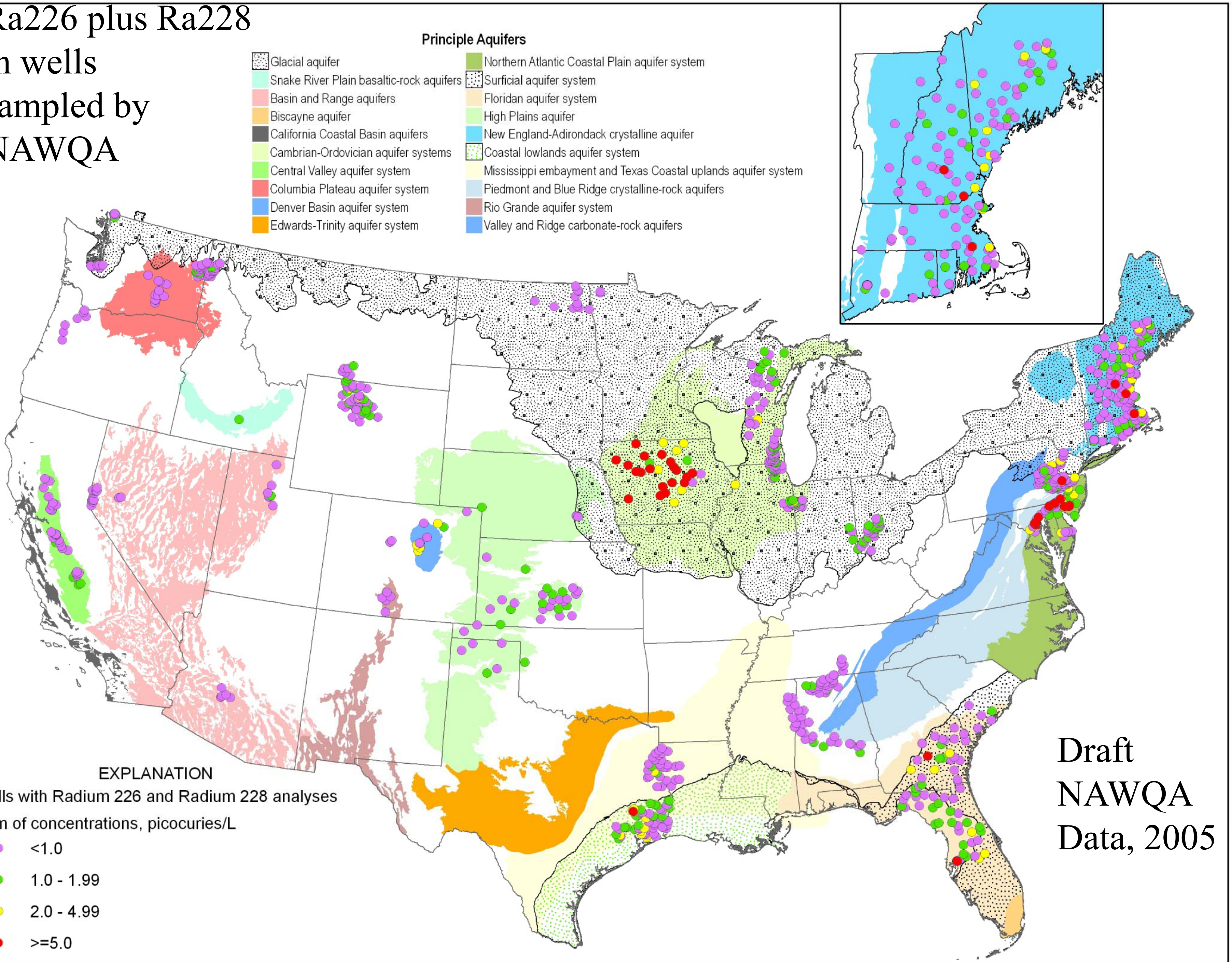
OXIC
U, 2.1 ug/L;
Ra <0.6 pCi/L;
Fe <0.1 mg/L

NJ Rock Borehole;
Geophysics and geochemistry; Szabo et al., 1997

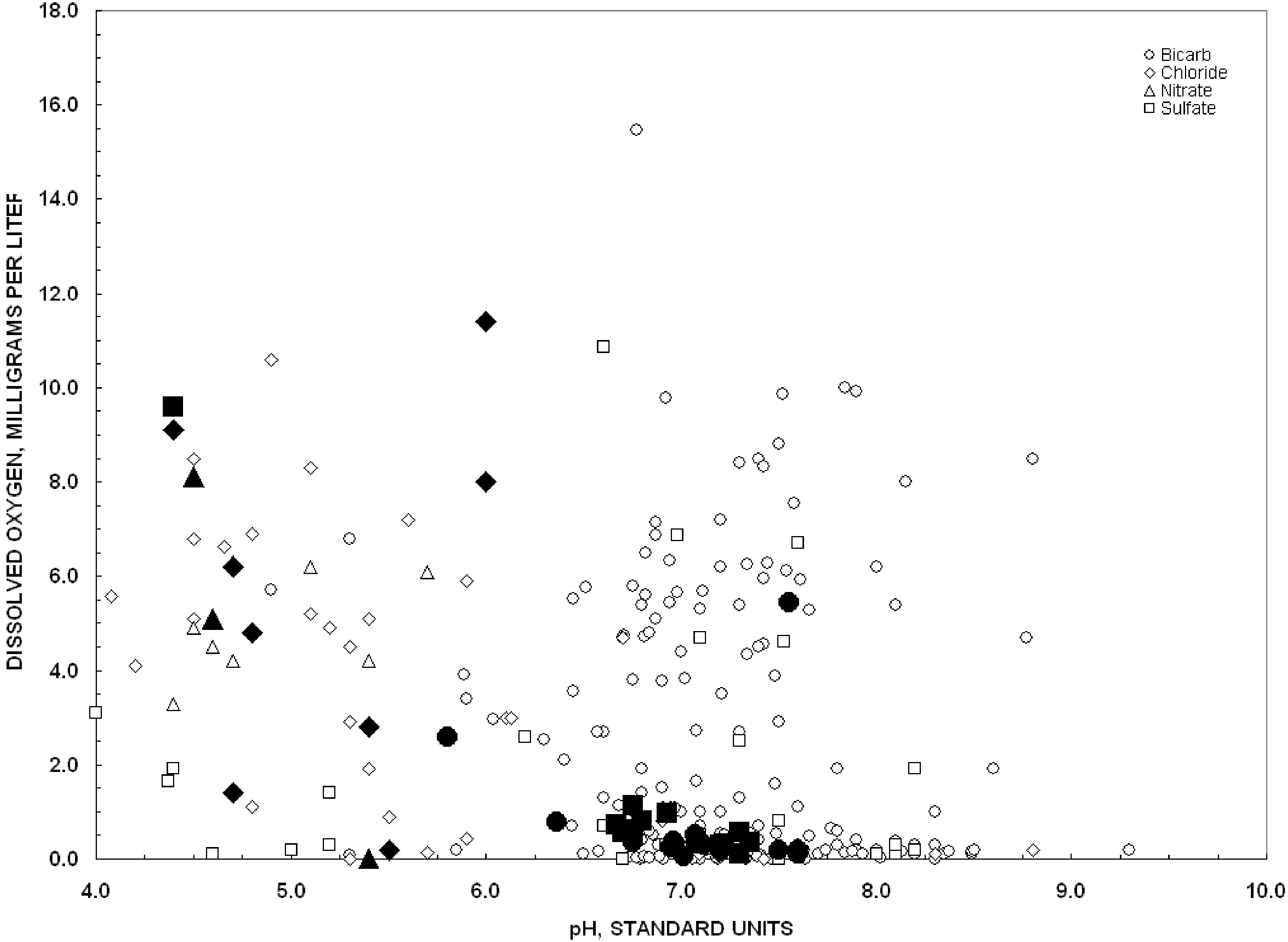
Ra distribution coefficients per g sorbent (Ames et al., 1983)



Ra226 plus Ra228 in wells sampled by NAWQA



Draft NAWQA Data, 2005

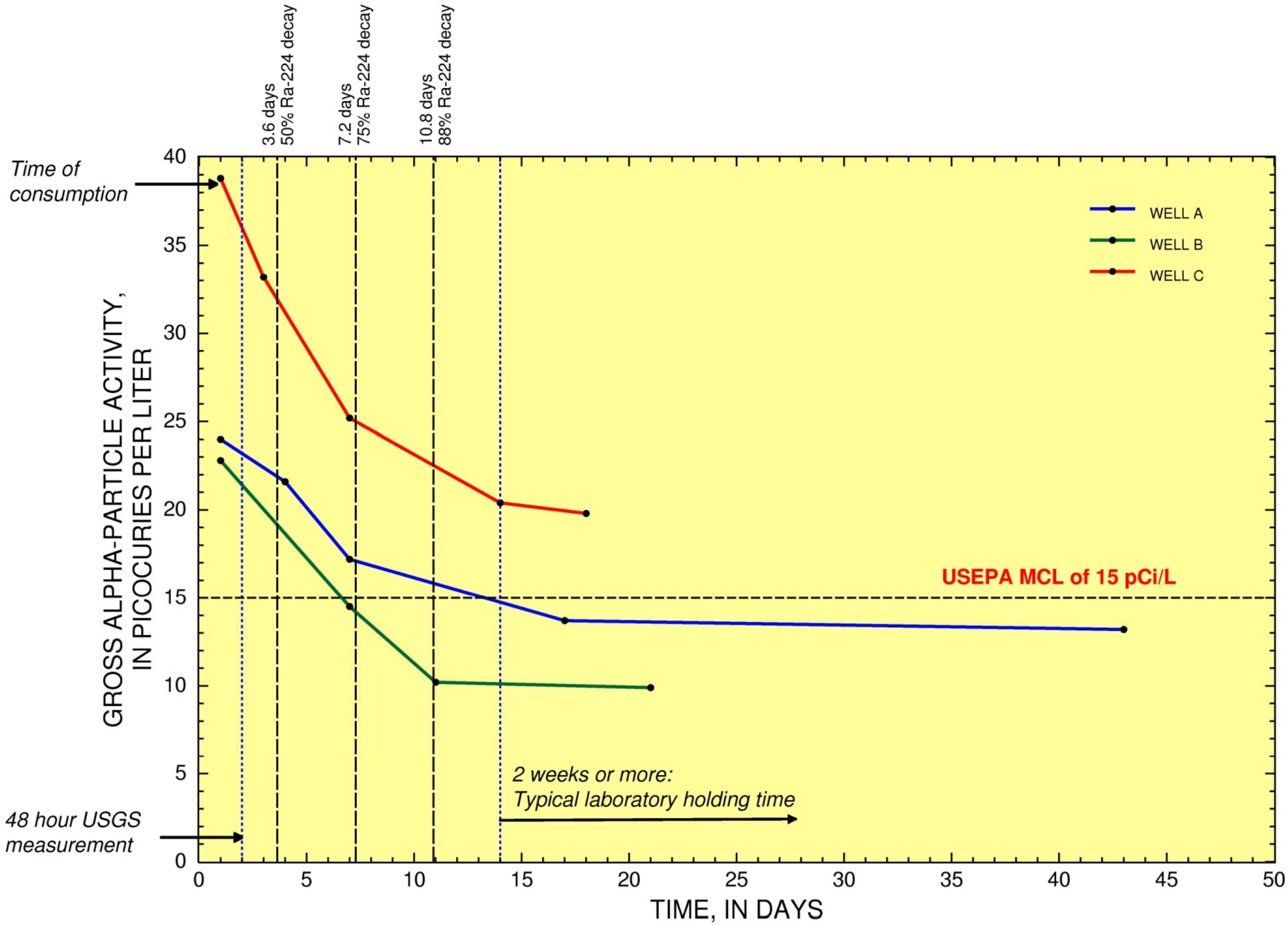


Draft NAWQA Combined Ra Data, 1990-2005. Detected Ra values, about 400 of 1200 samples. Solid, $\geq$ 5 pCi/L; open, 1-5 pCi/L. ND mostly cluster in upper right.

Understand Gross Alpha!

- ALPHA-EMITTER
- Ra-224 (3.6 days)
- Pb-212 (10 hrs)
- Rn progeny (variable)
- Po-210 (100 days)
- Ra-226 (1600 yrs)
- U, Th isotopes (very long-lived!)

- NON-ALPHA
- Ra-228 (beta); usually equals Ra-224
- Pb-210 (beta – no screen)
- Rn (gas, not detected, progeny?)
- Most man-made nuclides (beta, gamma)
- K-40 (beta "noise")



Decline of *gross alpha-particle activity through time in samples from selected public-supply wells, southern New Jersey, 1997.*

Variable alpha and gamma energies for a single nuclide: the key to gamma and alpha spectrometry – different energies can be detected and quantified

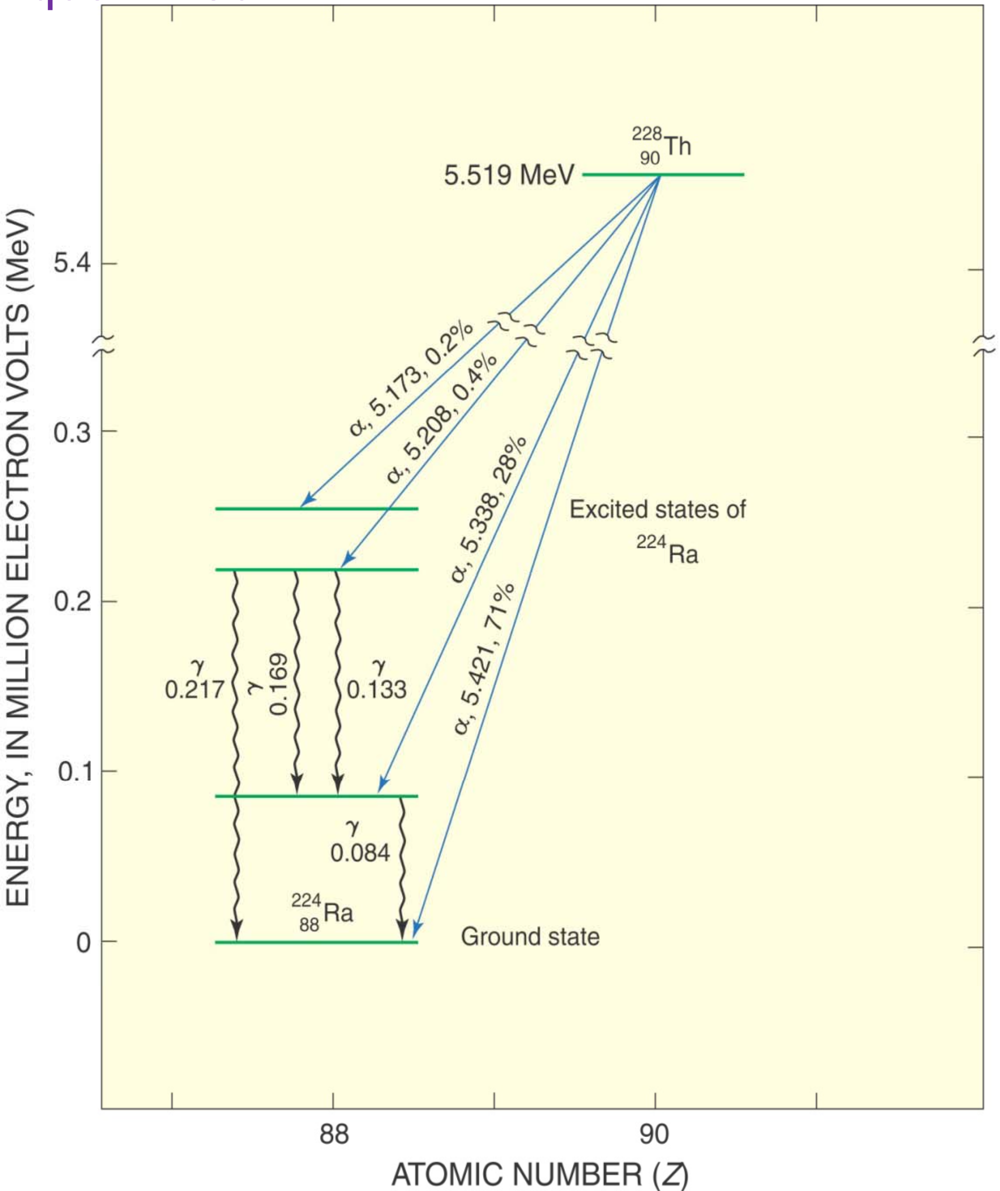
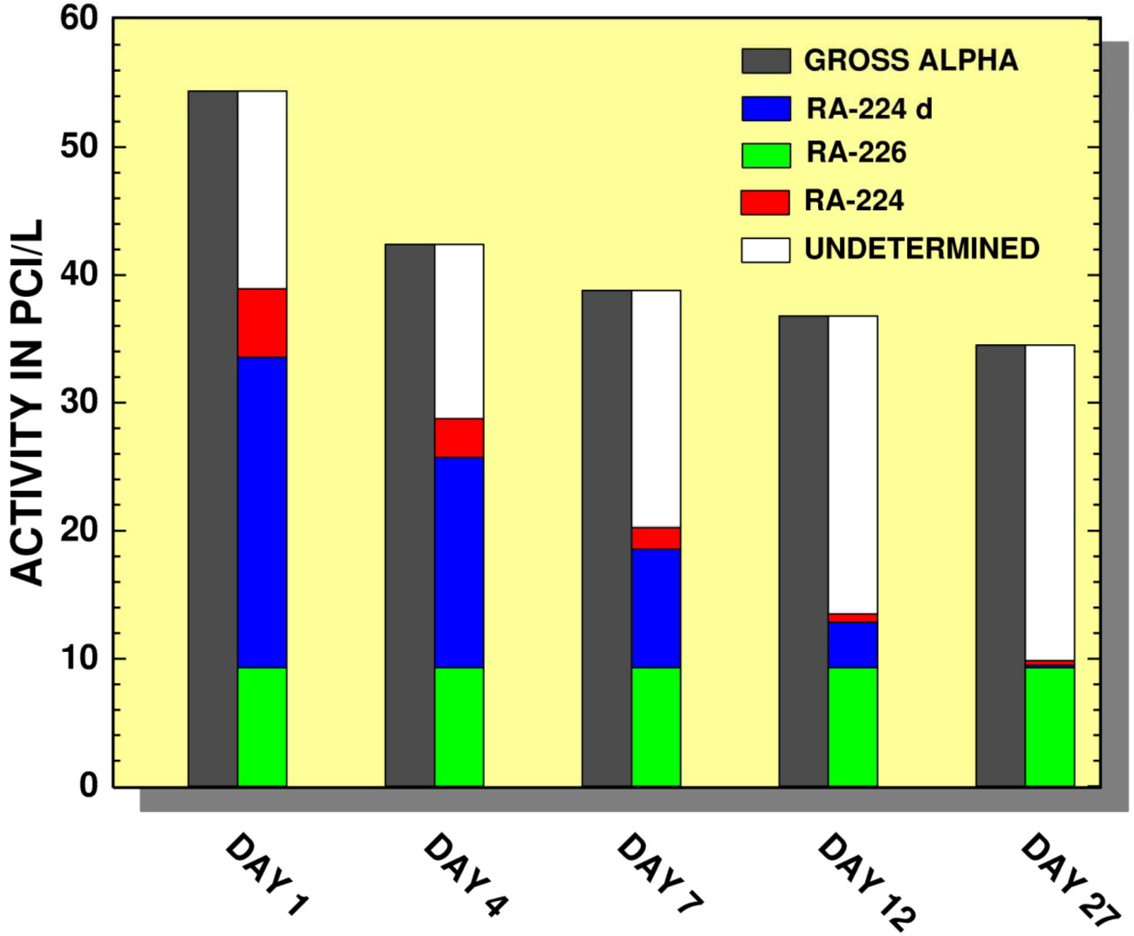
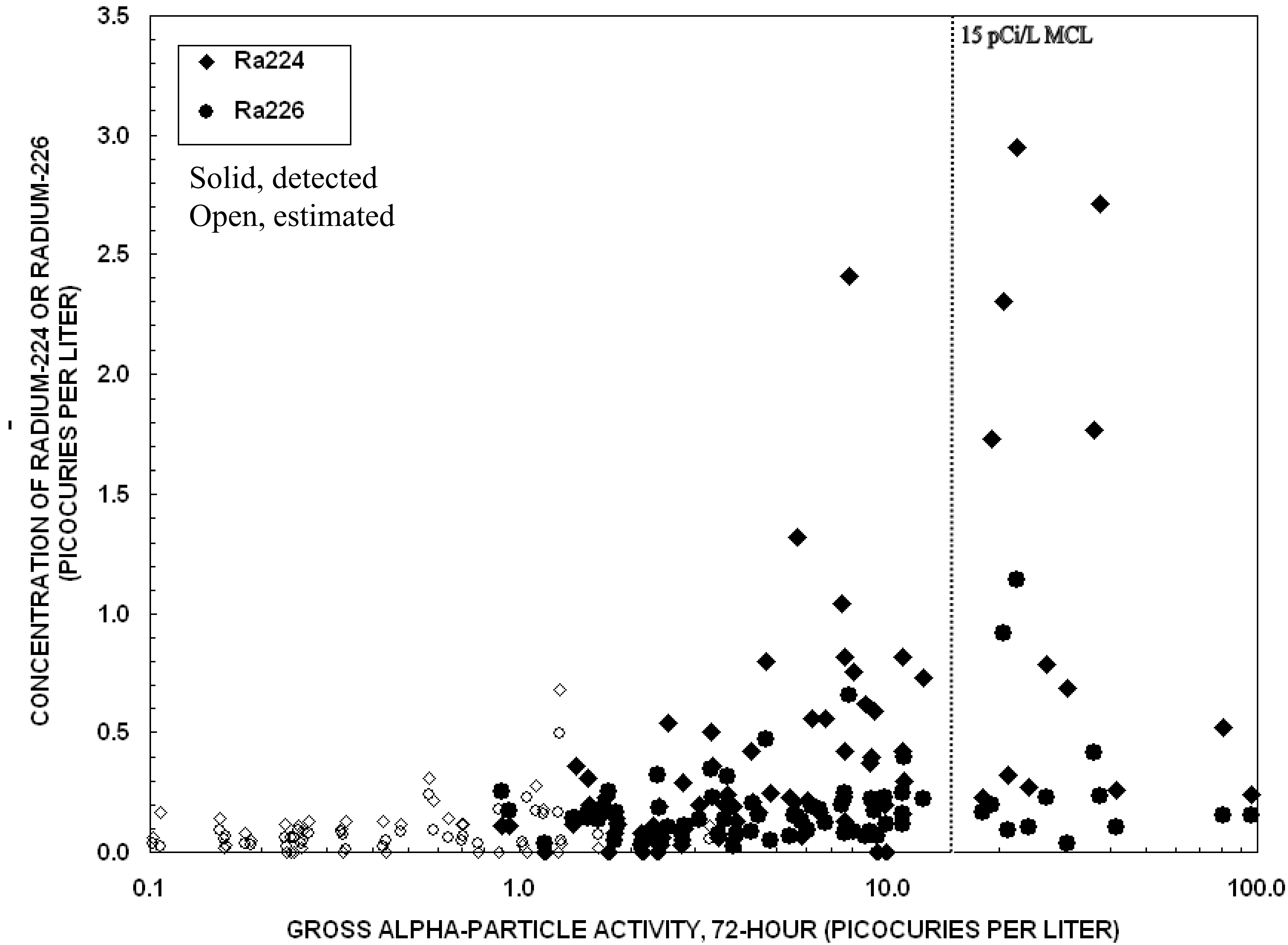


Figure 3.12 Decay scheme diagram for the alpha decay of $^{228}_{90}Th$ to $^{224}_{88}Ra$. In this case, four different alpha particles are emitted with four complementary gamma rays. (After Friedlander et al. 1964.)

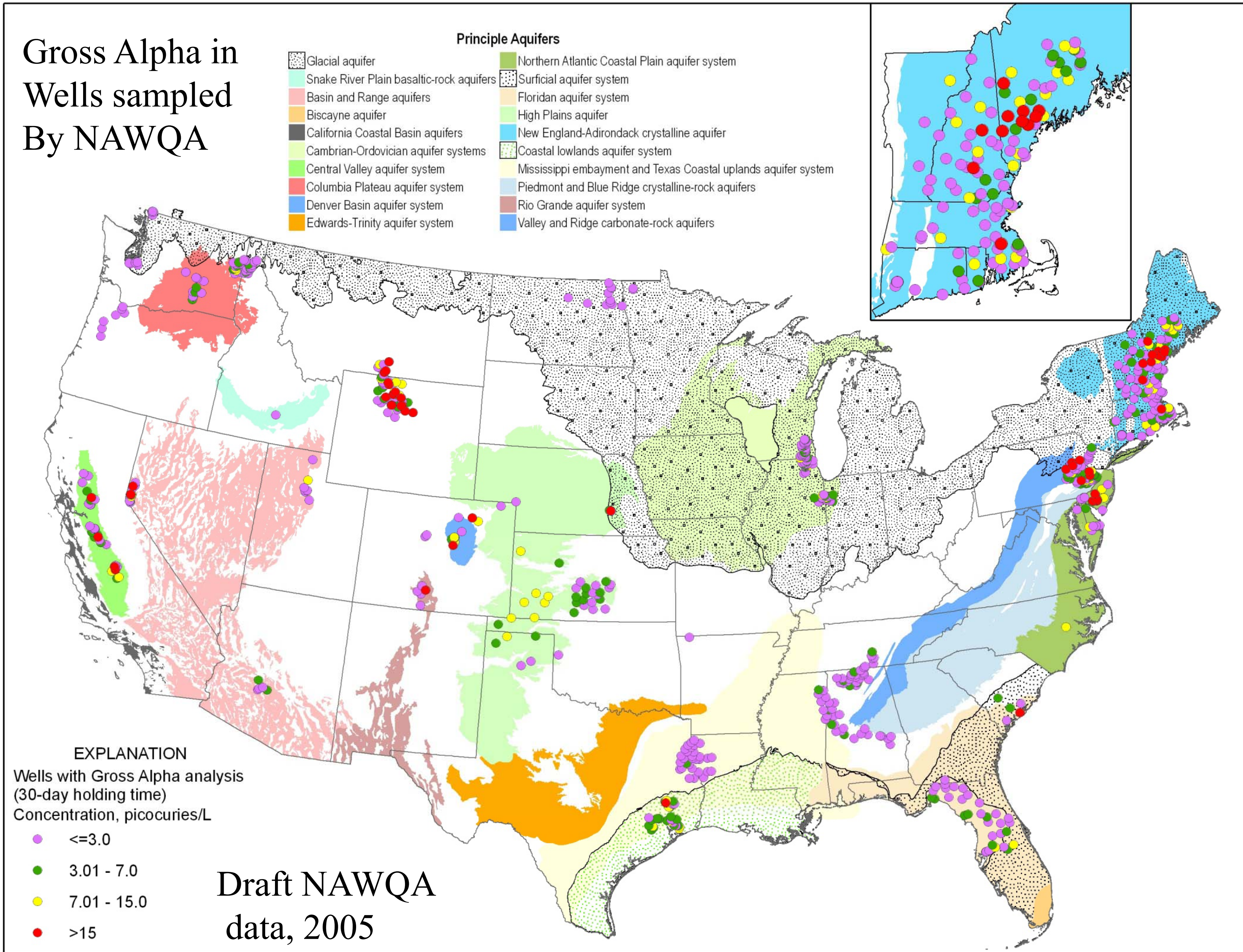


Change in components of gross alpha-particle activity through time, southern New Jersey



Western USA, 2004; draft NAWQA data; Szabo et al., in press.

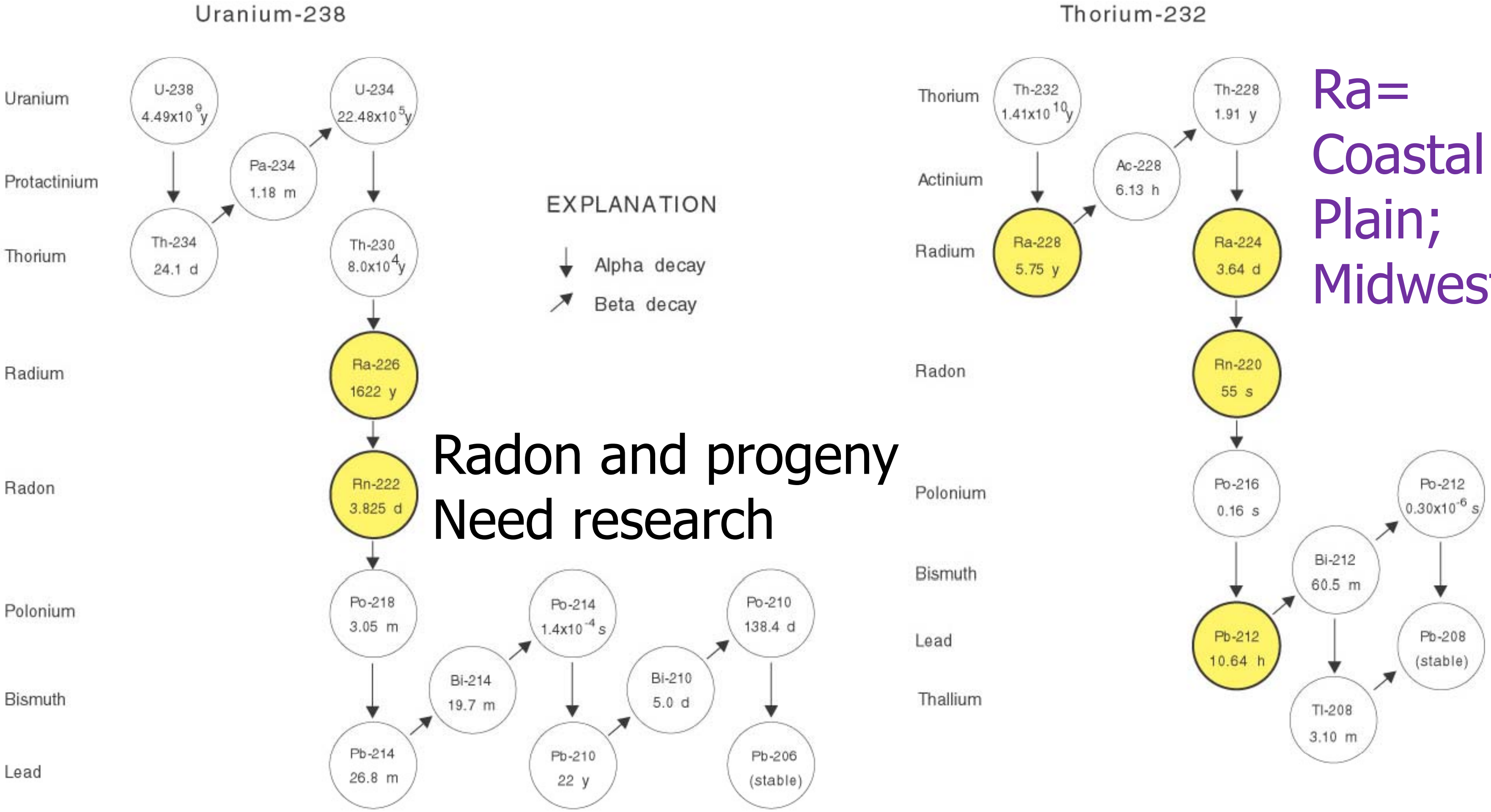
Gross Alpha in Wells sampled By NAWQA



Draft NAWQA data, 2005

U = Northeast USA bedrock
Western USA

Ra= Coastal Plain; Midwest

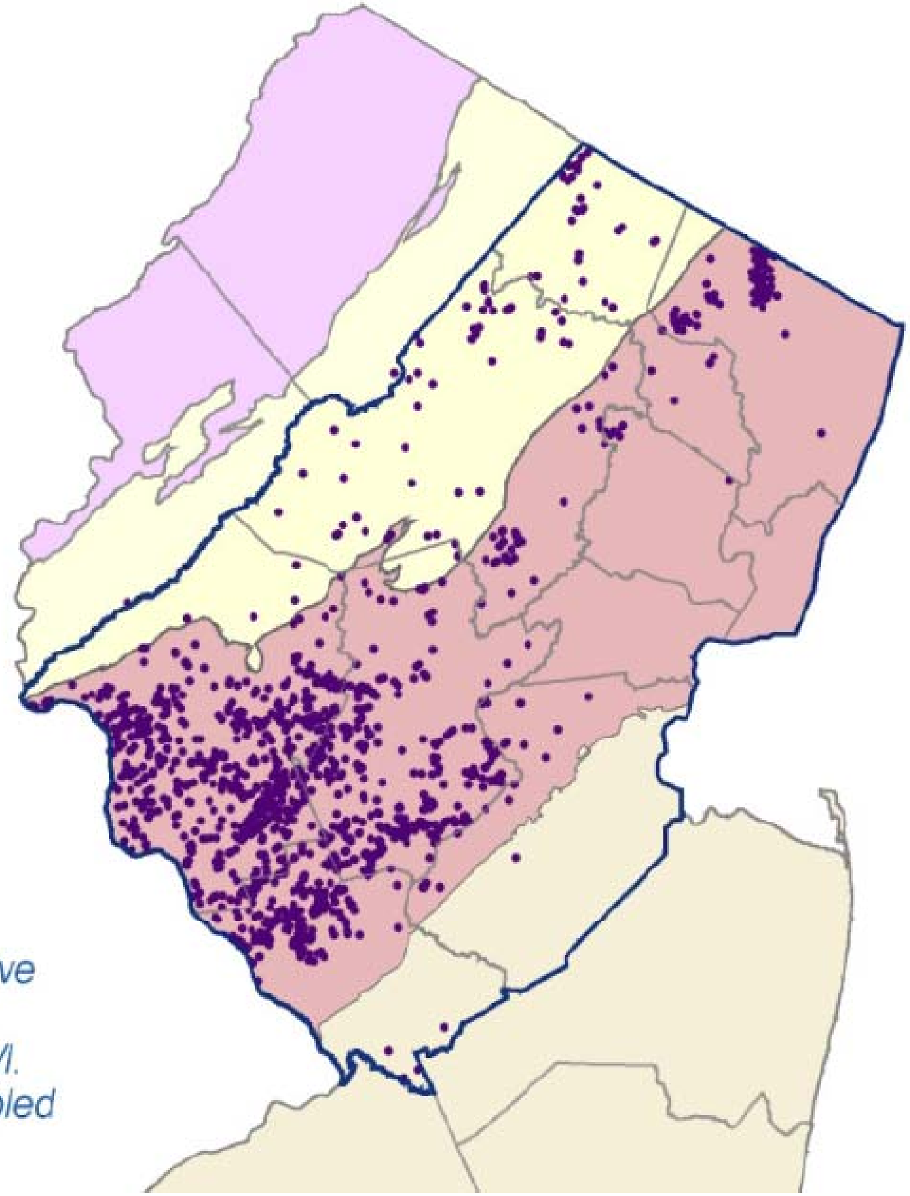


Radon and progeny
Need research

Figure 1. Diagram showing uranium-238 and thorium-232 radioactive decay series. (Radionuclides of interest in this study are shaded). [Times shown are half-lives: y, years; d, days; h, hours; m, minutes; s, seconds] (From Hall and others, 1985)

Gross alpha = may be one or many individual isotope contributions!

● Failed for Arsenic at 5 ug/l



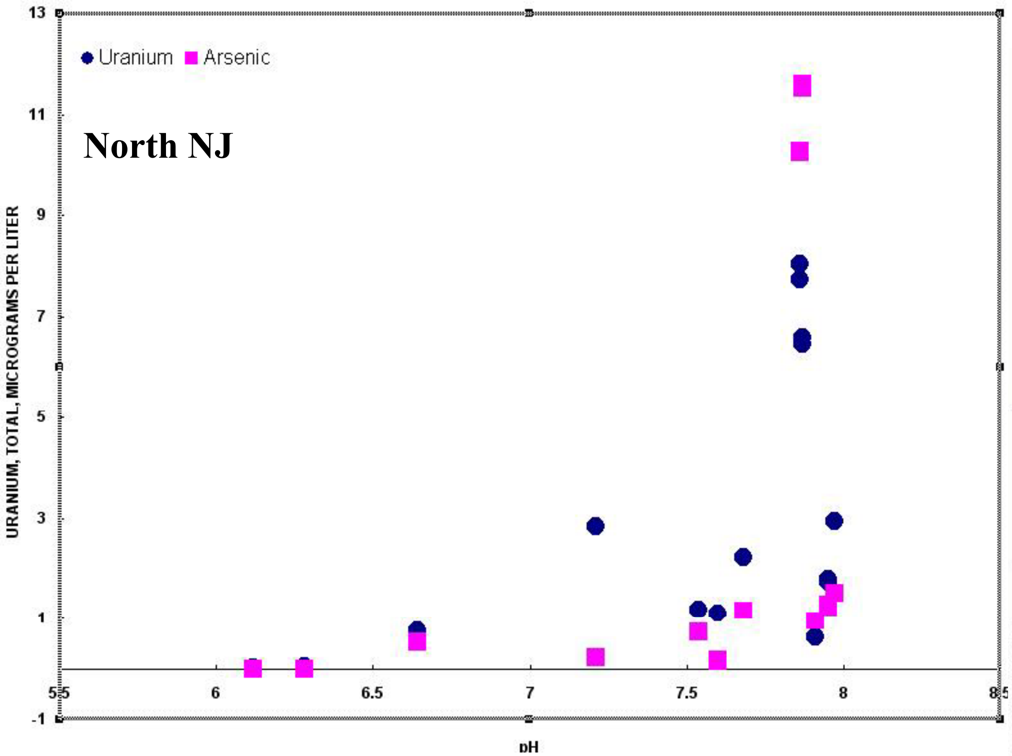
Those counties sampled for arsenic contamination are outlined in blue.

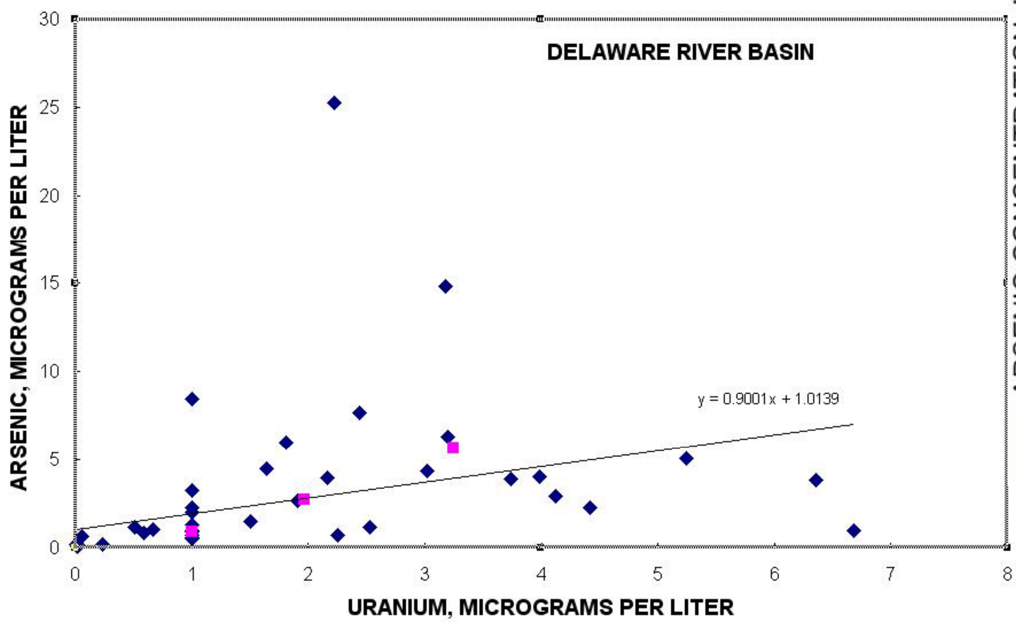
1,445 Private Wells, of the 12,263 wells analyzed for arsenic using sensitive analytical methods, failed to pass the State Drinking Water Standard of 5 ug/l. That is 11.8% of the 12,263 wells sampled and appropriately analyzed.

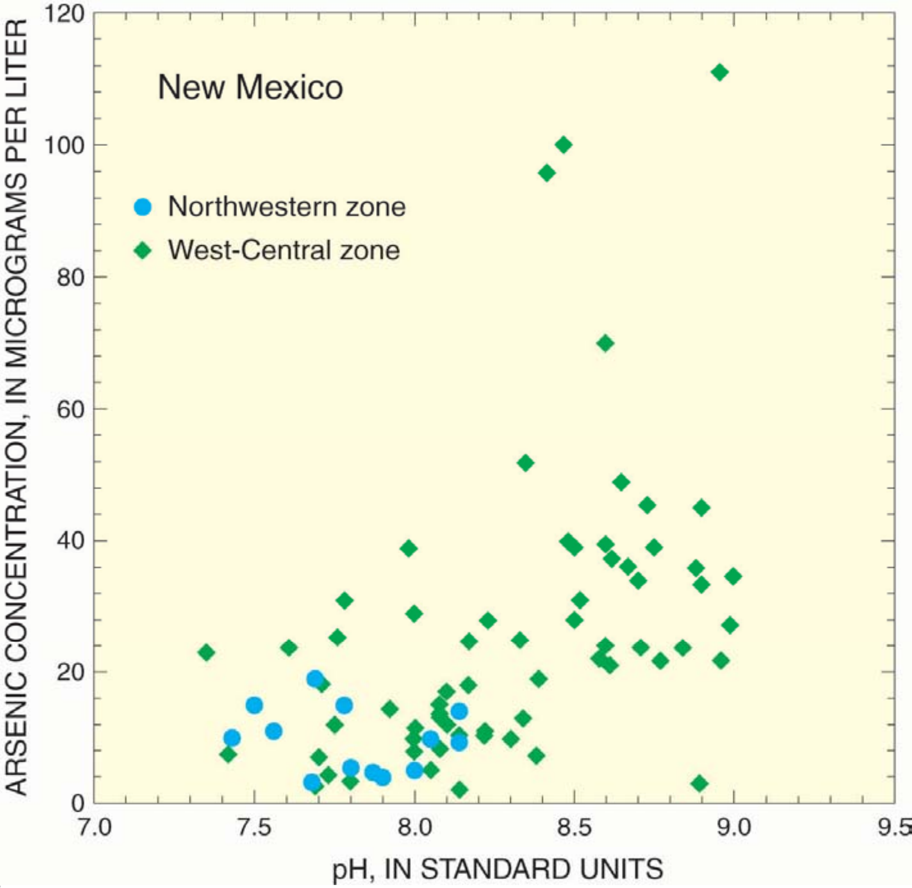
NJ Private Well Testing for Arsenic

*www.state.nj.us/dep/**pwta***

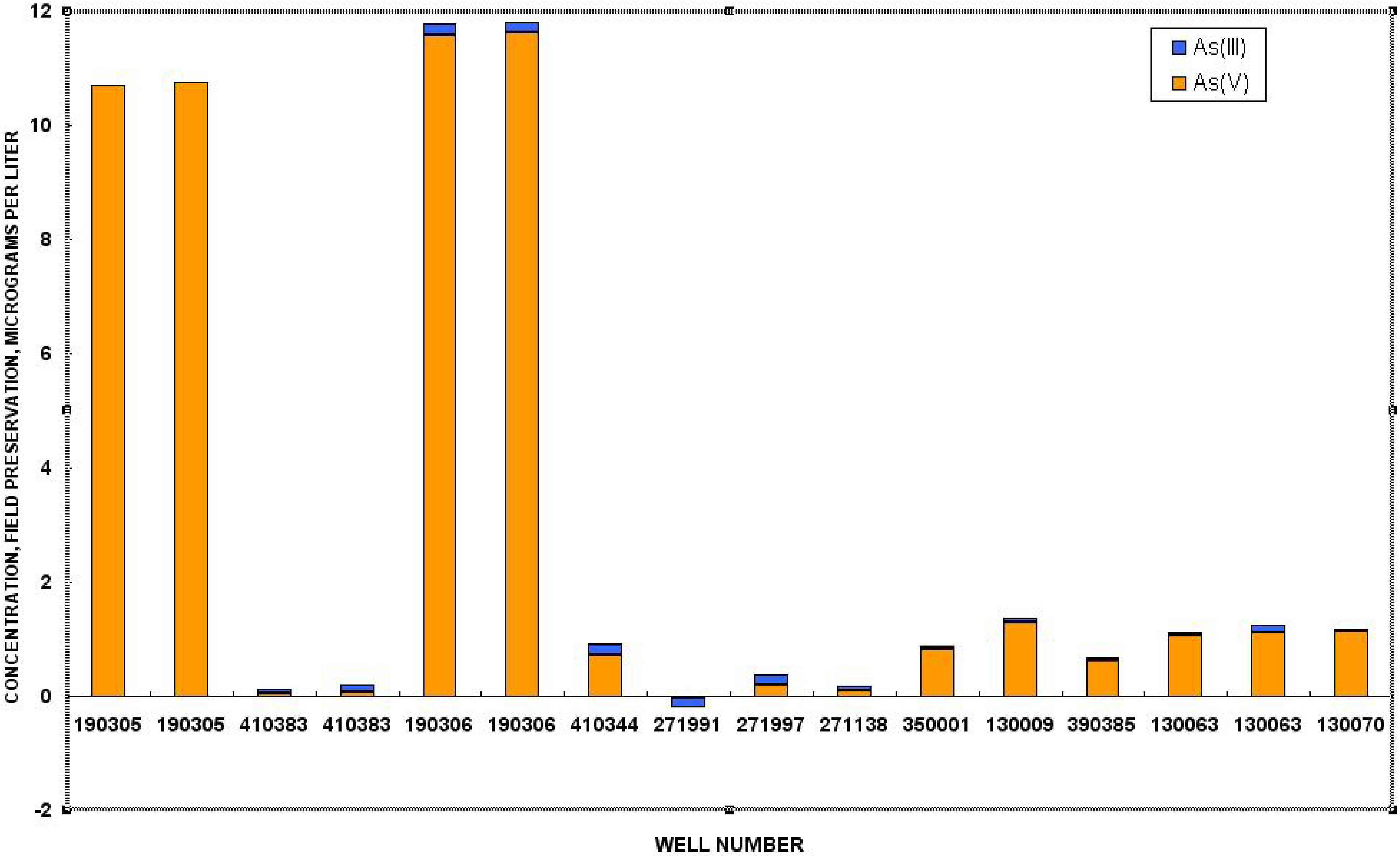
U(VI) & Arsenic(V) sorption decreases sharply about pH 8; Mobile in alkaline oxidizing environments

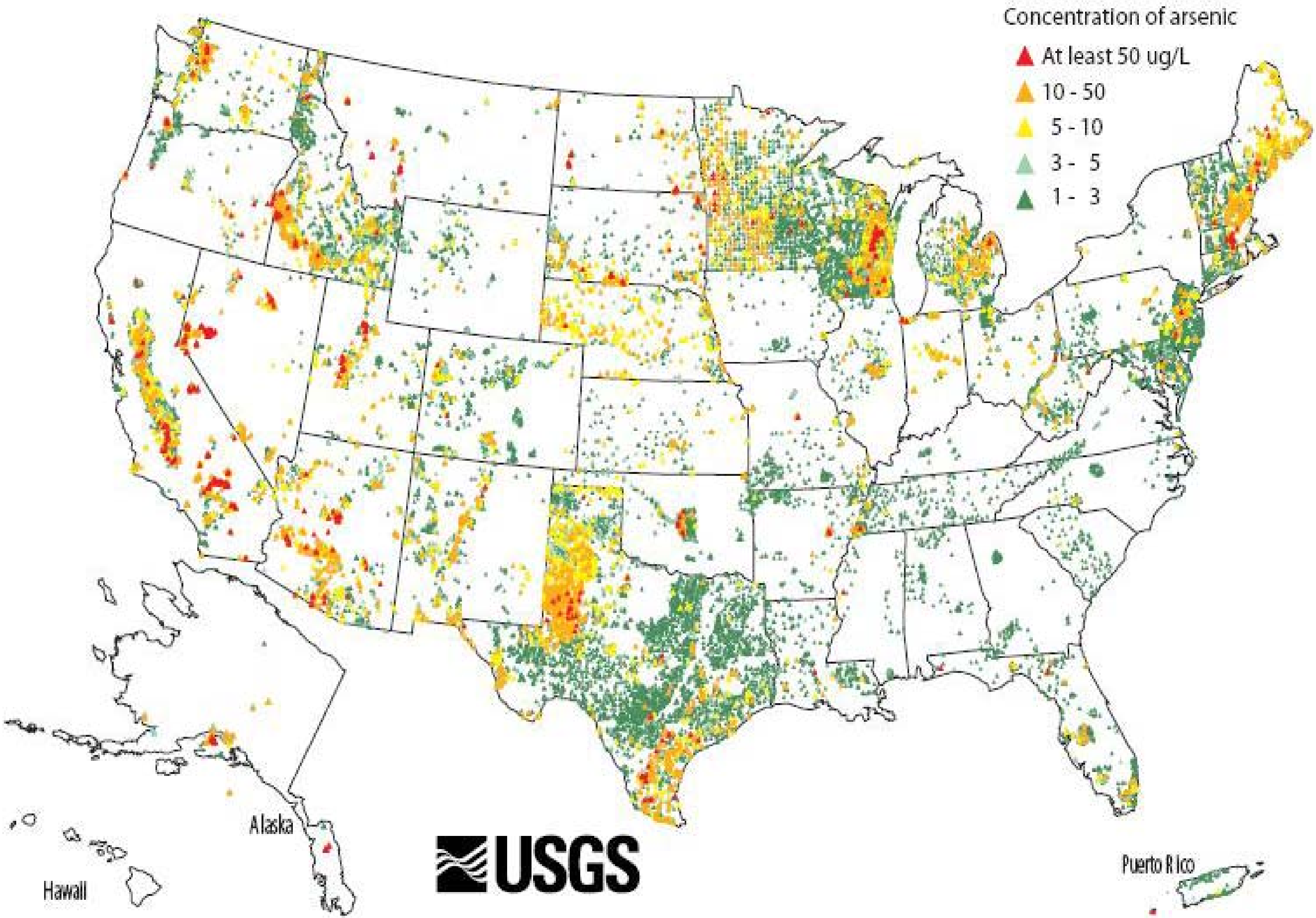






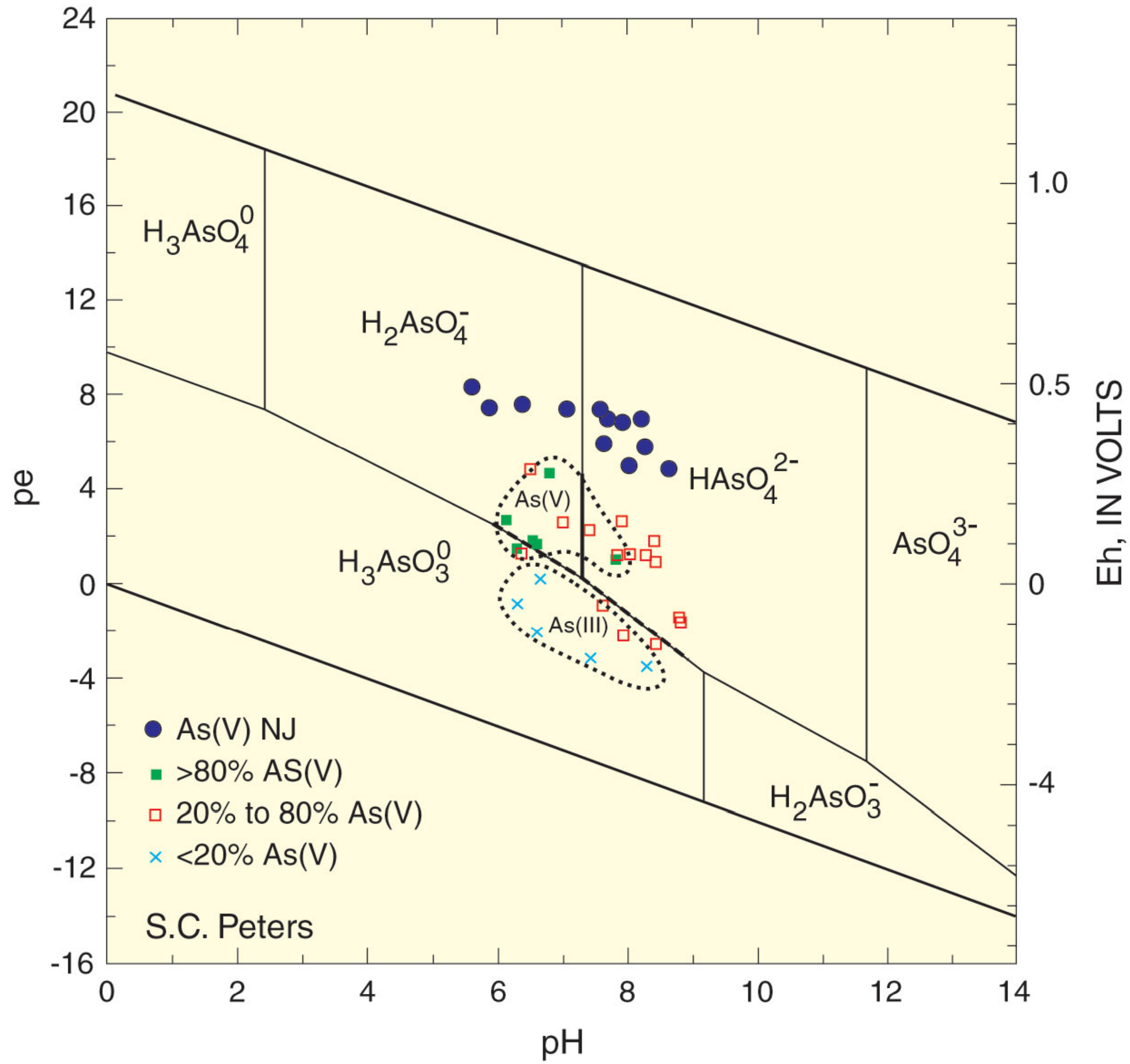
North NJ ground water, Arsenic species, mostly As(V)

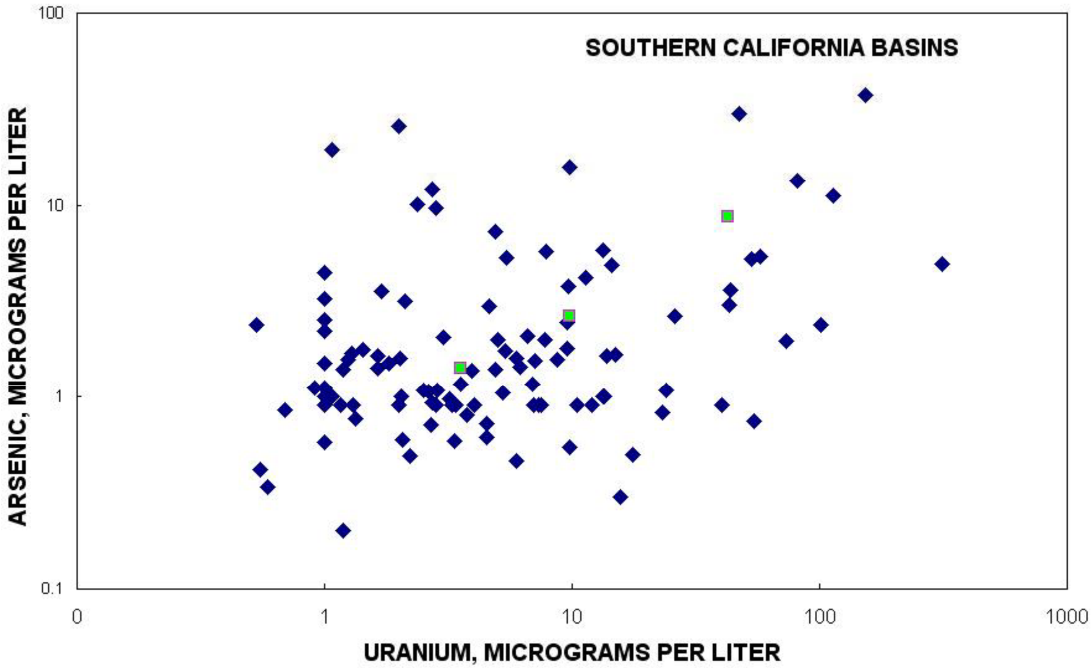




[http://water.usgs.gov/nawqa/trace/arsenic]
Focazio et al., 2006

1. Arsenic thermodynamic data and environmental geochemistry





Alkaline Oxidizing Environments

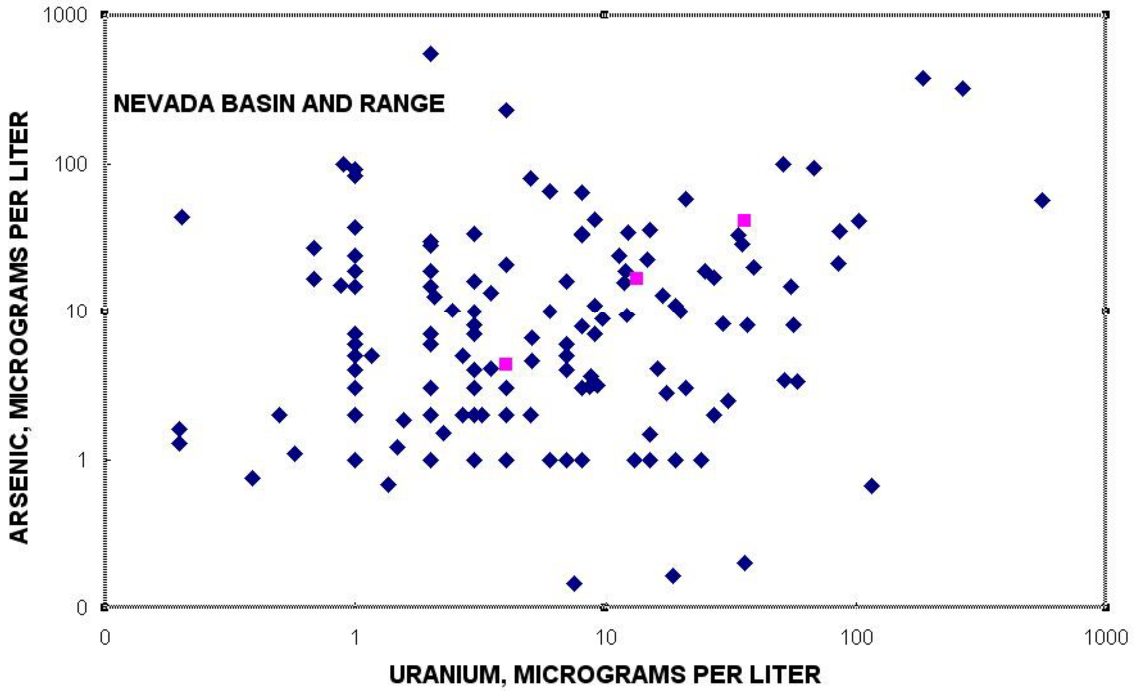
Asssume As = As(V)

Assume U =U(VI)

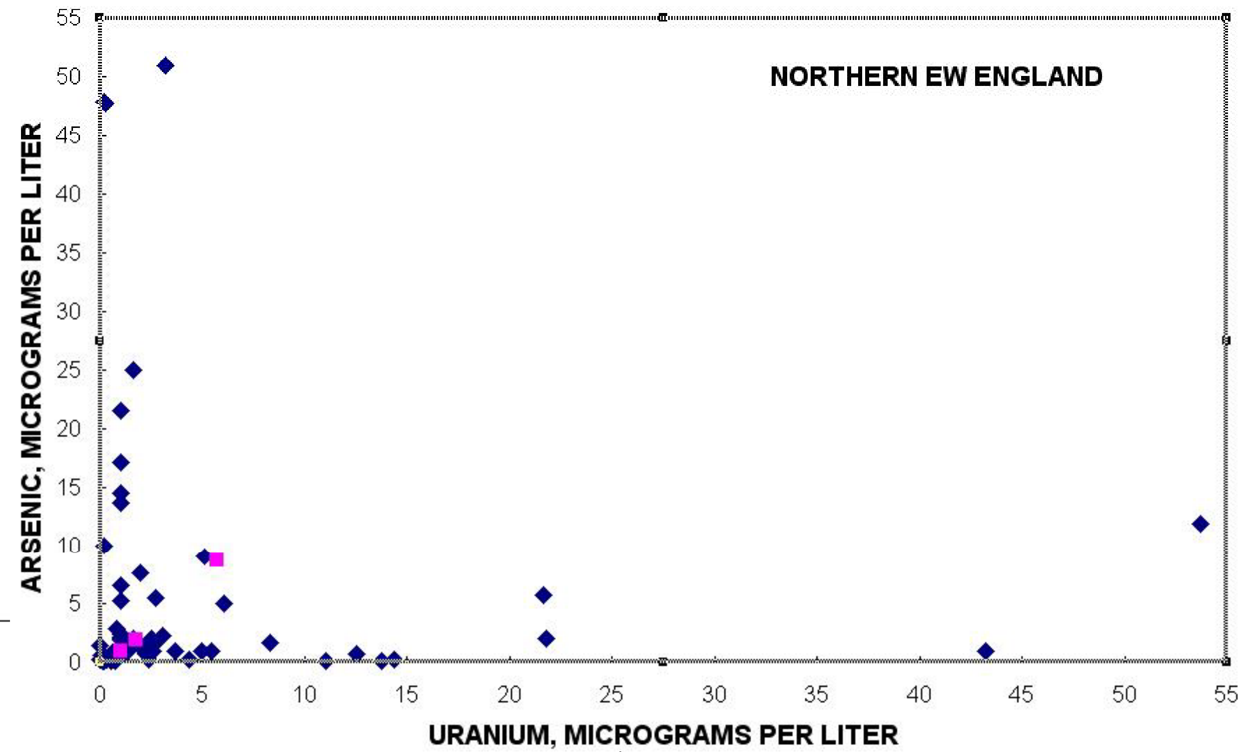
Assume Ra is sorbed

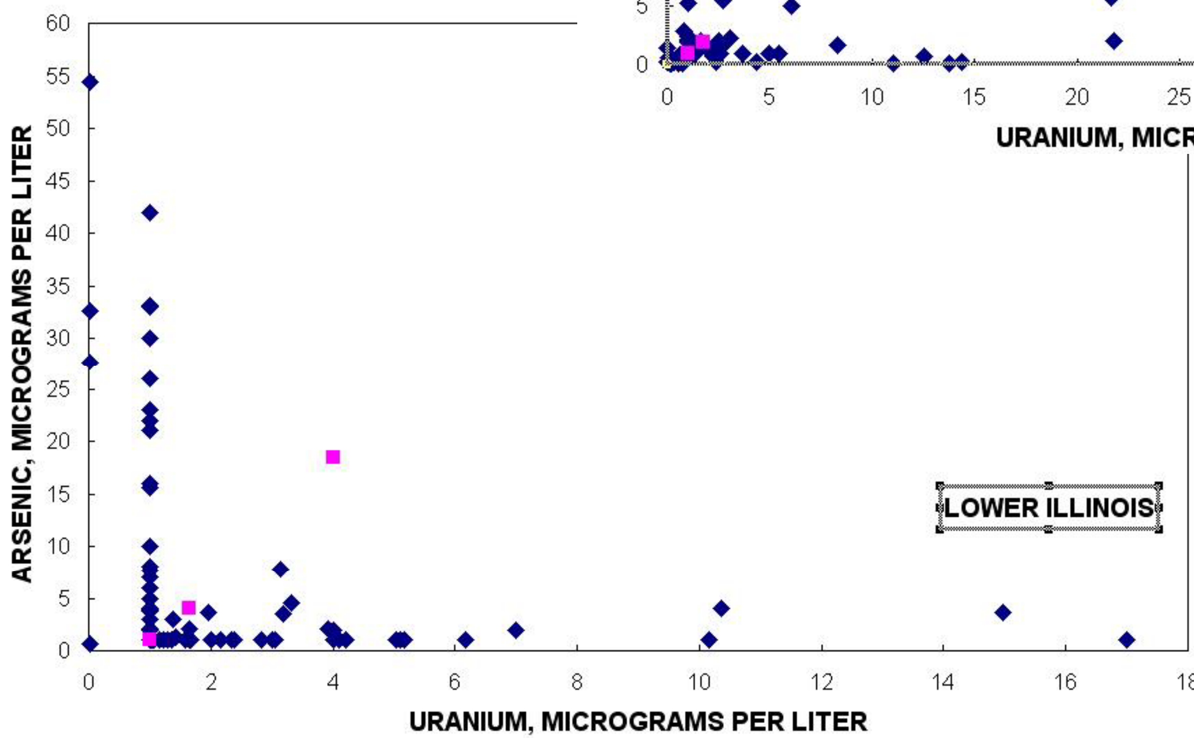
(draft NAWQA data)

Broad U & As Concurrence



EXCLUSIONARY U & As occurrence at all but the lowest concentrations



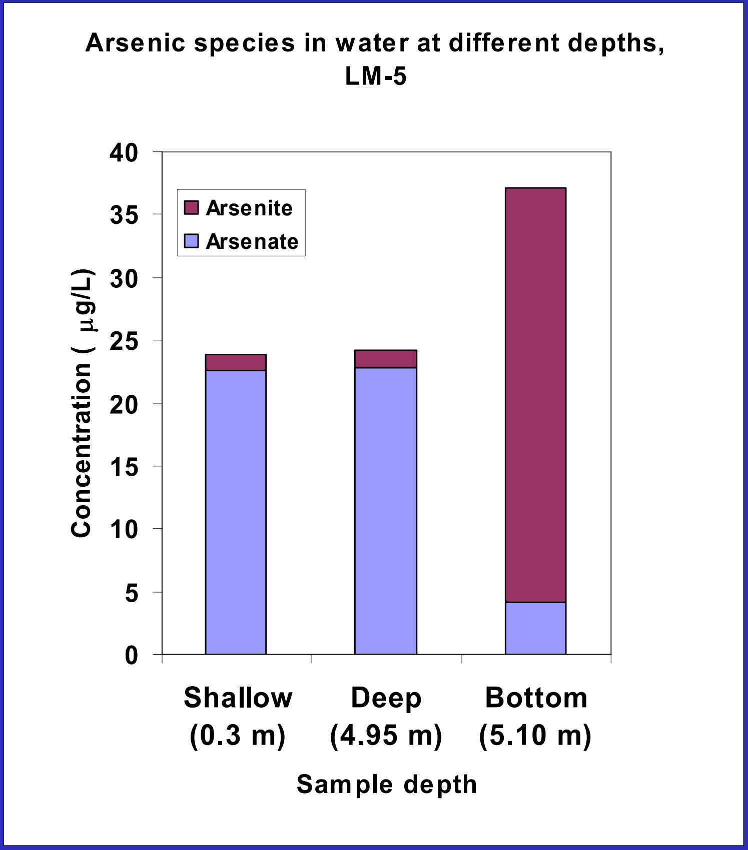


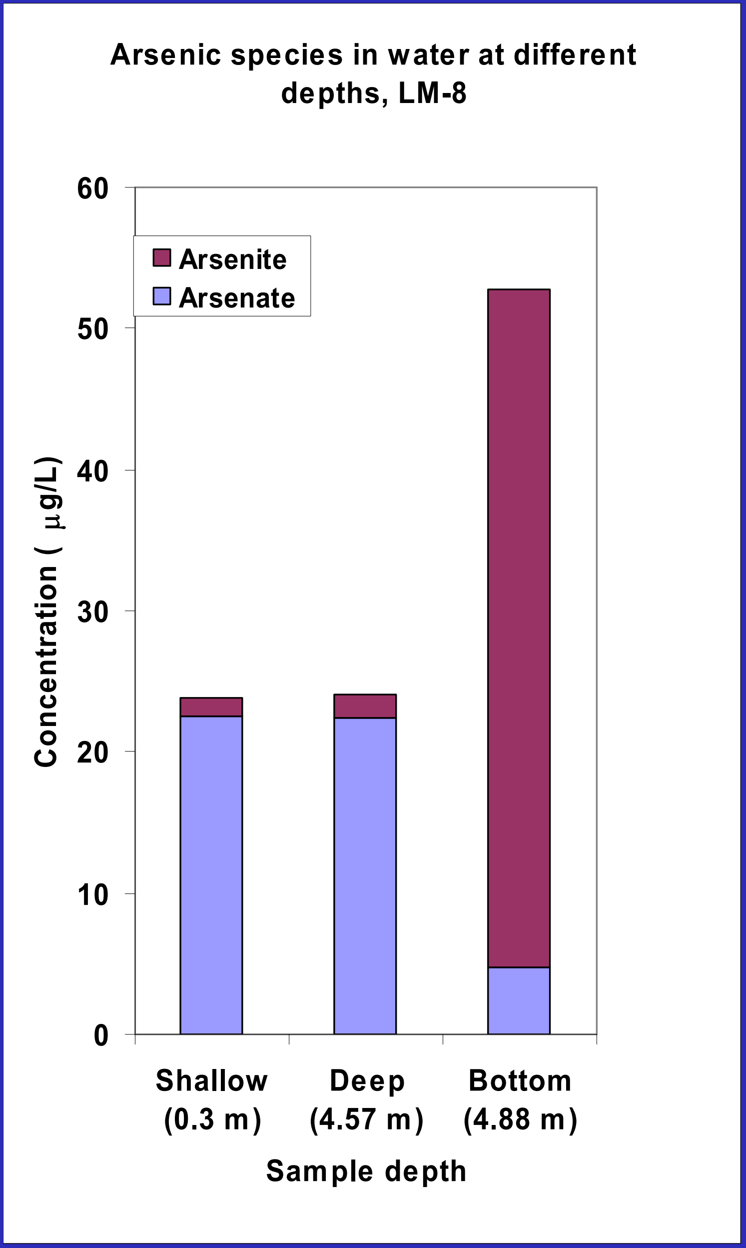
Reducing Environments As = As(III)

(draft NAWQA data)

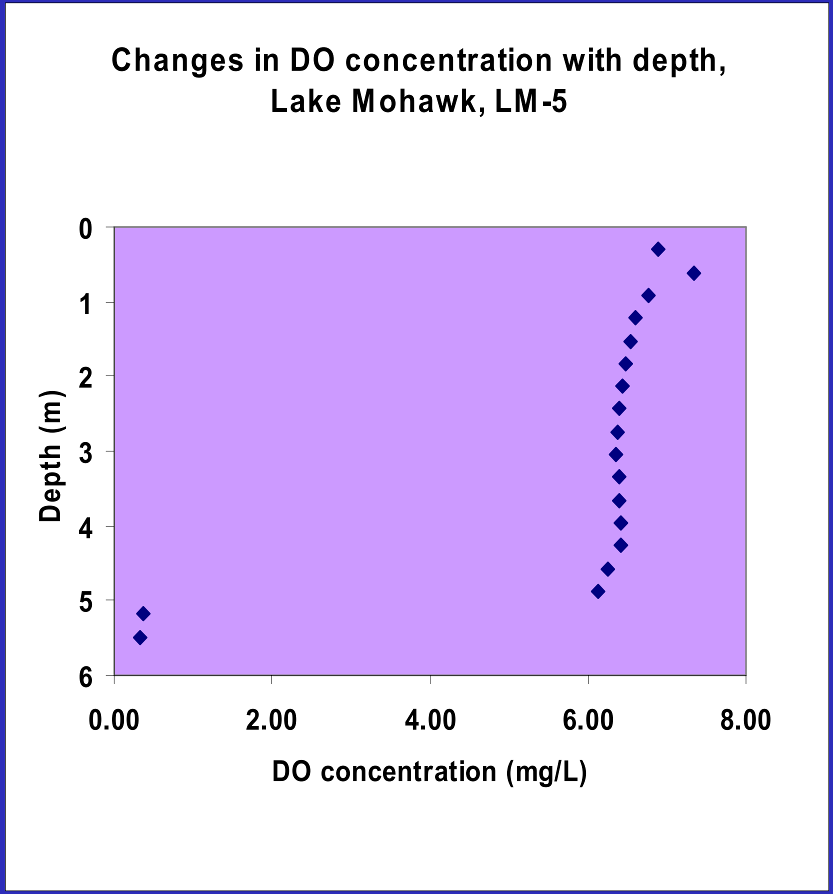
Arsenic species distribution, Lake M, NJ.

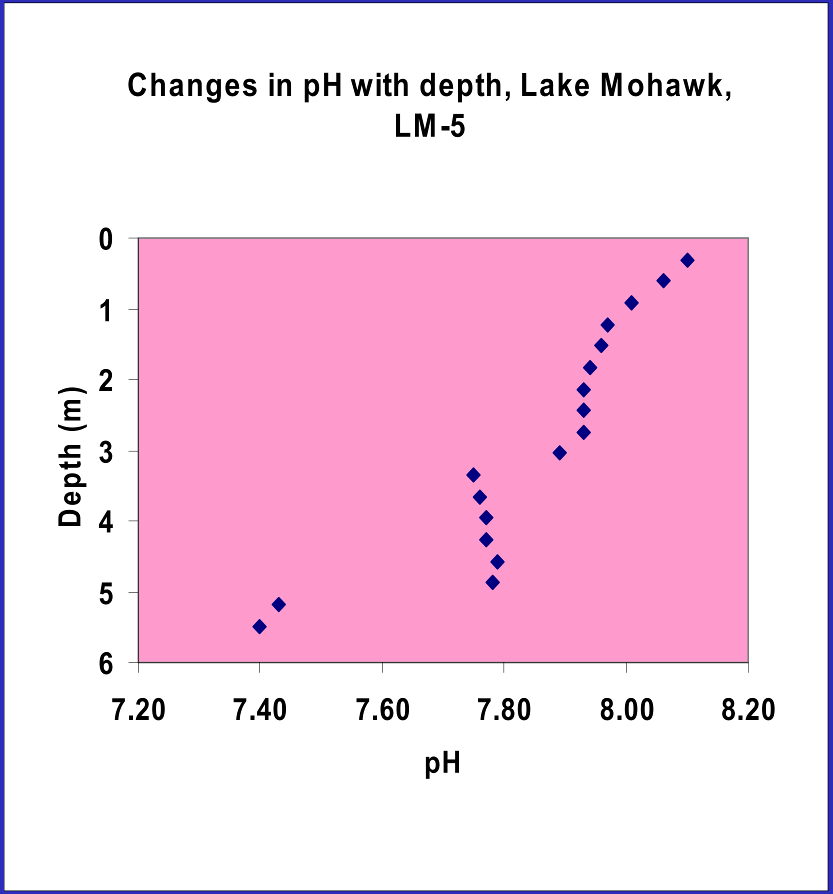
(Barringer, Szabo, and others, in press)



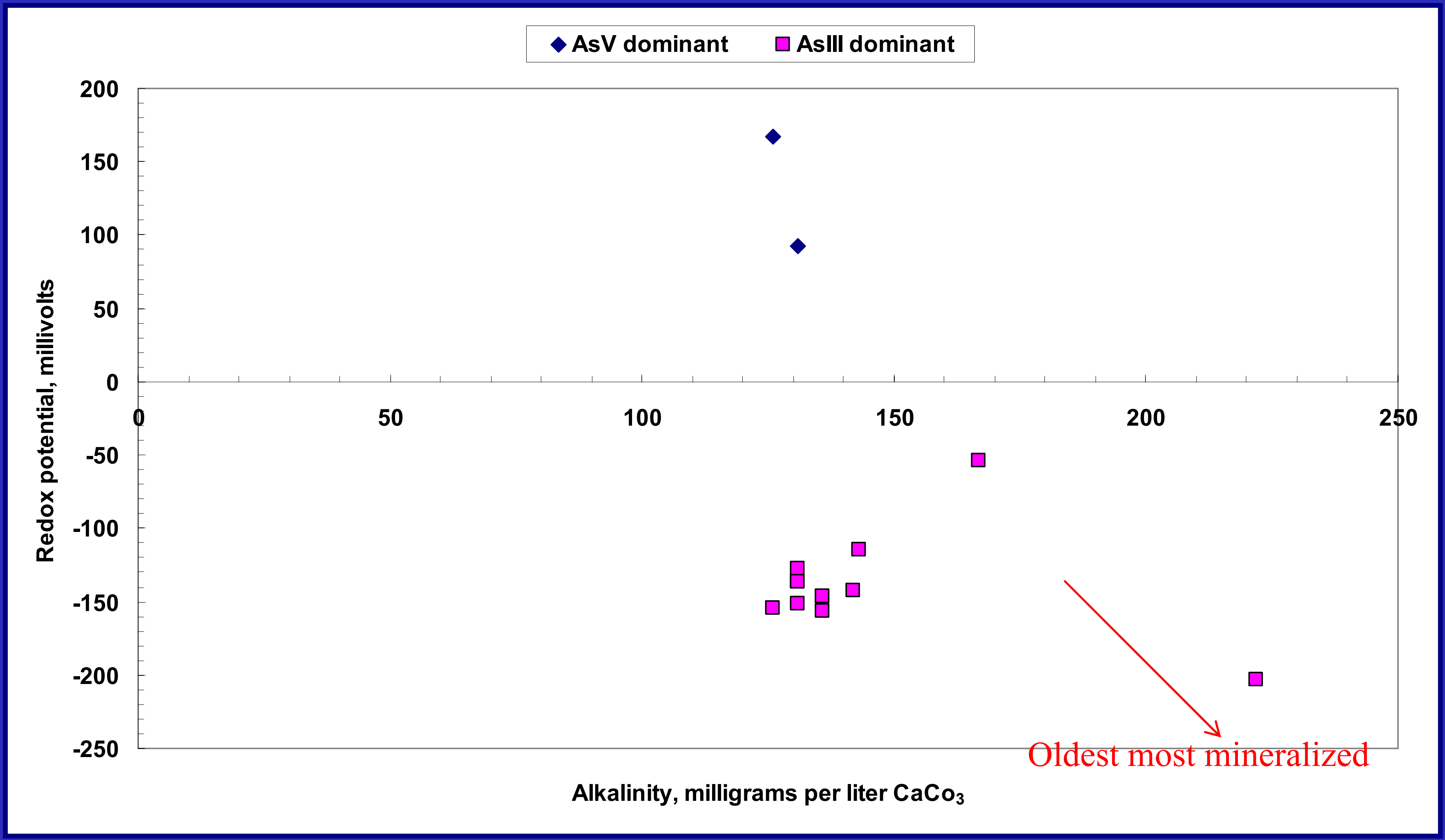


At site LM-5 at the deepest part of Lake M, decrease in DO and pH was abrupt. The organic-rich sediment layer is ~ 1 m thick there and is reducing.
(Barringer, Szabo, and others, in press)





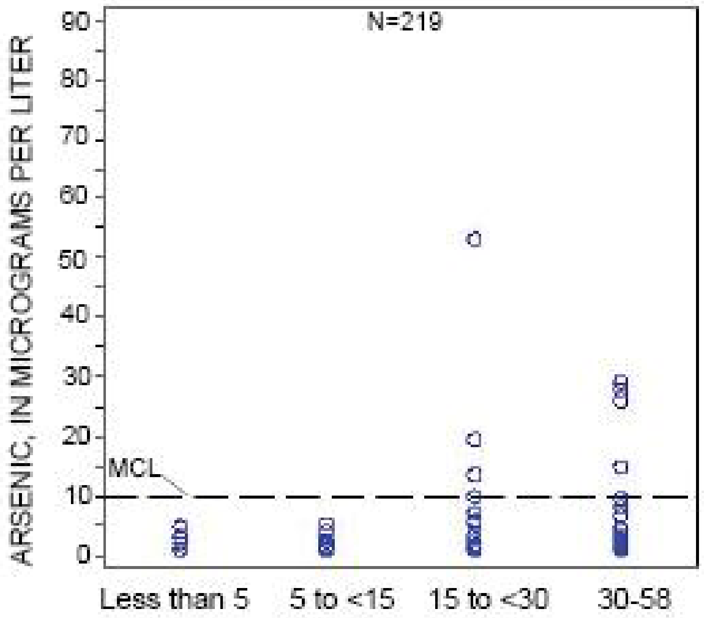
Arsenic species vs. ORP and alkalinity, Ground water, Texas Gulf Coastal aquifer



Oden et al., 2008

Residence time and mineralization (salinity) can be indicative of elevated trace element concentrations provided geochemistry allows for dissolution

Arsenic Concentrations and Related Factors in the Glacial Aquifer System



Age, in years,
based on chloroflurocarbon, sulfur hexafluoride,
or tritium/helium-3 data

	Less than 5	5 to <15	15 to <30	30 to 58
Number of samples	48	63	59	49
Percentage of samples with arsenic ≥10 µg/L[1]	0	0	7	8

[1] µg/L, micrograms per liter

Thomas, 2007

IMPLICATIONS: Treatment and Distribution

- Consider geochemistry for treatment and distribution systems as well.
- Arsenic speciation affects treatability.
- Ra-224 can occur and perhaps other short-lived isotopes can be present.
- Monitoring fate of radionuclides may be important for treatment and distribution systems.

Ra-224 data, Alpha radioactivity, and Short-lived Progeny in various portions of the water supply delivery System. What are their Sources?

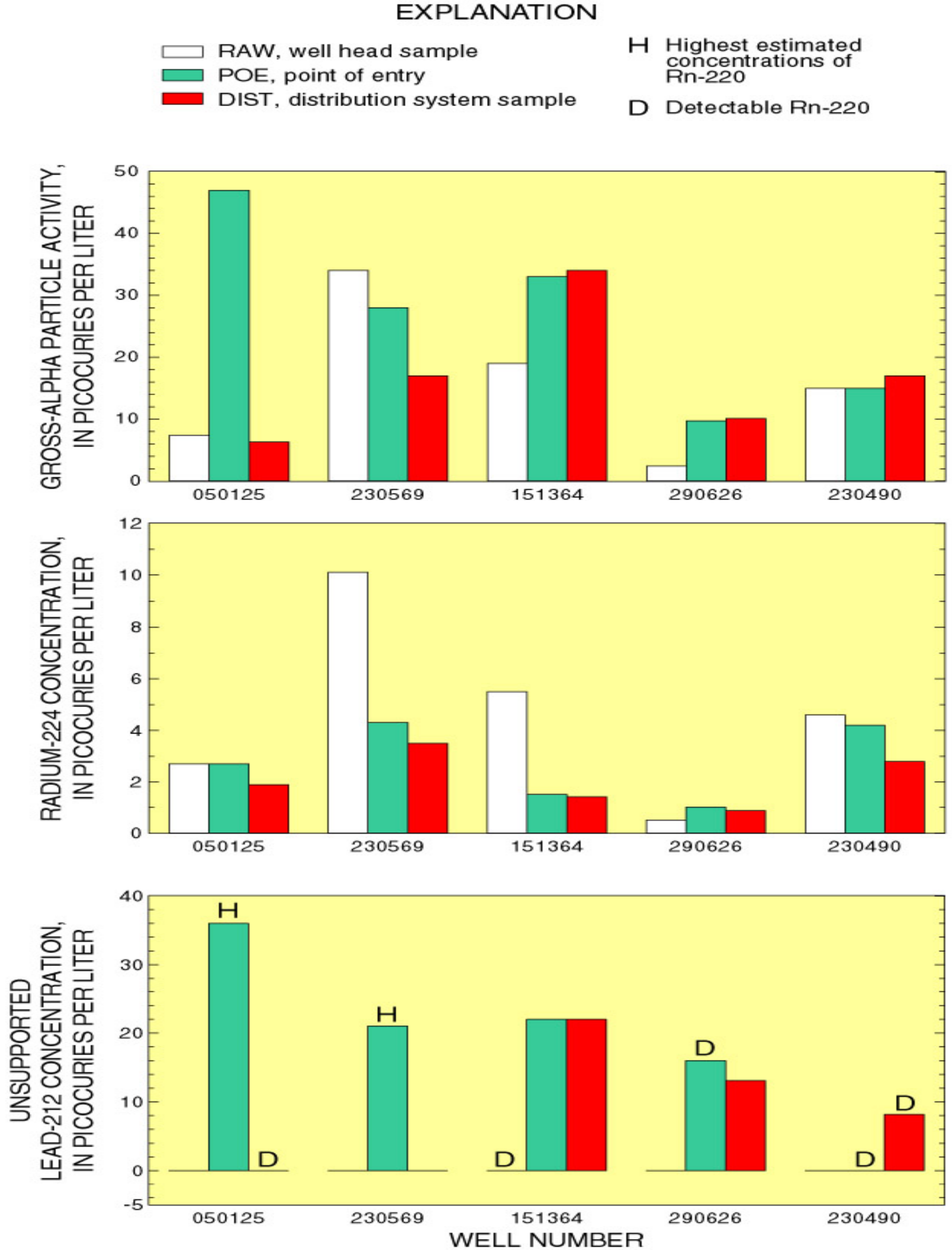
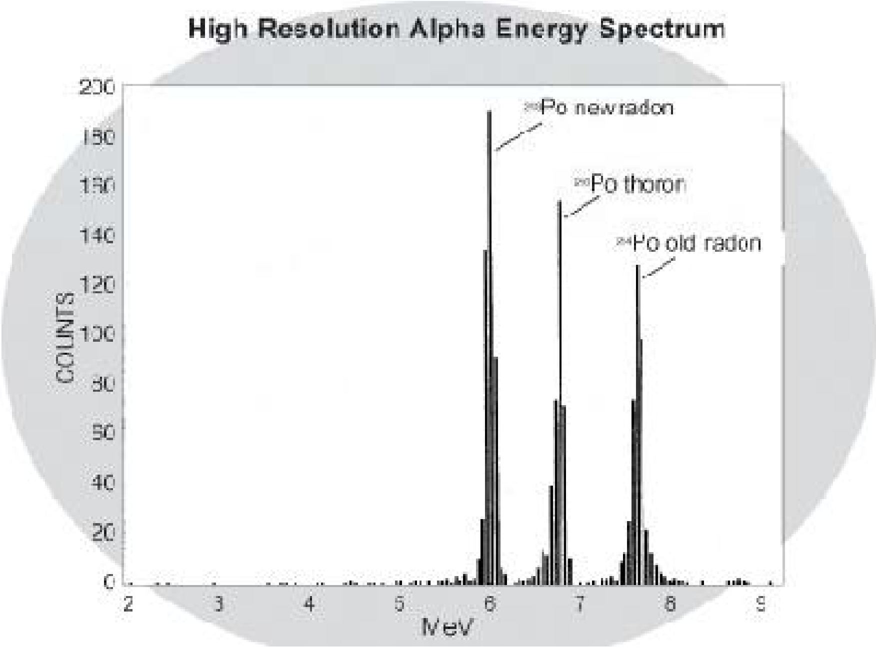


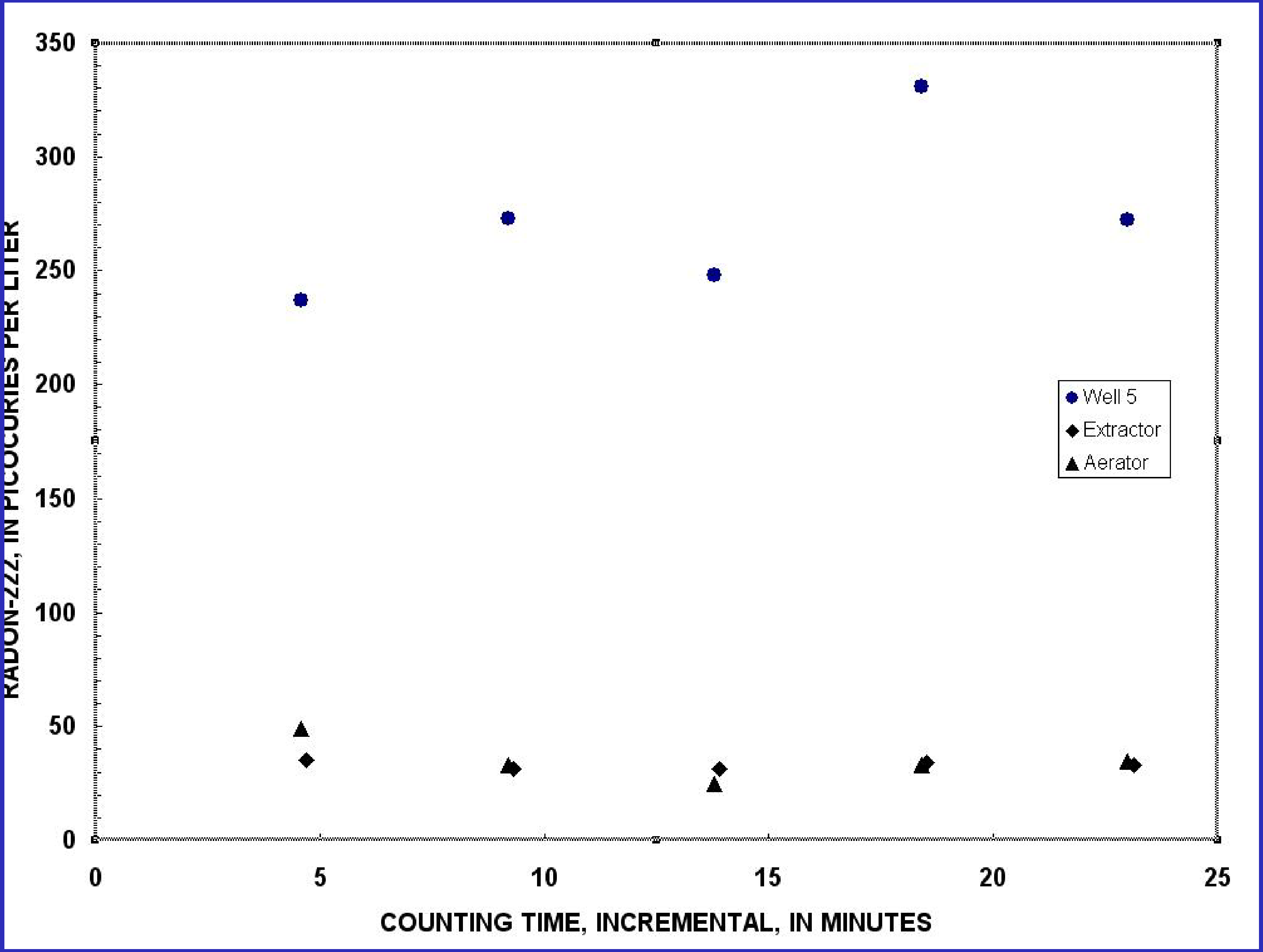
Figure 4. Comparison of radioactivity in raw, point-of-entry, and distribution system samples from selected wells, withdrawing water from the Potomac-Raritan-Magothy aquifer system, New Jersey, 2000.

Field Portable Alpha Spectrometer – different energies of the various radon progeny can be detected and quantified. A useful screen in the distribution system.

- Thoron-220 detected



Field study completed in a matter of hours, southern NJ air-stripping tower



IMPLICATIONS

- **Additional active monitoring is needed to better understand radionuclide and As occurrences**
- **Consider geology, hydrology, geochemistry.**
- **Arsenic speciation allows for mobility in many environments.**
- **Ra-224 can occur and other short-lived isotopes can be present.**
- **Conventional monitoring inadequate for :**
  - **Ra-224 (gross-alpha screen)**
  - **Pb-212 (gross-alpha screen)**
  - **Po isotopes (gross-alpha screen)**
  - **U isotopes (gross alpha-screen)**

IMPLICATIONS: INNOVATIVE TECHNOLOGY

- Understanding Arsenic speciation allows predicting mobility in many environments.
- Ra-224 and short-lived isotopes can be detected by alpha- or gamma-spectroscopy
- Field portable alpha spectrometry is useful for radionuclides. Voltametry may allow Arsenic determination in the field
- Additional monitoring needs are better measurements of redox in field
- Gross alpha monitoring needs holding times
- Improved methods needed for:
  - Pb-212 , Pb-210, Po isotopes, U isotopes

[http://water.usgs.gov/nawqa/trace/arsenic][http://pubs.er.usgs.gov/pubs/]

Gundersen, L.C.S. and Szabo, Zoltan, 1995, Natural radionuclides in earth, air, and water, and the effect on human health: *in* Carter, L.M.H., ed., U.S. Geological Survey Circular 1108 p.22-24.

Focazio, M.J., Welch, A.H., Watkins, S.A., Helsel, D.R., and Horn, M.A., 1999, A retrospective analysis on the occurrence of As in ground water resources of the United States and limitations in drinking-water supply characterizations: [http://pubs.er.usgs.gov/usgspubs/wri/wri994279]

Focazio, M.J., Szabo, Zoltan, Kraemer, T.F., Mullin, A.H., Barringer, T.H. and dePaul, V.T., 2001, Occurrence of selected radionuclides in ground water used for drinking water in the United States: A reconnaissance Survey, 1998: [http://water.usgs.gov/pubs/wri/wri004273/pdf/wri004273.pdf]

Szabo, Zoltan and Zapecza, O.S., 1991, Geologic and geochemical factors controlling natural radioactivity in ground water, Newark basin, New Jersey: *in* Gundersen, L.C.S., and Wanty, R.B., eds., U.S. Geological Survey Bulletin 1971, p. 243-266. p. 566-586.

Szabo, Zoltan, Taylor, T.A., Payne, D.F. and Ivahnenko, Tamara, 1997, Relation of hydrogeologic characteristics to distribution of radioactivity in ground water, Newark Basin, New Jersey: [http://pubs.er.usgs.gov/usgspubs/wri/wri954136]

Szabo, Zoltan and dePaul, V.T., 1998, Radium-226 and Radium-228 in shallow ground water, southern New Jersey: [http://nj.usgs.gov/publications/FS/FS-062-98.pdf]

Szabo, Zoltan, dePaul, V.T., Kraemer, T.F., Parsa, Bahman, 2005, Occurrence of radium-224 and comparison to that of radium-226 and radium-228 in water from the unconfined Kirkwood-Cohansey Aquifer System, Southern New Jersey: [http://pubs.er.usgs.gov/pubs/sir/sir20045224]

zszabo@usgs.gov Please contact me via e-mail for copies of articles “in press” or otherwise cited.

SUMMARY

1. U & As occur in concentrations of concern especially in the alakline western third of the USA, also in the Midwest and Northeast
2. Ra occurrs primarily in sandstone and sand aquifers usually in acidic regions of the Coastal Plain and reducing areas in the Central USA
3. Co-occurrence of U and As is greatest in alkaline oxidizing regions, indicating geochemical control & prevelance of As(V)
4. Exclusionary occurrence of U & As in Midwest, Northeast indicates prevalance of As(III) in those regions
5. Characterization of pH, DO, SC, gross alpha, and other master geochemical variables is warranted!

USGS
science for a changing world