Characterization of Contaminant Transport Using Naturally-Occurring U– and Th–Series Disequilibria

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First study of its kind — in situ study of transport on geologic timescale

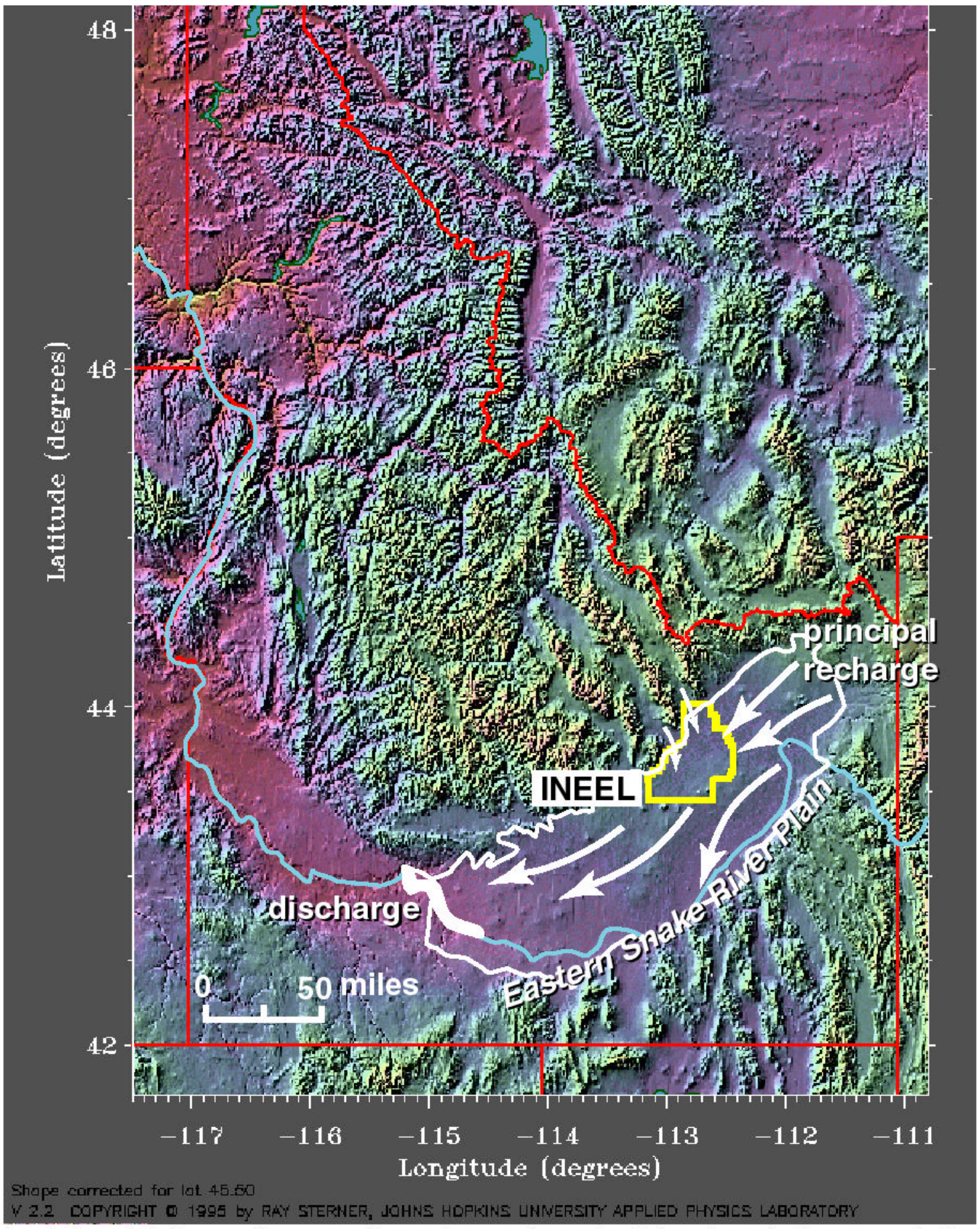
- Provides information not accessible with other methods
- Help in INEEL risk assessment
- Applicable to other sites

Goals

- Improved Characterization of Snake River Plain Aquifer Below INEEL
  1) Detailed delineation of flow pathways
  2) Identification of mixing patterns and calculation of relative water volumes
  3) Relative roles of mixing vs. water/rock interaction
- Quantify Contaminant Transport Rates at INEEL
  1) Rate of sorption–desorption and precipitation
  2) Retardation factors
  3) Rock/water interaction times
  4) Rock dissolution rates

Methods

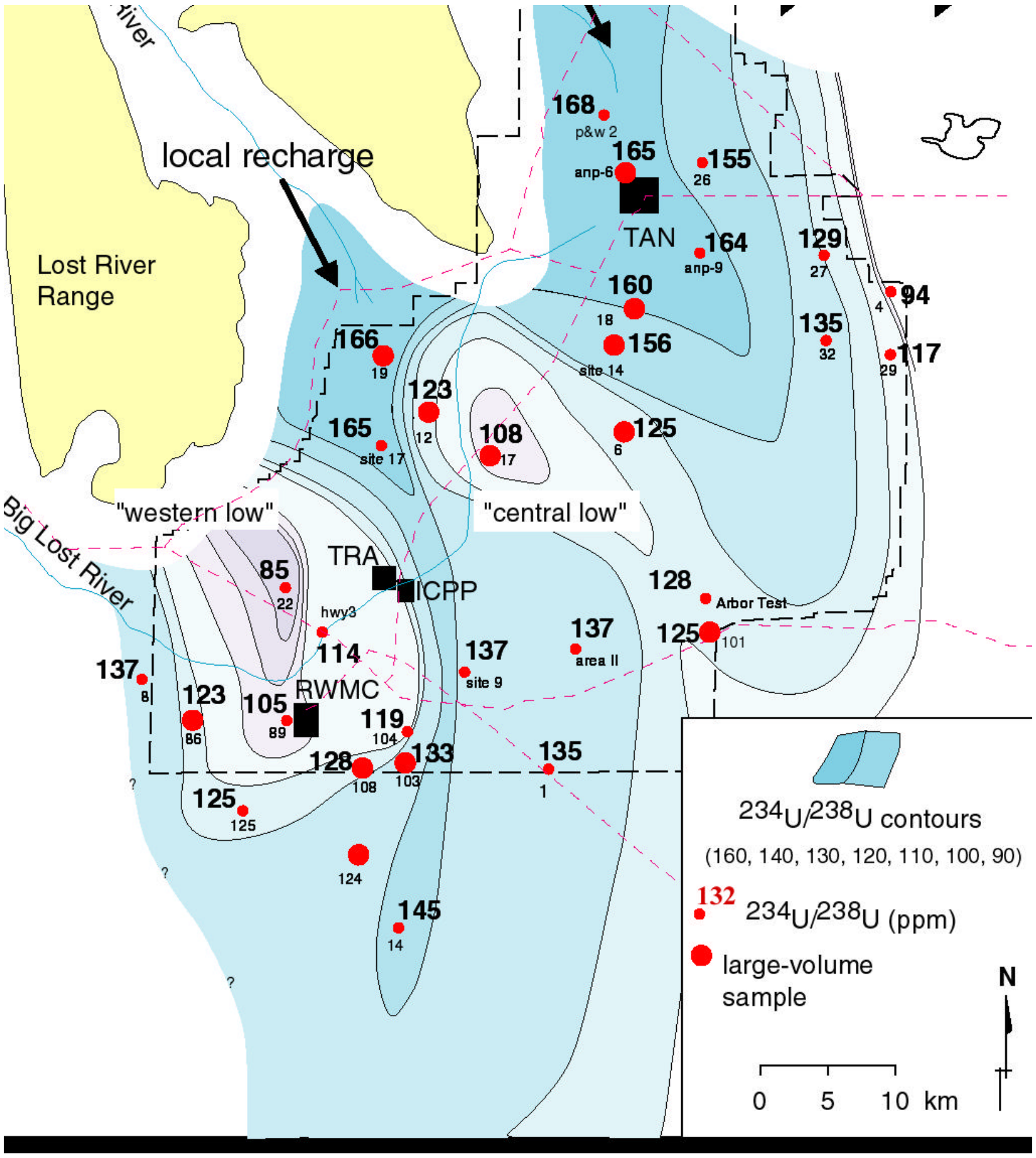
- Samples
  - Waters
    - Groundwaters (12, ~1000L samples collected using MnO_2 impregnated filters, and 50, 0.5L samples thus far)
    - Surface waters
  - Rocks
    - Core sections
    - Surface coatings
    - Fracture filling materials
- Measurements
  - Short-lived: ^{234}Th, ^{228}Th, ^{228}Ra, ^{224}Ra, ^{222}Rn, ^{210}Po by high sensitivity gamma counting (USC team)
  - Long-lived: ^{238}U, ^{235}U, ^{234}U, ^{232}Th, ^{230}Th, ^{226}Ra, ^{231}Pa by thermal ionization mass spectrometry (LANL team)



Snake River Plain aquifer consists of a series of olivine basalt flows and discontin
bedded sediments. Groundwater flow in the aquifer is fracture dominated and is fa
gh highly permeable rubble zones, which typify the tops and bases of individual flows
volcanic features such as lava tubes. Groundwater flow is heterogeneous ar
rally controlled by the orientation and interconnection of the high-permeability zo
of the recharge into the Snake River Plain aquifer occurs in the northeastern part o

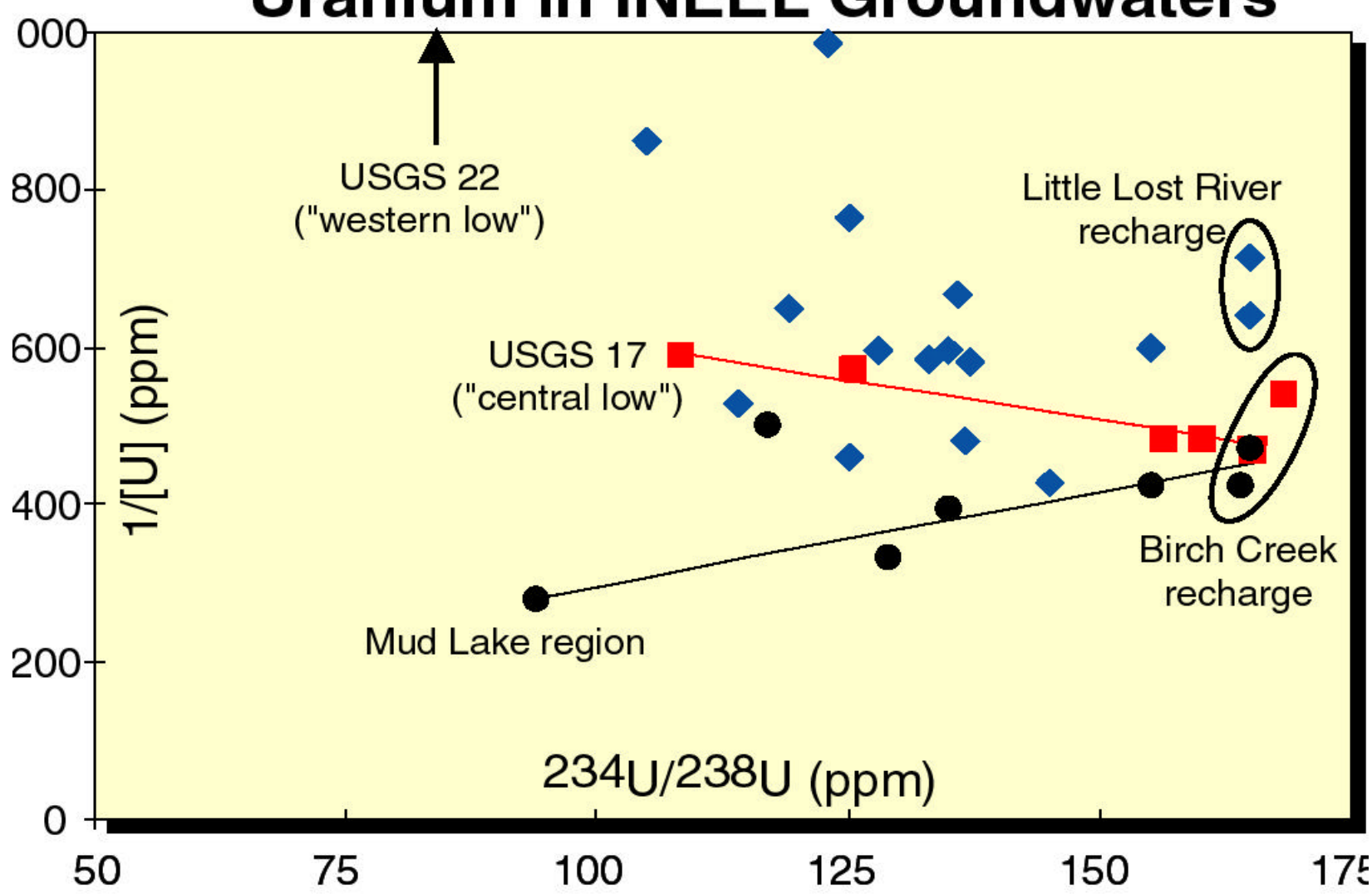
Summary: Uranium Isotopes

- Uranium data define multiple endmembers; can locally constrain mixing volumes
- Uranium isotopics define preferential flow paths (high $^{234}U/^{238}U$) and isolated pockets (stagnant areas?) with low $^{234}U/^{238}U$
- $^{234}U/^{238}U$ ratios and $^{87}Sr/^{86}Sr$ are lowered along flow paths
  - Dissolution/ion exchange dominate over recoil and selective leaching processes for uranium
  - Reactive phase composition modeled from U and Sr data does not fit bulk basalt - suspect incongruent dissolution of glassy components



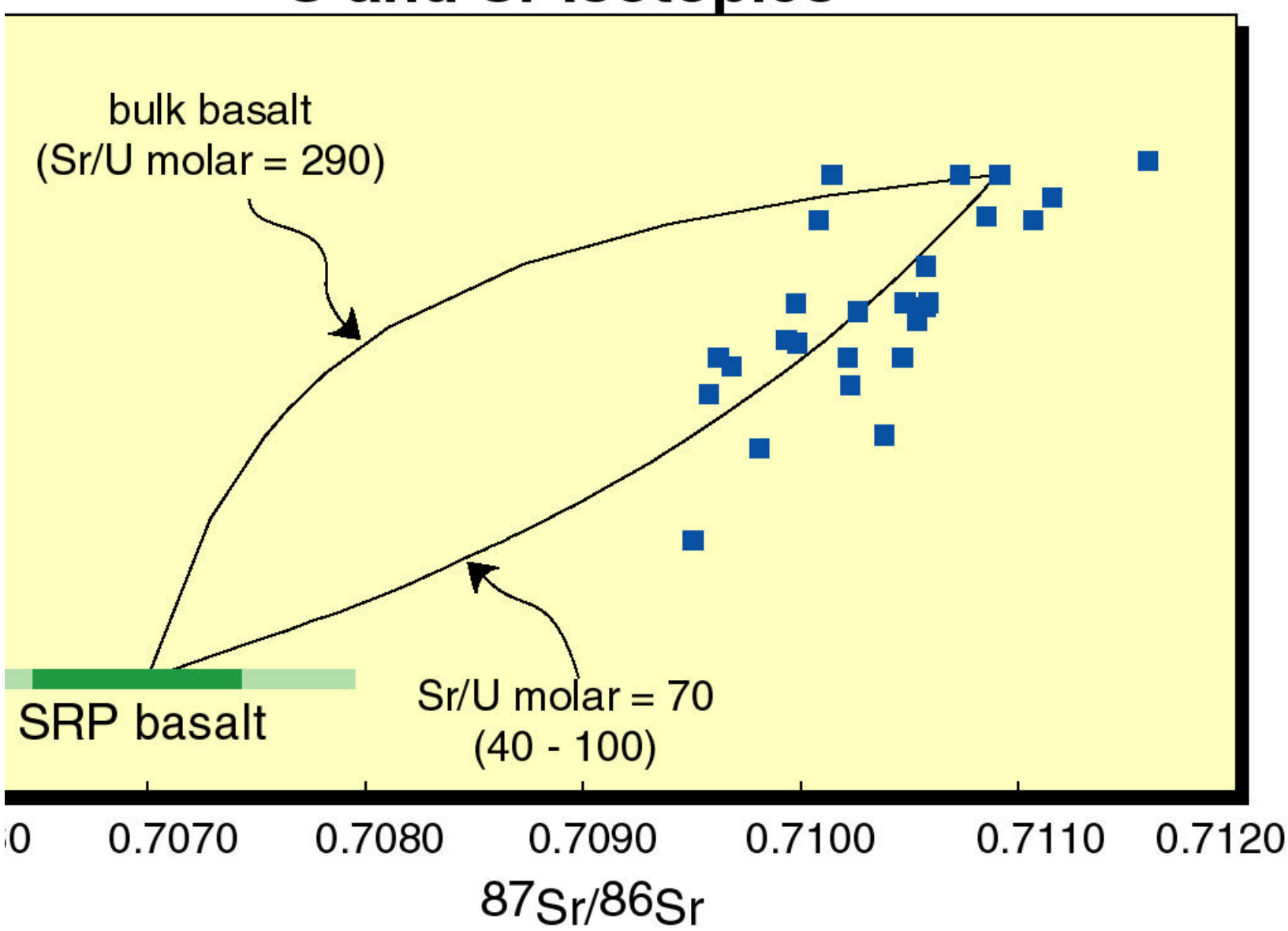
' groundwater samples have been analyzed for uranium isotopics and concentr
ured $^{234}U/^{238}U$ ratios vary from 85 to 168 ppm (atom ratio) and concentrations
0.3 to 3.6 ppb. These values are higher than secular equilibrium but are typical of
enated groundwater with ^{234}U additions from recoil and selective leaching. We have
patial distribution of $^{234}U/^{238}U$ to constrain flow at the INEEL. The contour map poin

Uranium in INEEL Groundwaters



ata set from INEEL document the presence of multiple end-members, defined b
position, concentration and geographic distribution. Isotopic modification of U re
ects of mixing and water rock interaction; differentiating between the two is chal
form linear arrays on a this type of plot. Mixing may be the dominant cause of
along two transects both of which start from the mouth of Birch Creek and go so
ud Lake area and southward toward the “central low”. Uranium data along thes
n roughly linear arrays. It is important to note that along these same transects,
ent pairs (e.g. Sr) do not form linear arrays suggesting that water/rock interactio
he systematics.

U and Sr Isotopics



d against $^{87}Sr/^{86}Sr$ show a good correlation with a corresponding decrease in both 8
ıtios. Sr isotopics are not affected by alpha recoil or selective leaching processes as a
This implies that dissolution or exchange dominate over these processes. Also note
isotopic composition of the basalt, by far the dominant rock type in the aquifer, implyi
re being modified through water/basalt interaction. A two end member model dissolvi
erbola) does not fit the data. The lower hyperbola, which is drawn to fit the data, requi
f reactant phases are lower than that of bulk basalt (40-100 vs~270).

Summary: The Short-lived Radionuclides

- Significant disequilibria exists among naturally occurring U- and Th-series nuclides in INEEL groundwater
- These disequilibria provide quantitative information pertinent to contaminant migration, including:
  - Preferential flow paths and residence time (ages)
  - In-situ retardation factors of contaminants (transport rate relative to fluid flow)
  - Removal rates of radionuclides from the fluid
  - Rock dissolution rates and their relation to flow paths and contaminant migration

Modeling Decay-Series Isotopes in Water-Rock Systems

- Model is based on mass balance: Concentration (C) of a radionuclde in groundwater is governed by the relationship:

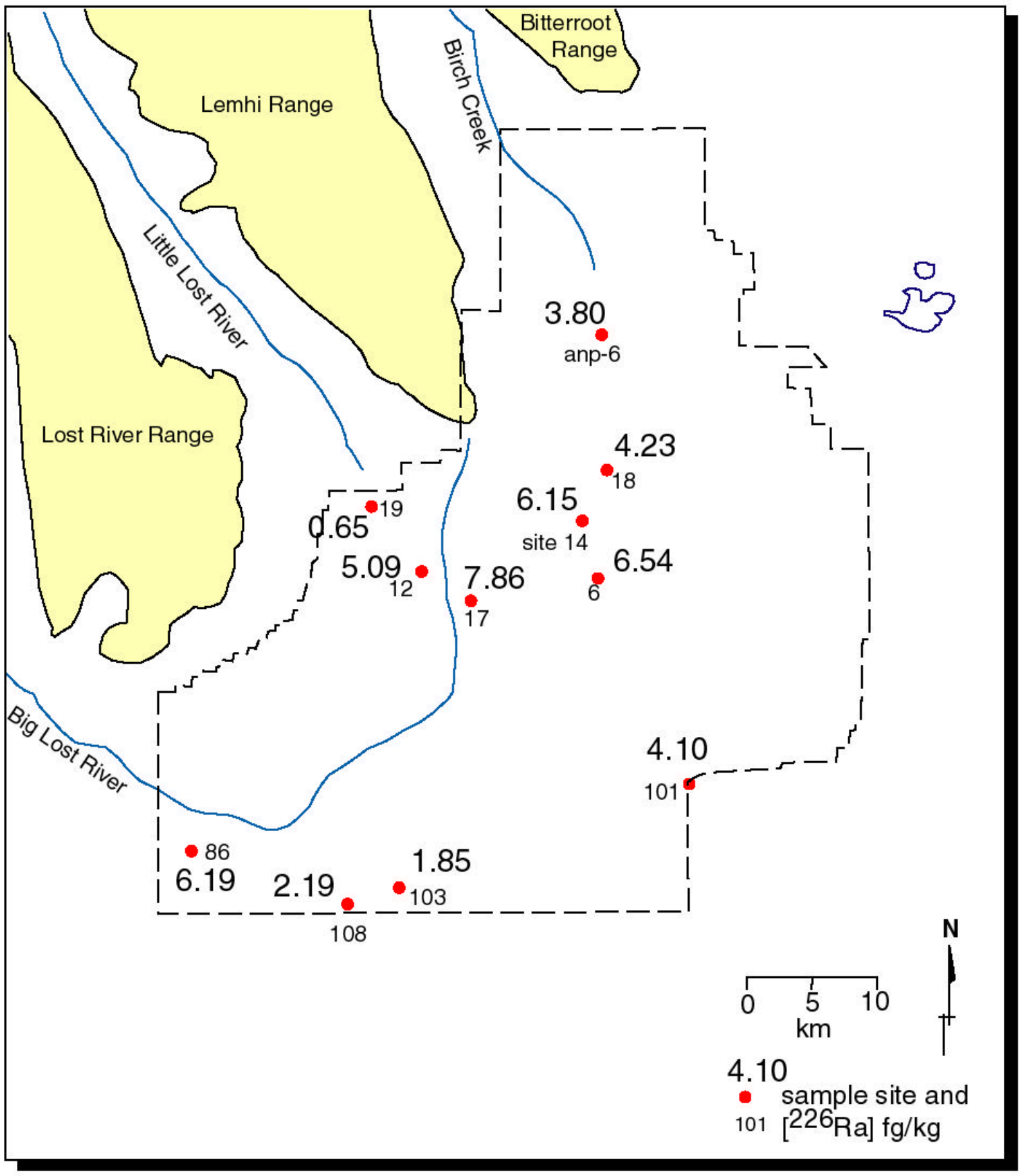
$$Q + P_d + P_r + \lambda' R_f' C' = k_p C + \lambda R_f C$$

Q = supply or removal rate by diffusion and advection
P_d = supply rate by dissolution
P_r = supply rate by alpha recoil
λ = decay constant
R_f = retardation factor
k_p = precipitation rate constant
Prime notation refers to the parent nuclide

- Model input
  - Measured acitvities in groundwater
    - U isotopes (^{238}U and ^{234}U)
    - Th isotopes (^{232}Th, ^{230}Th, ^{228}Th , and ^{234}Th)
    - Ra isotopes (^{226}Ra, ^{228}Ra, and ^{224}Ra)
  - Known values for the site:
    - ^{222}Rn activity in groundwater: 340±40 dpm/l (Orr et al., 1991)
    - ^{232}Th activity in rocks = 0.31±0.02 dpm/g (Knobel and Cecil, 1995)
    - $^{238}U/^{232}Th$ activity ratio in rocks = 0.90±0.06 (Knobel and Cecil, 1995)
- Model output
  - Fluid residence times and preferential flow paths.
  - Retardation factors of Ra, Th, and U isotopes.
  - Adsorption and desorption rates of Ra and Th.
  - Rock dissolution rates
  - Precipitation rates of Th, Ra and U

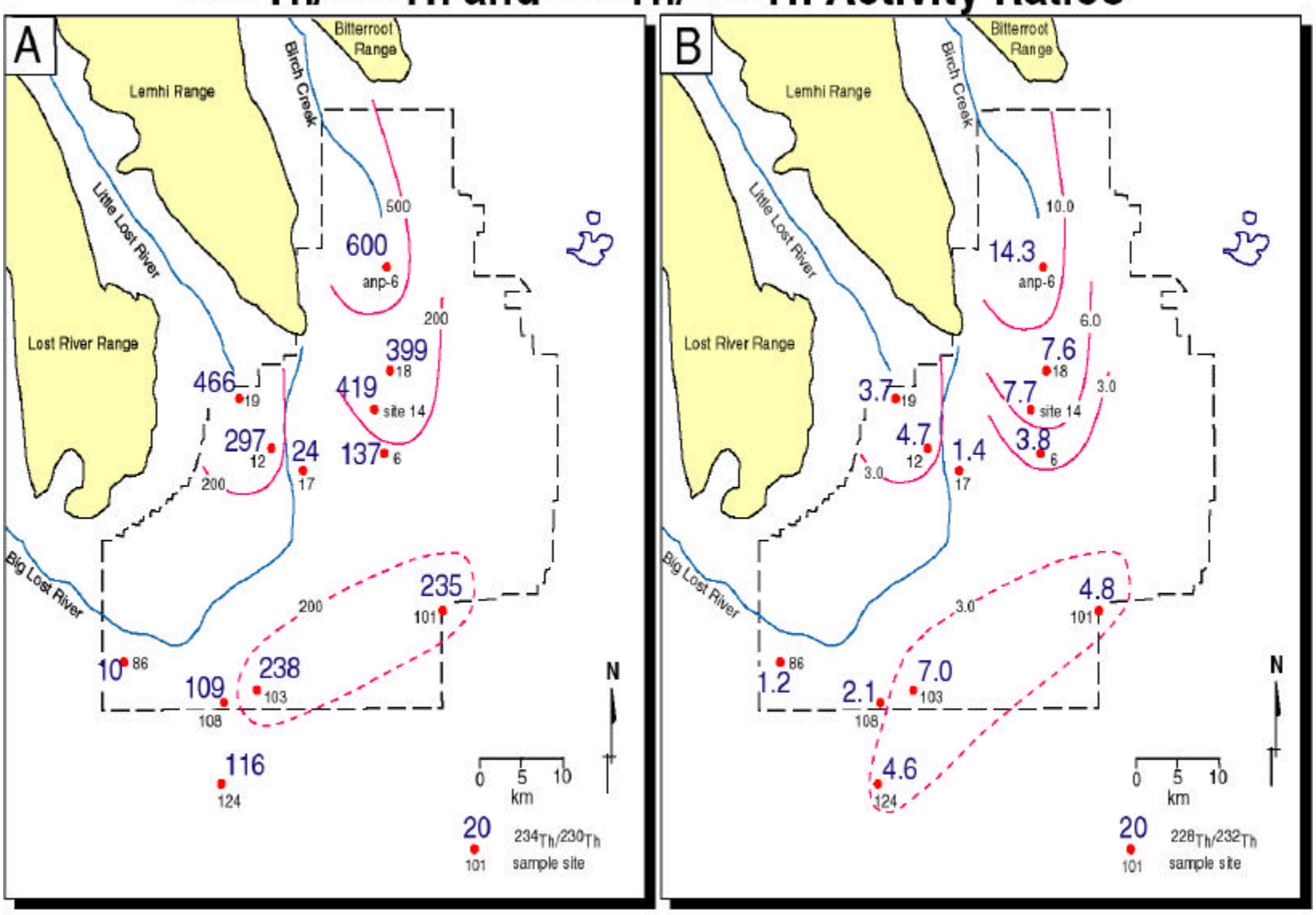
Quantitative Estimates of Contaminant Transport

- Fluid residence time:
  - range from ~1 year in the north to ~100 years in the central and southwestern parts of the INEEL
- In-situ retardation factors:
  - Th (and lanthanides): ~2 x 10^6
  - Ra (and Ba, Cs, Sr): ~2 x 10^4
  - U (and transuranics): ~1 x 10^3
- Precipitation rate constants:
  - Th (and lanthanides): 0.02 to 1.0 x10^3 y^{-1}
  - Ra (and Ba, Cs, Sr): 0.04 to 1.7 x 10^2 y^{-1}
  - U (and transuranics): 0.14 to 1.7 x10^{-1} y^{-1}
- Dissolution rates:
  - ~200mg/L/y in the north where in contact with “young” groundwater from Birch Creek and Little Lost River
  - ~50mg/L/y in the south where in contact with older (~100 y) groundwater



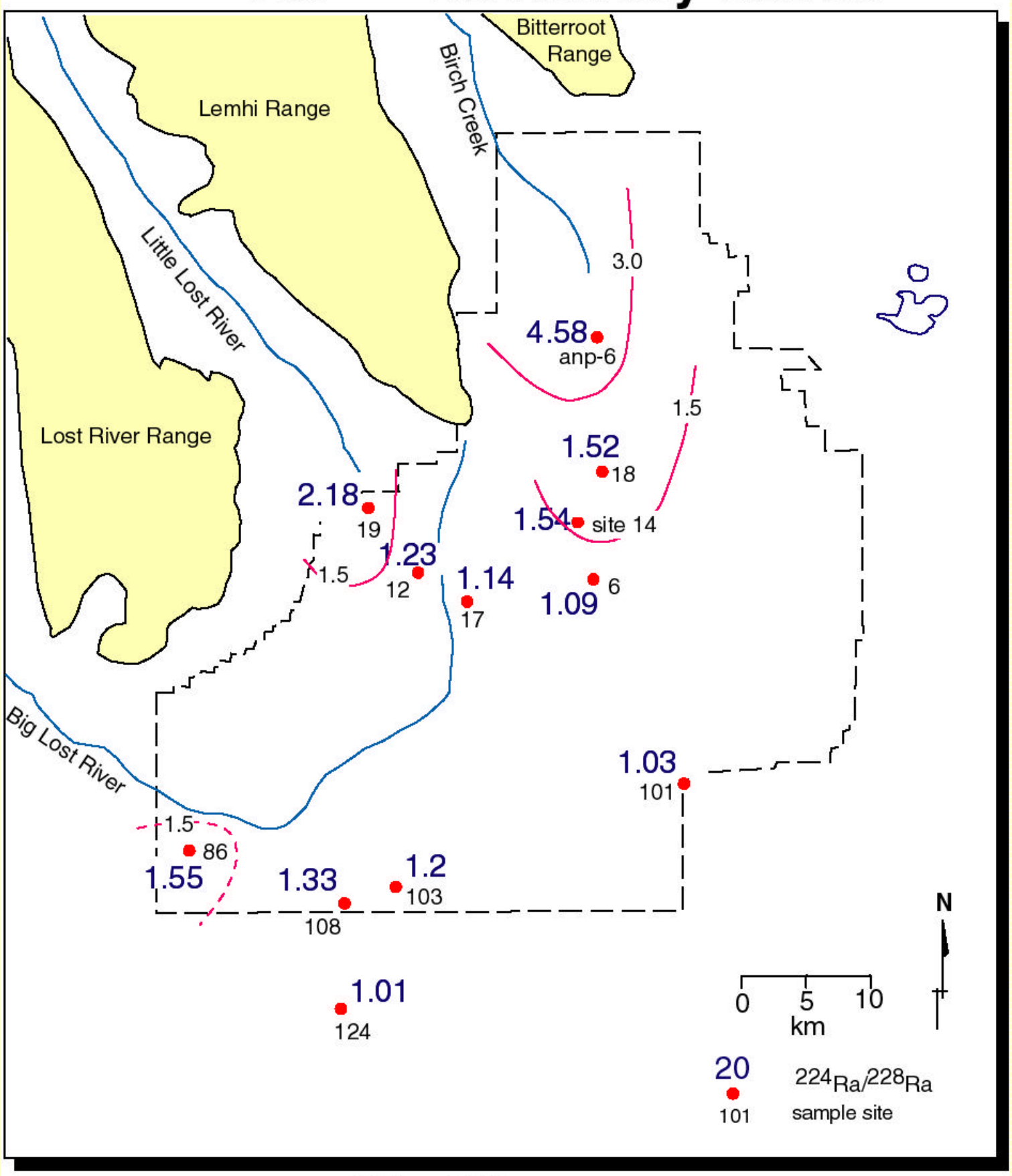
^{226}Ra concentrations range from 0.65 to 7.86 fg/kg. Recharge groundwater from Birch Creek and Little Lost River have relatively low concentrations of Ra. Groundwater nearest the areas with low ^{234}U/^{238}U ratios also have high concentrations of ^{226}Ra.

$^{234}Th/^{230}Th$ and $^{228}Th/^{232}Th$ Activity Ratios



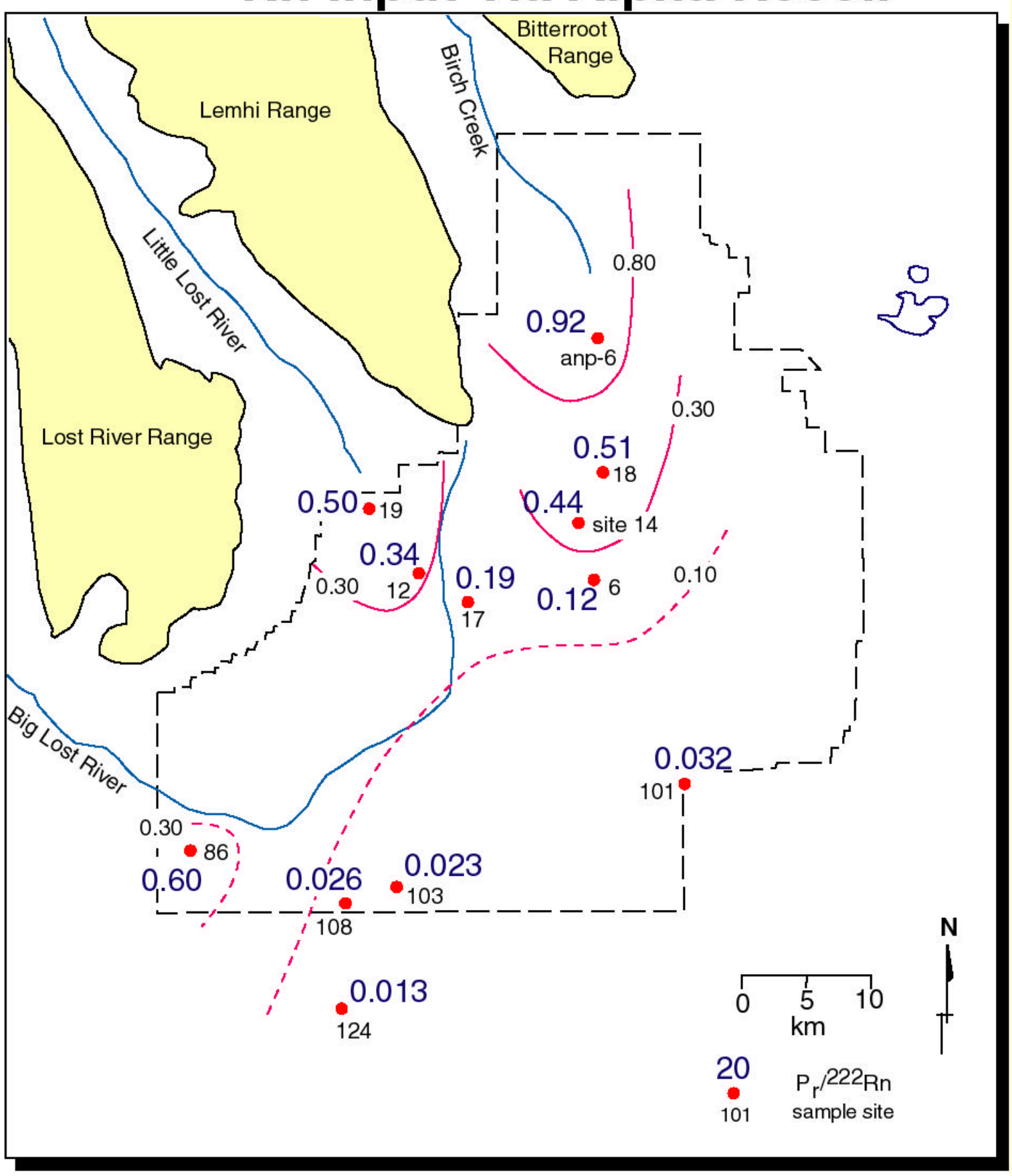
Southward decrease of (a) $^{234}Th/^{230}Th$ and (b) $^{228}Th/^{232}Th$ activity ratios along major flow paths.

$^{224}Ra/^{228}Ra$ Activity Ratios



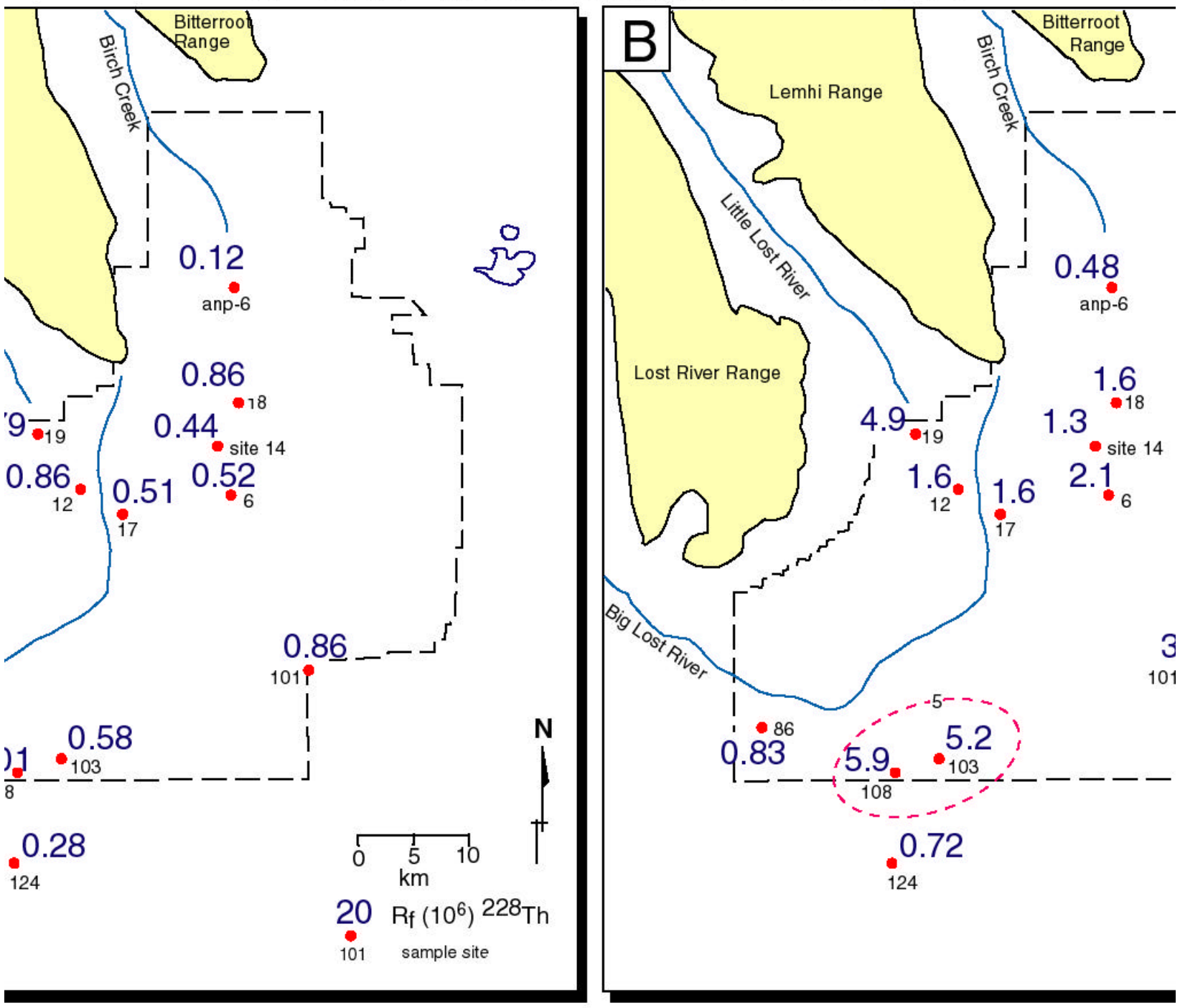
Southward decrease of $^{224}Ra/^{228}Ra$ activity ratios along major flow paths. High $^{224}Ra/^{228}Ra$ ratios are attributable to enhanced alpha-recoil – they are less affected by dissolution/precipitation due to the short half-lives of the Ra isotopes.

^{222}Rn Input Via Alpha Recoil



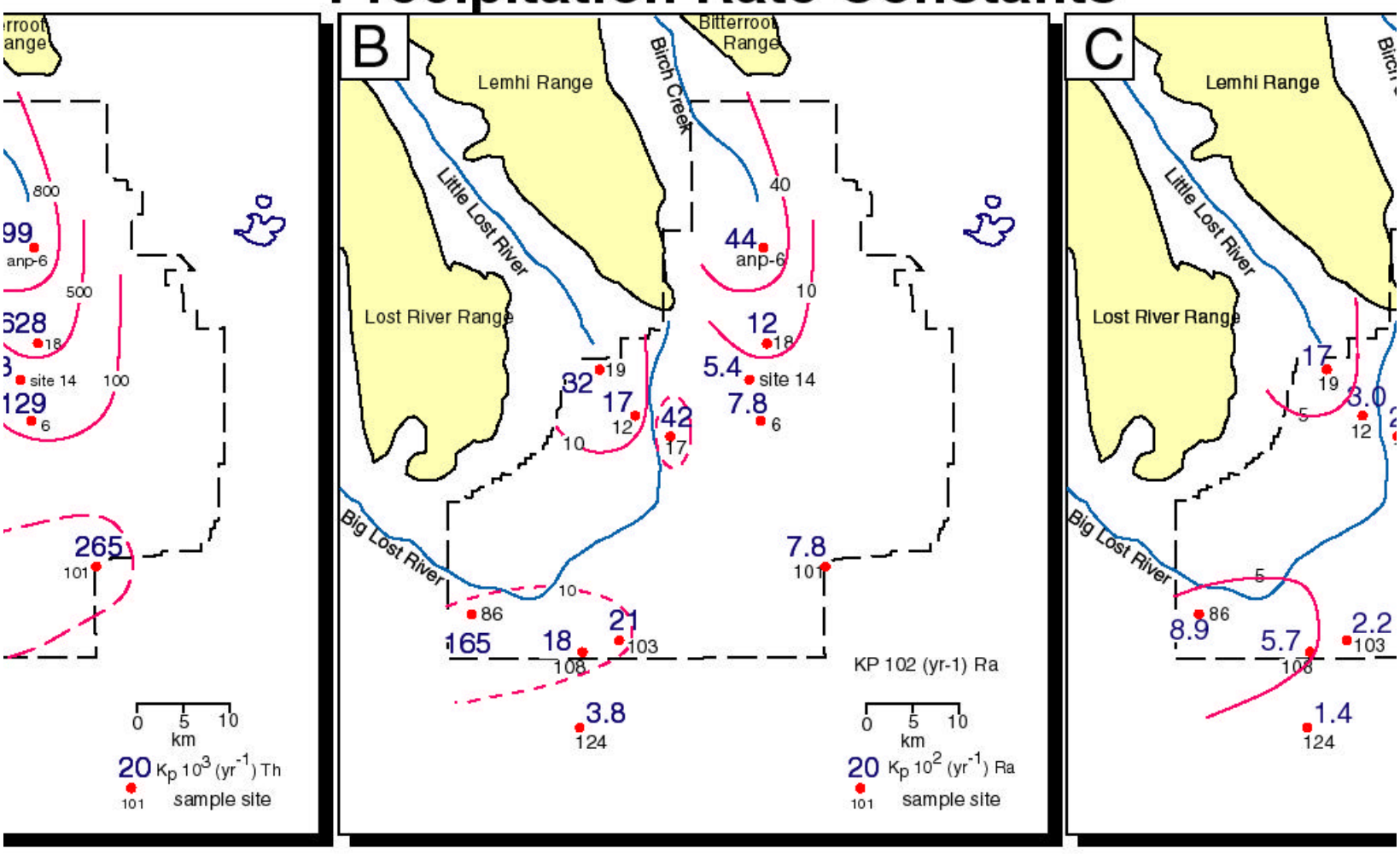
Southward decrease of P_r/Rn222 along major flow paths. This ratio reflects the input of ^{222}Rn to groundwater via alpha recoil relative to that from decay of ^{226}Ra in dissolved and sorbed pools of the aquifer system.

In-situ Retardation Factors



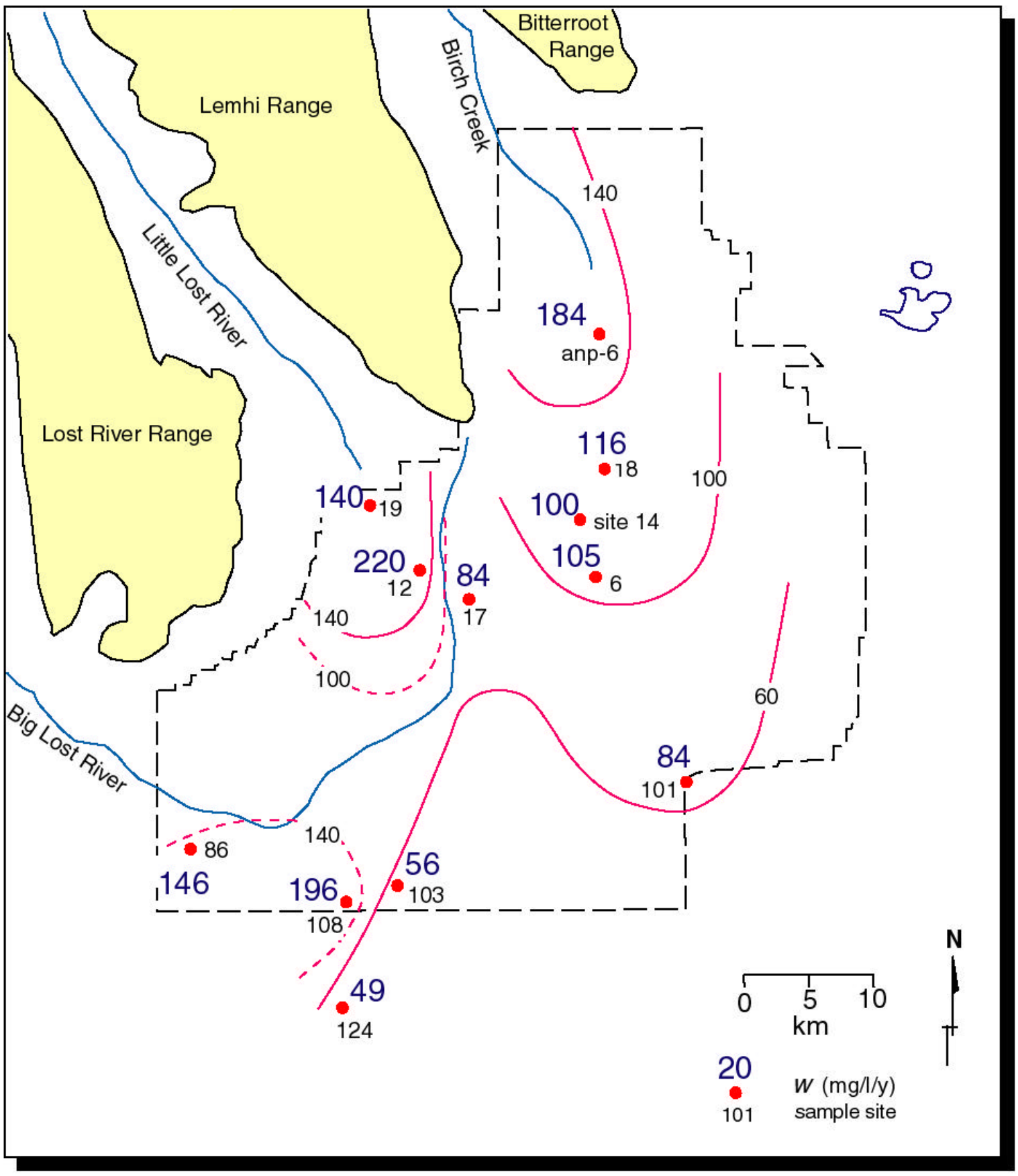
tardation factors (R*f*) of (a) ^{228}Th, (b) Ra (^{226}Ra, ^{228}Ra, and ^{224}Ra), an
tio of flow rate of fluid to that of dissolved radionuclides. The mean values of
±1.9) x 10^4 for Ra, and (0.9±0.3) x 10^3 for U. Because desorption of Th takes
and R*f* for ^{234}Th is ~0.7 times, that of ^{228}Th. All three Ra isotopes have t
ption rate constants are much greater than the decay constant of ^{224}Ra.

Precipitation Rate Constants



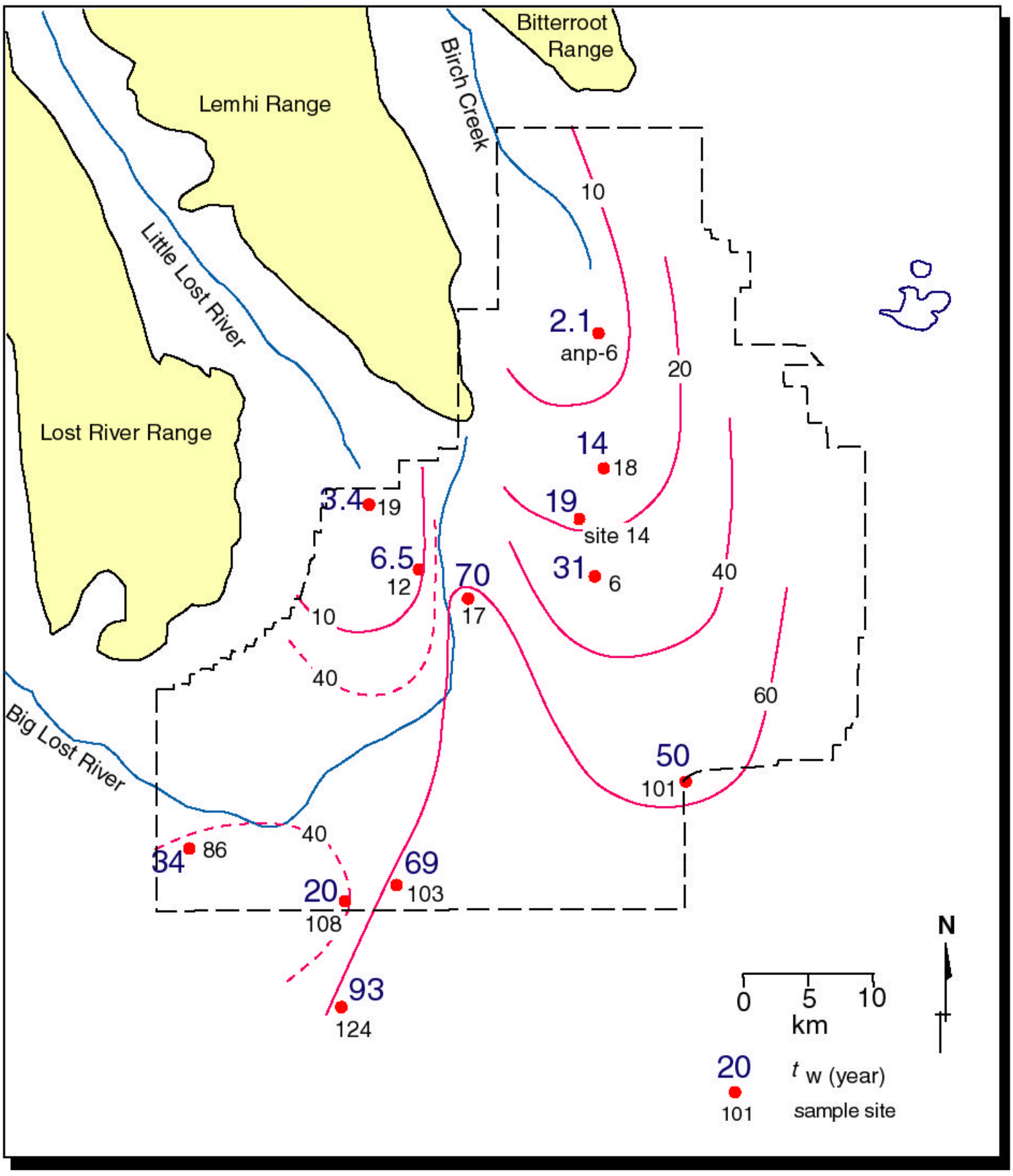
nstants (k_p) of (a) Th, (b) Ra, and (c) U showing that high precipitation rates occur chiefly southward along major flow paths. Precipitation of Th, Ra, and U takes 0.4–21 days for Th, 2

Rock Dissolution Rates



Southward decrease of rock dissolution rates (*w*) along major flow paths. High dissolution rates are usually accompanied by high precipitation rates, suggesting that enhanced rock weathering occurs in young groundwater regimes.

Groundwater Residence Times



Modeled groundwater residence times showing that the oldest waters occur in the central and southeastern parts of INEEL. The contours delineate major southward flow paths from the Birch Creek and Little Lost River recharge areas .

Plans for Summer 98/ Conclusions

- Second large-volume sampling trip in August
- Analysis of new water samples and rock samples
- Continued modeling
- Publications
- Currently evaluating this approach at Rock Flats, CO