

⁹⁹Tc, ²³⁶U, and ²³⁷Np in the Snake River Plain Aquifer at the Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho

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The Idaho National Engineering and Environmental Laboratory (INEEL) is located on the eastern Snake River Plain in southeastern Idaho; it is a multipurpose complex operated by the U.S. Department of Energy. Among its installations is the Idaho Chemical Processing Plant (ICPP), a facility designed principally to recover highly enriched uranium ($\geq 93\%$ ²³⁵U) from different nuclear fuel types used in naval propulsion, research, and test reactors. Starting in 1952 and continuing until 1984, low-level radioactive waste was discharged from the ICPP directly to the Snake River Plain aquifer by means of an injection well and seepage ponds. Over time, a suite of radionuclides have been measured in the aquifer including ³H, ³⁶Cl, ⁹⁰Sr, ¹³⁷Cs, ¹²⁹I, and Pu isotopes. Reported here are the first measurements of the long-lived radionuclides ⁹⁹Tc, ²³⁶U, and ²³⁷Np in the aquifer and their downgradient concentration changes during water transport through fractured basalt. Like ³⁶Cl, ⁹⁹Tc behaves conservatively during transport while ¹²⁹I, ²³⁶U, and ²³⁷Np indicate retardation.

Introduction

In 1983, the National Research Council published a report entitled "A Study of the Isolation System for Geological Disposal of Radioactive Wastes" (1). At that time, the four candidate geologic media for a high-level waste repository were (i) basalt, (ii) granite, (iii) salt, and (iv) tuff. Model calculations were used to predict the transport of radionuclides from a hypothetical breached repository to surface and groundwaters accessible to human populations and to predict the resulting radiation dose estimates for individuals using those waters. Hydrogeologic parameters for the modeling were chosen to reasonably represent the geographical locations under consideration for the repository at that time. As an example, Figure 1 shows the calculated relative radiation dose received by individuals, over time, from the release of selected radionuclides resulting from the dissolution of uranium fuel elements stored in basalt (1). Given a water travel time of 1000 yr, Figure 1 is also indicative

of first-arrival times of the radionuclides shown and, a posteriori, the effect of interaction (retardation) of the radionuclides in the subsurface. A conservative (noninteractive) behavior is predicted for ¹⁴C ($T_{1/2} = 5.73 \times 10^3$ yr) and ¹²⁹I ($T_{1/2} = 1.6 \times 10^7$ yr) in basalt over that for ⁹⁹Tc ($T_{1/2} = 3.05 \times 10^5$ yr) and ²³⁷Np ($T_{1/2} = 2.1 \times 10^6$ yr). While not shown, the behavior of U in basalts, under oxidizing conditions, is comparable to that of ²³⁷Np. The high relative dose received from ¹⁴C is due to its enhanced production from nitrogen impurities in the uranium fuel during the irradiation cycle [¹⁴N(n,p)¹⁴C], its predicted conservative behavior in the subsurface, and its uptake and retention in tissues following ingestion. Not considered in the repository study was the isotope ³⁶Cl, whose presence in irradiated nuclear fuels was first demonstrated in 1992 (2).

The degree of sorption of ionic species to mineral surfaces is operationally quantified by the retardation factor (RF). The RF is defined as the ratio of pore velocity of groundwater to the net velocity of transport of a dissolved contaminant, assuming local chemical equilibrium of the contaminant dissolved in the liquid and that sorbed (*I*). For species that behave conservatively in groundwater, RF = 1; for species sorbed to surfaces, RF > 1. The 'best-estimate' RFs used for calculating water transport of ⁹⁹Tc, ¹²⁹I, U, and ²³⁷Np in the basalt repository study were 5, 1, 50, and 100, respectively.

The geochemical parameters necessary for constructing transport models are principally obtained from laboratory experiments, but testing their validity under field conditions is seldom practical. Waste disposal practices at the INEEL have introduced a suite of radionuclides directly to the fractured basalts underlying the U.S. Department of Energy's Idaho National Engineering and Environmental Laboratory (INEEL), and their transport away from the site of introduction can be used to contrast their relative mobilities.

We report here the first measurements of ⁹⁹Tc, ²³⁶U ($T_{1/2} = 2.3 \times 10^7$ yr), and ²³⁷Np in the Snake River Plain aquifer resulting from radioactive waste discharges at the INEEL. Our principal interest was to derive an aquifer inventory for ⁹⁹Tc and, secondarily, to compare the distances that ⁹⁹Tc, ²³⁶U, and ²³⁷Np have been transported downgradient from their common point of introduction to those previously observed for ³⁶Cl and ¹²⁹I. The scope of our study did not include ancillary measurements necessary to evaluate complex questions of speciation as it effects the subsurface mobility of the radionuclides measured. Rather, the intent was to provide "first-order" comparisons of the relative rates of transport for ⁹⁹Tc, ¹²⁹I, ²³⁶U, and ²³⁷Np for contrast with those predicted in the waste repository study.

Study Area

The INEEL is one of the largest (~2300 km²) of the Department of Energy's nuclear complexes. It is situated on the eastern Snake River Plain (SRP) in southeastern Idaho (Figure 2), and facilities there use groundwater from the Snake River Plain aquifer as both process and potable water. For most of the eastern SRP, the subsurface is comprised of Quaternary to Tertiary age basalts of differing flow histories that are, in places, several thousand feet thick. Water in the aquifer is unconfined, and the tops of the basalt are highly fractured (effective porosity = 0.23; 3) leading to high hydraulic conductivities (4). Lindholm (4) estimated that between 200 and 300 million acre-ft [(2.5–3.7) × 10¹¹ m³] of water are held in the upper 170 m of the eastern SRP basalt, a volume comparable to that of Lake Erie (~5 × 10¹¹ m³). Nearly 70% of the groundwater discharge from the eastern SRP occurs

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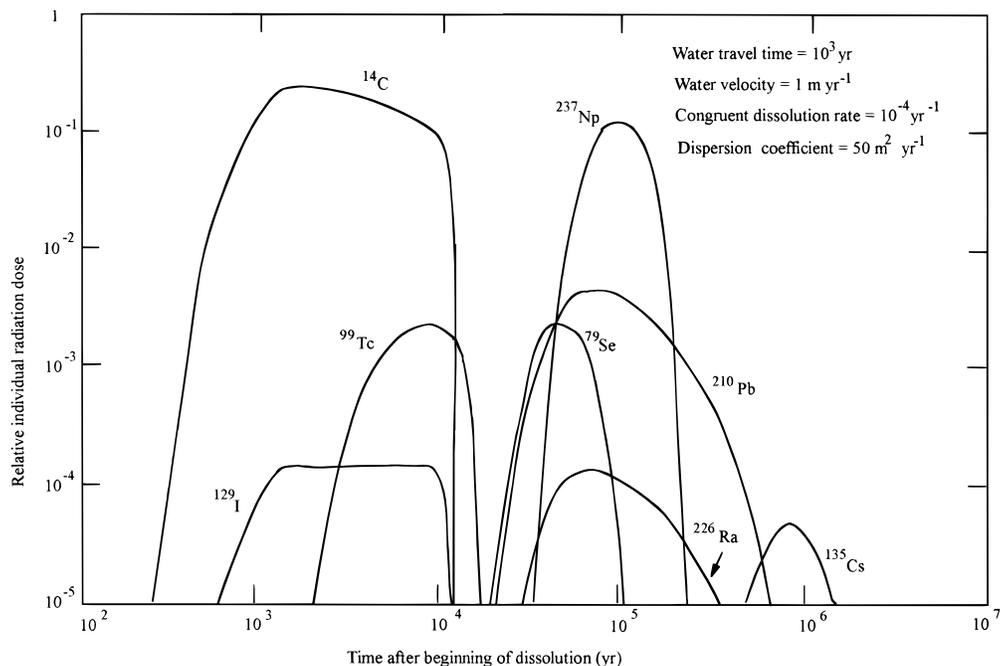


FIGURE 1. Calculated relative radiation dose received by individuals following release from a hypothetical repository located 1 km from point of groundwater use assuming constant, congruent dissolution rate of all radionuclides, e.g., the ratio of dissolution rates is proportional to concentration ratios. (Reproduced by permission of the National Academy Press).

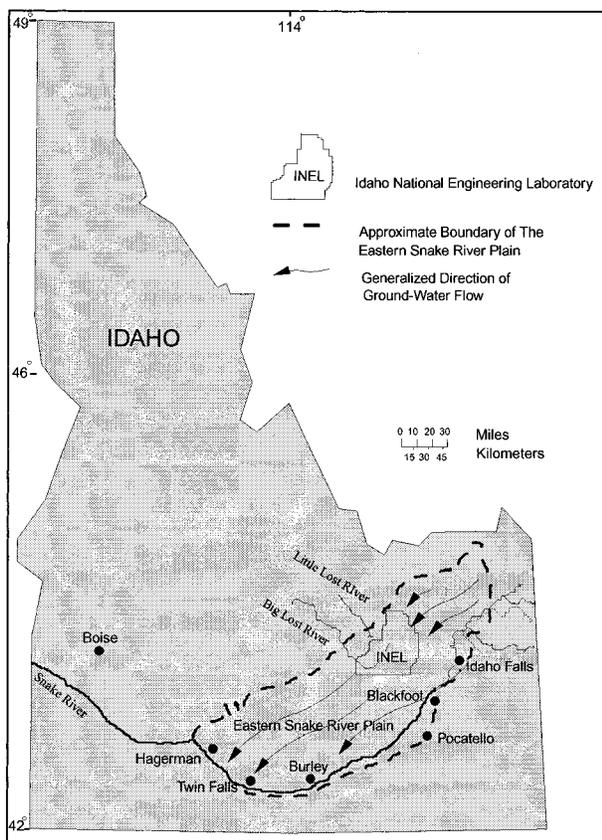


FIGURE 2. Location of the Idaho National Engineering and Environmental Laboratory, the eastern Snake River Plain, and regional groundwater flow lines.

from springs that flow to the Snake River between Twin Falls and Hagerman, ID (Figure 2; 4); the average groundwater discharge in 1993 was $144 \text{ m}^3 \text{ s}^{-1}$ (comparable to that of 1917; 5). Assuming steady state, the calculated residence time, $\tau_{(r)}$, of water within the eastern SRP is between 55 and

82 yr ($\tau_{(r)} = \text{reservoir volume} \div \text{discharge rate}$), although water travel times within different parts of the aquifer from recharge to discharge are estimated to range between 12 and 350 yr (5).

The locations of selected facilities at the INEEL are shown in Figure 3. Groundwater flow is from the northeast to the southwest, and depth to water ranges from $\sim 60 \text{ m}$ at the northern site boundary to $\sim 275 \text{ m}$ at the southern site boundary. The average hydraulic gradient across the INEEL is $\sim 2 \text{ m km}^{-1}$ (6), and water travel times between the ICPP and the southern site boundary have recently been estimated at 2 m d^{-1} (7). A more detailed description of the geohydrological setting of the INEEL and its operational history can be found in ref 6–8 and references therein.

For more than 30 years (1952–1984), low-level radioactive waste was discharged directly into the Snake River Plain aquifer from the ICPP (Figure 3) through an $\sim 182 \text{ m}$ deep injection well. Since 1984, waste has been discharged to disposal ponds (Figure 3) where liquids must infiltrate $\sim 140 \text{ m}$ of vadose zone (unconsolidated sedimentary rock/alluvium and basalt) before reaching the aquifer (6). During the years 1988–1994, radioactivity discharges to the disposal ponds decreased to $<1\%$ of those which occurred in 1985, and no discharges occurred for the years 1989, 1993, and 1994 (6). From 1959 through 1976, the Test Reactor Area (TRA) discharged low-level radioactive waste to unlined infiltration and evaporation ponds, and from 1965 to 1982, a disposal well was also in operation (injection depth $>400 \text{ m}$; Figure 3). However, the type and amounts of radioactivity discharged from the TRA were distinctly different than those at the ICPP. Prior to 1980, 70% of the discharged radioactivity at the TRA was comprised of activation and fission products with half-lives of several weeks or less, and virtually no transuranic radionuclides (or ^{129}I) were contained in the waste (8, 9). Moreover, between 1976 and 1993, two lined evaporation ponds replaced the radioactive waste-infiltration ponds that effectively prevented radioactivity from entering the vadose zone after that time. Consequently, the radionuclides discussed here most certainly were introduced into the aquifer via the ICPP disposal well between 1952 and 1984.

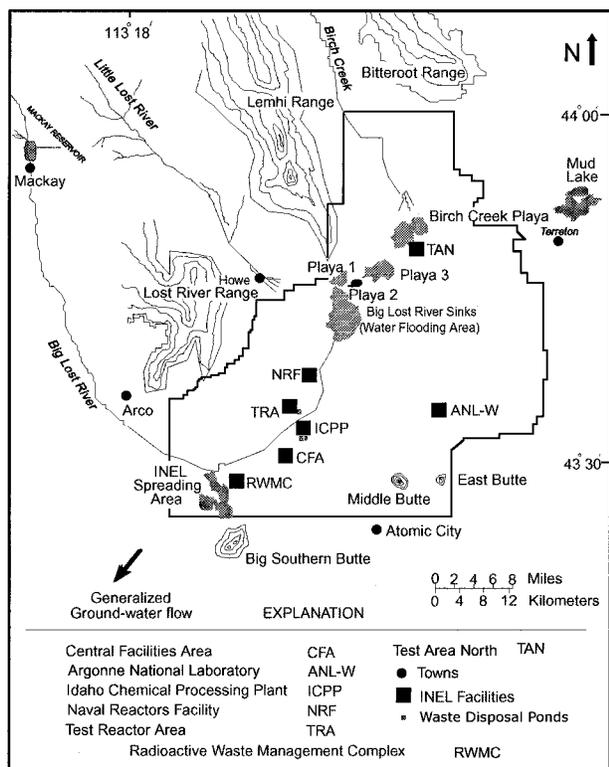


FIGURE 3. Location of selected facilities at the Idaho National Engineering and Environmental Laboratory. Water from the Big Lost River is diverted to spreading areas to prevent incursion into INEEL facilities.

Of the radionuclides detected in monitoring wells downgradient from the ICPP and TRA, ^3H ($T_{1/2} = 12.3$ yr) is present in the highest activity. It is a product of "ternary fission" in which three fission products arise during the fission process, one of which is ^3H ; the yield is ~ 1 ^3H atom in 10^4 fissions (10). Between 1952 and 1988, approximately 1.2 PBq (3×10^4 Ci) of ^3H was released in wastewater at the ICPP and TRA. Because of radioactive decay, only 0.38 PBq of ^3H was estimated to remain in the Snake River Plain aquifer by 1988 (11). In the early 1990s, site-derived ^{36}Cl (produced by neutron activation of stable chloride) was measured in the Snake River Plain aquifer (12), and its areal distribution was shown to mimic that of ^3H . The area occupied by the ^{36}Cl plume was ~ 240 km 2 and contained 19 GBq (~ 0.5 Ci) of ^{36}Cl (13). The distribution of ^{129}I in the aquifer has also been determined (14), and the inventory of fission product-derived ^{129}I in the early 1990s over a plume area comparable to that of ^{36}Cl is estimated at 4.4 GBq (~ 0.12 Ci). The total number of atoms of ^3H , ^{36}Cl , and ^{129}I represented by these inventories is $\sim 6 \times 10^{23}$, $\sim 2 \times 10^{23}$, and $\sim 3 \times 10^{24}$, respectively.

Sampling and Analysis

Well waters were collected following standard U.S. Geological Survey (USGS) procedures (15), and special precautions were taken to prevent contamination by resuspended surface soils. Quantitative measurements of ^{99}Tc concentrations were made using isotope dilution, thermal ionization mass spectrometry (TIMS), the technique of choice in measuring low levels of long-lived radionuclides. When sophisticated purification procedures are employed that effectively remove trace interferences, advanced state-of-the-art TIMS techniques can accurately measure as few as a million atoms of U and Np. However, ^{99}Tc measurements require higher atom abundances, even where near-point sources of ^{99}Tc can be prepared for good focusing during the initial ionization stages

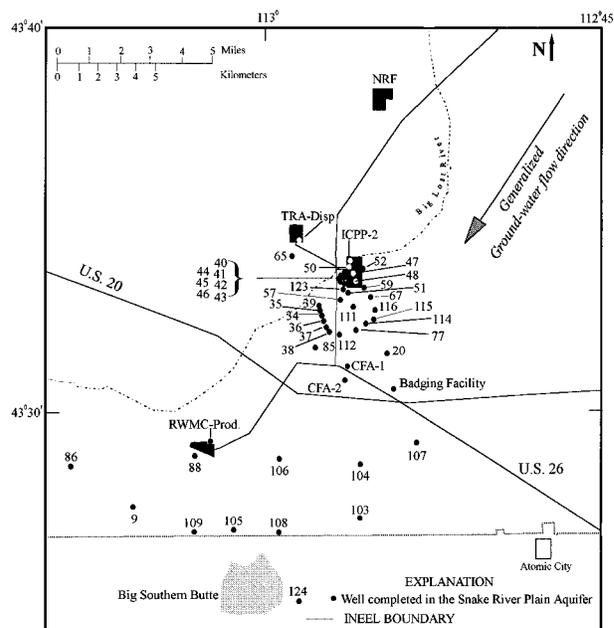


FIGURE 4. Location of groundwater monitoring wells at the Idaho National Engineering and Environmental Laboratory (INEEL) that were sampled for radionuclide measurements. Well 50 draws water from a perched water zone.

of analysis (16). Even so, ^{99}Tc TIMS measurements are an order of magnitude more sensitive in determining ^{99}Tc than are radiometric, β -particle counting techniques. For example, the straightforward determination of 0.01 ng of ^{99}Tc in a 1-L water sample using TIMS techniques represents only 6 mBq (0.006 disintegrations s^{-1}), an activity level requiring very long counting times and exceptionally low background-counting equipment.

Because the analytical protocols used for isolating, purifying, and measuring ^{99}Tc in environmental samples have recently been described (17), as have those for the actinide elements discussed here (18, 19), they are not repeated. It is important to note, however, that calibrated, high-purity ^{97}Tc was used as the yield determinant for quantifying ^{99}Tc recoveries and standardized ^{233}U and ^{236}Np were used, respectively, as yield determinants for U isotopic (^{235}U , ^{236}U) and ^{237}Np quantification. Samples for transuranic analysis were acidified to pH 1 (in their original sampling bottles), yield determinants were added and, over a 3-week period, intermittently mixed to ensure desorption from the glass container walls (20).

Results and Discussion

Locations of the INEEL monitoring wells sampled are shown in Figure 4, and measured ^{99}Tc concentrations and activities are listed in Table 1. In general, the wells are listed in the downgradient direction from the ICPP and TRA. Not all of the well waters shown were collected in the same years. The majority were collected in 1991–1992; wells 109, 9, 103, 104, 105, 106, 108, 124, the Badging Facility, and CFA-1/CFA-2 were collected in 1994. On the assumption that ^{99}Tc and ^{36}Cl would behave similarly in the subsurface, viz., conservatively, ^{36}Cl was measured in the 1994 collections for comparison to their 1991–92 values. Our intention was to use the 1991–1992 and 1994 ^{36}Cl ratios to adjust the 1994 ^{99}Tc concentrations to 1991–1992 values and then compare concentrations of different isotopes in selected wells for this earlier period. As a new monitoring well, 124 was only available for sampling in 1994.

TABLE 1. Technetium-99 in Water Samples Collected from the Snake River Plain Aquifer, Idaho

| well identifier | ⁹⁹ Tc (ngL ⁻¹) | ⁹⁹ Tc (mBqL ⁻¹) ^a | well identifier | ⁹⁹ Tc (ngL ⁻¹) | ⁹⁹ Tc (mBqL ⁻¹) ^a |
|-----------------------|---------------------------------------|---|------------------|---------------------------------------|---|
| TRA-disp ^b | ≤0.0007 | ≤0.0005 | 59 | 0.092 ± 0.002 | 58 ± 1 |
| ICPP-2 | 0.0051 ± 0.0003 ^c | 3 ± 0.2 | 57 | 0.776 ± 0.014 | 486 ± 9 |
| 65 | 0.043 ± 0.010 | 27 ± 6 | 67 ^b | 1.94 ± 0.17 | 1210 ± 105 |
| 50 | 3.29 ± 0.025 | 2060 ± 16 | 111 | 1.34 ± 0.006 | 840 ± 4 |
| 40 | 0.133 ± 0.002 | 83 ± 1 | 39 ^b | 0.023 ± 0.001 | 14 ± 1 |
| 41 | 0.115 ± 0.003 | 72 ± 2 | 35 | 0.150 ± 0.004 | 94 ± 3 |
| 42 | 0.020 ± 0.0003 | 12 ± 1 | 34 | 0.061 ± 0.004 | 38 ± 3 |
| 43 ^b | 0.110 ± 0.008 | 69 ± 5 | 36 | 0.318 ± 0.006 | 199 ± 4 |
| 44 ^b | 0.0014 ± 0.0001 | 0.85 ± 0.1 | 37 ^b | 0.426 ± 0.001 | 267 ± 1 |
| 45 | 0.078 ± 0.006 | 48 ± 4 | 38 | 0.643 ± 0.013 | 402 ± 1 |
| 46 | 0.256 ± 0.023 | 160 ± 14 | 116 ^b | 0.871 ± 0.16 | 542 ± 100 |
| 47 | 0.409 ± 0.008 | 256 ± 5 | 114 ^b | 0.532 ± 0.014 | 333 ± 9 |
| 52 | 0.106 ± 0.044 | 66 ± 28 | 115 ^b | 1.08 ± 0.15 | 676 ± 93 |
| 48 | 0.165 ± 0.012 | 103 ± 7 | 77 | 0.491 ± 0.012 | 307 ± 8 |
| 51 ^b | 0.136 ± 0.023 | 85 ± 14 | 112 ^b | 0.737 ± 0.023 | 462 ± 14 |
| 85 ^b | 0.542 ± 0.045 | 339 ± 28 | RWMC | 0.0025 ± 0.0005 | 2 ± 0.3 |
| 20 | 0.018 ± 0.003 | 11 ± 2 | 106 ^b | 0.0451 ± 0.002 | 28 ± 1 |
| CFA-1 ^b | 0.089 ± 0.012 | 56 ± 7 | 104 ^b | 0.0069 ± 0.002 | 4 ± 0.1 |
| CFA-2 ^b | 0.202 ± 0.028 | 126 ± 18 | 9 ^b | ≤0.0002 | ≤0.0001 |
| badge fac. | ≤0.0002 | ≤0.0001 | 109 | ≤0.0003 | ≤0.0002 |
| 86 | ≤0.0002 | ≤0.0001 | 105 ^b | 0.0036 ± 0.0008 | 2 ± 0.5 |
| 88 | ≤0.0002 | ≤0.0001 | 108 ^b | 0.0014 ± 0.0004 | 0.9 ± 0.3 |
| 103 | ≤0.0002 | ≤0.0001 | 124 | 0.0026 ± 0.0002 | 1.6 ± 0.1 |

^a mBq = millibecquerel; 1 mBq = 0.001 dis sec⁻¹. ^b Represents mean and standard deviation of two or more analyses. ^c Uncertainties at 67% confidence interval.

TABLE 2. Comparison of ³⁶Cl Concentrations in Selected Wells at the INEEL Collected during 1991–1992 and 1994^a

| well identifier | 1991–1992 | 1994 |
|--------------------------|---------------------|---------------|
| CFA-1/CFA-2 ^b | 80 ± 4 ^c | 70 ± 2 |
| badging facility | 0.050 ± 0.003 | 0.052 ± 0.001 |
| 9 | 0.11 ± 0.01 | 0.14 ± 0.03 |
| 109 | 0.040 ± 0.002 | 0.56 ± 0.01 |
| 103 | 0.039 ± 0.002 | 0.026 ± 0.003 |
| 104 | 5.7 ± 0.1 | 5.9 ± 0.2 |
| 105 | 0.76 ± 0.03 | 1.22 ± 0.02 |
| 106 | 7.0 ± 0.2 | 6.8 ± 0.2 |
| 108 | 0.55 ± 0.02 | 0.32 ± 0.03 |
| 107 | 0.011 ± 0.001 | 0.013 ± 0.001 |
| 124 | | 1.00 ± 0.03 |

^a ³⁶Cl concentrations are given in units of 10¹⁰ atoms L⁻¹. Uncertainties are propagated at the 67% confidence interval (1σ). ^b Values measured at these two wells in 1994 were virtually identical; only CFA-1 was measured in 1991–1992. ^c Read as (80 ± 4) × 10¹⁰ atoms L⁻¹. Results represent the analysis of a single sample.

The ³⁶Cl atom concentrations for the two time periods are listed in Table 2. Significant changes occurred at wells 109, 103, 105, and 108; ³⁶Cl concentrations at wells CFA-1/CFA-2 changed by less than 15%. There was an increase in the ³⁶Cl concentrations at well 109 in the intervening ~3 yr period, but because the measured ⁹⁹Tc concentration in 1994 was ≤0.0003 ng L⁻¹, concentrations at this well in 1991–1992 would presumably have been even lower as would those for well 103. For well 105, the calculated 1991–1992 ⁹⁹Tc concentration is 0.0022 ± 0.0005 ng L⁻¹ [(0.0036 ± 0.0008) × (0.76/1.22)], a decrease of some 60% from the measured 1994 value. Similarly, the calculated 1991–1992 ⁹⁹Tc concentration at well 108 increases to 0.0024 ± 0.0006 ng L⁻¹.

Quality assurance for the ⁹⁹Tc measurements was monitored by analyzing blind replicates of selected wells (20, 38, 57, 116, ICPP-2) over the course of the research. With the exception of a single duplicate from ICPP-2, which had a low ⁹⁹Tc concentration (Table 1), all analyses overlapped at the 67% (1σ) confidence interval, and the duplicate for ICPP-2 did overlap at the 95% confidence interval. Process blanks (n = 24) averaged 0.0044 ± 0.0060 ngL⁻¹.

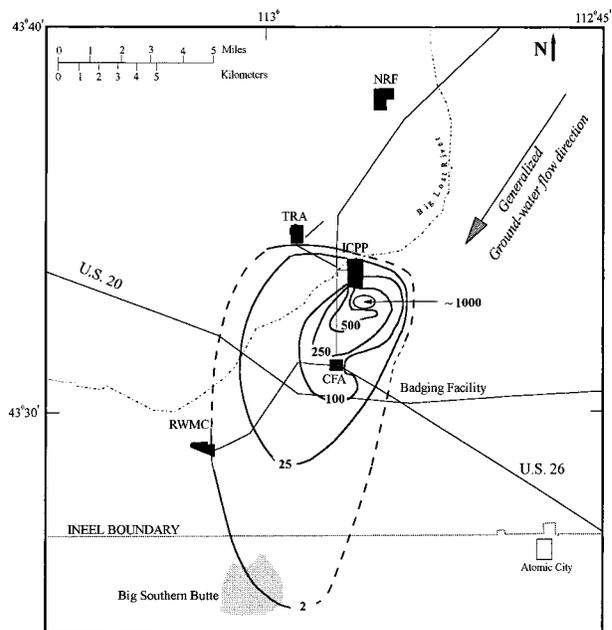


FIGURE 5. Isopleths of ⁹⁹Tc (mBq L⁻¹) in the Snake River Plain aquifer. The total plume area is 136 km² (53 mi²) and contains 554 GBq (~15 Ci) of ⁹⁹Tc. The dashed line for the 2 mBq L⁻¹ contour is intended to indicate uncertainty in its exact position because of the number of values used in its construction. The inventory and plume area are for the period 1991–1992.

Inventory of ⁹⁹Tc in the Snake River Plain Aquifer. To estimate the site-derived inventory of ⁹⁹Tc in waters down-gradient from the ICPP, we plotted the data of Table 1 to determine the areal distribution of ⁹⁹Tc. The activity at well 50 was excluded because this well samples perched water and not aquifer water. Figure 5 shows this distribution and broadly delineates isopleths of ⁹⁹Tc activity. The inventory is calculated as the product of the area within an isopleth (m²), the depth of contaminated water (m), the effective basalt porosity (0.23, unitless), and the ⁹⁹Tc activity (mBq m⁻³). The latter is taken as the mean activity between isopleths, e.g.,

TABLE 3. Uranium and Neptunium Atom Concentrations and Ratios in Selected Monitoring Wells at the INEEL

| well identifier | $^{235}\text{U}/^{238}\text{U}^a$ (atom/atom) | ^{236}U (atoms L^{-1}) | ^{237}Np (atoms L^{-1}) |
|-----------------|--|--|---|
| 65 | 0.007269 ± 0.000044 | $1.39 \pm 0.38 (10^8)^b$ | $5.65 \pm 0.80 (10^5)^c$ |
| 45 | 0.007394 ± 0.000044 | $9.91 \pm 0.22 (10^{10})$ | $3.61 \pm 0.08 (10^8)$ |
| 48 | 0.007987 ± 0.000048 | $1.94 \pm 0.04 (10^{11})$ | $7.67 \pm 0.17 (10^8)$ |
| 123 | 0.007984 ± 0.000018 | $2.65 \pm 0.04 (10^{11})$ | $1.09 \pm 0.04 (10^9)$ |
| 57 | 0.007693 ± 0.000046 | $1.94 \pm 0.04 (10^{11})$ | $9.19 \pm 0.21 (10^8)$ |
| 112 | 0.007602 ± 0.000046 | $2.02 \pm 0.05 (10^{11})$ | $3.03 \pm 0.08 (10^8)$ |
| CFA-1 | 0.007320 ± 0.000044 | $4.58 \pm 0.15 (10^9)$ | $<3 (10^5)$ |
| 106 | 0.007254 ± 0.000044 | $2.05 \pm 0.30 (10^8)$ | $<6 (10^5)$ |

^a The $^{235}\text{U}/^{238}\text{U}$ atom ratio in natural uranium is 0.007253 (25). ^b Read as $(1.39 \pm 0.38) \times 10^8$. ^c Propagated uncertainties at 1σ . Results represent the analysis of a single sample.

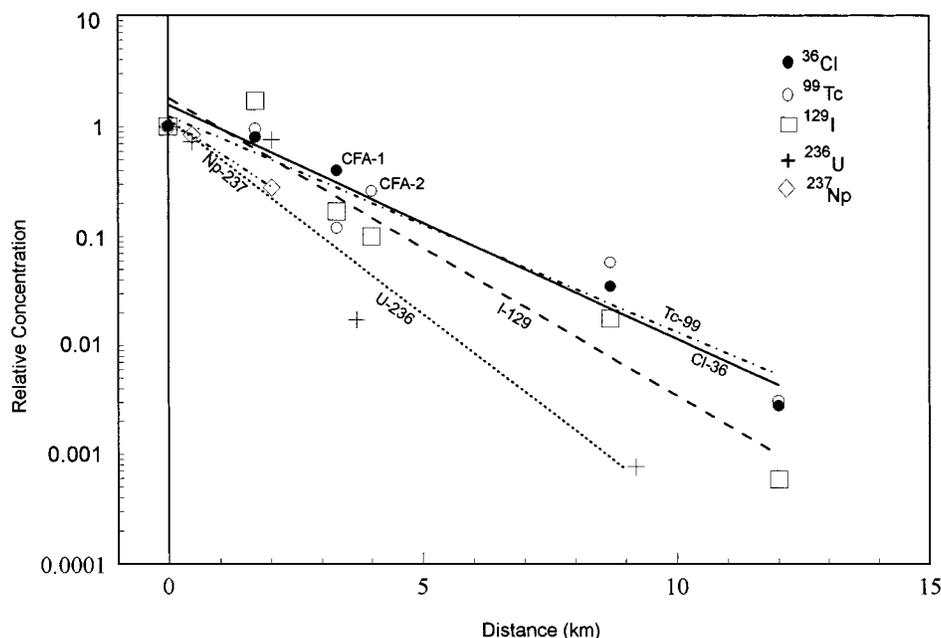


FIGURE 6. Decrease in relative concentrations of selected radionuclides in the Snake River Plain aquifer with distance from the Idaho Chemical Processing Plant. For ^{36}Cl , ^{99}Tc , and ^{129}I , the values are normalized to their concentrations in well 57 (Figure 4); for ^{236}U and ^{237}Np , the reference well is 123.

the area between the 25 and 100 mBq L^{-1} isopleths (Figure 5) is assigned a value of 62.5 mBq L^{-1} . We chose 50 m as the depth of contaminated water since this depth closely approximates the depth of waste introduction from the ICPP to the aquifer (14) and because in balancing ^3H subsurface discharge estimates and ^3H aquifer inventories (13), a depth interval of 50 m produced concordant results.

We estimate the total area occupied by the ^{99}Tc plume at 136 km^2 (53 mi^2) and the ^{99}Tc inventory within the plume at some 554 GBq (~ 15 Ci). The total number of ^{99}Tc atoms in the plume is therefore 5.4×10^{24} , a value slightly larger than that of the ^{129}I inventory ($\sim 3 \times 10^{24}$ atoms) discussed earlier. Because ^{99}Tc has never been reported in liquid (or airborne) effluent releases from the ICPP (6), it is not possible to compare our plume inventory with estimated ^{99}Tc discharges to the aquifer. However, such estimates have been made for ^{129}I . Through 1990, between 21 and 32 GBq of ^{129}I is believed to have been discharged directly to the aquifer (9), representing the input of between $(1.5 \text{ and } 3.2) \times 10^{25}$ atoms of ^{129}I . Therefore, at best, the ^{129}I plume inventory can account for only 10–20% of this estimated discharge, suggesting that a substantial fraction of the ^{129}I is retained in the basalt rock and sedimentary deposits that constitute the aquifer near the ICPP.

U Isotopes and ^{237}Np in the Snake River Plain Aquifer. The results of uranium and ^{237}Np atom concentrations and

ratios in selected wells at the INEEL are shown in Table 3. Uranium-236 arises from thermal neutron capture in ^{235}U ; thermal neutron capture in ^{236}U produces ^{237}U ($T_{1/2} = 6.75$ d), which then decays by β -particle emission to ^{237}Np (19). In highly enriched uranium fuels ($\sim 93\%$ ^{235}U), substantial amounts of these radionuclides can be produced especially with sustained irradiation times (high fuel burnup).

The deviation of the $^{235}\text{U}/^{238}\text{U}$ atom ratios for wells 45 through CFA-1 from that expected in natural uranium (Table 3) and the presence of ^{236}U in all wells measured confirm the discharge of small amounts of enriched uranium from the ICPP to the aquifer. Neptunium-237 is measurable in six of the eight wells sampled but fell below our detection limit at wells CFA-1 and 106. The sample size taken for U and ^{237}Np analysis was 1 L, and it is probable that with larger sample sizes (~ 10 L) ^{237}Np would also have been detected in wells CFA-1 and 106.

Relative Mobility of ^{36}Cl , ^{99}Tc , ^{129}I , ^{236}U , and ^{237}Np . To determine the relative mobilities of the radionuclides reported here, we normalized individual radionuclide activities in wells near the ICPP to those at a distance. In the case of ^{36}Cl , ^{99}Tc , and ^{129}I , downgradient concentrations were normalized to their concentration in well 57. For ^{236}U and ^{237}Np , downgradient concentrations were normalized to well 123 (Figure 4) because 1991–1992 waters from well 57 were exhausted in analyses of ^{99}Tc and ^{129}I . Figure 6 shows a best fit,

semilogarithmic plot of these normalizations for each radionuclide. The close correspondence in the decrease of ^{36}Cl and ^{99}Tc with distance from the ICPP argues that ^{99}Tc , like ^{36}Cl , behaves conservatively in the fractured basalt and that concentration decreases observed occur only as a result of dilution and dispersion. Iodine-129 is attenuated and ^{237}Np and ^{238}U more so. Consistent with the repository study, there appears to be no retention differences between ^{237}Np and ^{238}U , although the paucity of ^{237}Np data requires confirmation of this observation through the analysis of a larger number of wells. In contrast, where the repository study predicted a greater mobility for ^{129}I in basalts over that of ^{99}Tc (Figure 1), our measured data shows the opposite.

Could the relationships shown in Figure 6 arise simply from variable discharge rates over time for the radionuclides shown? None of the radionuclides discussed here were routinely monitored in the low-level waste streams discharged from the ICPP. Therefore we cannot, ex cathedra, discount this possibility. However, it is reasonable to assume that while the absolute amounts of radioactivity discharged to the aquifer and waste disposal ponds most certainly varied over time, the ratios of radionuclides in the discharges may well have shown constancy. The rationale for such an assumption relates to the fuel processing protocols of the ICPP. Because of national security concerns, facility operations were likely focused on process efficiency to recover and purify unspent ^{235}U (21). Any changes in processing protocol, over time, would have been aimed at maintaining or increasing the level of ^{235}U recovery but at reduced processing costs, thus leaving the relative composition of the radioactivity in the waste streams unaffected.

An important parameter in the behavior of any trace constituent in the subsurface is its physical/chemical form. Because of the chemical separation techniques used at the ICPP [pulsed and packed column extraction into tributyl phosphate (TBP) from nitric acid solutions (21)], the most probable valence state of the radionuclides in the waste stream would be (i) U (uranyl, +6), (ii) Np (neptunyl, +5), (iii) Tc (pertechnetate, +7), and (iv) Cl (chloride, -1). These valence states are concordant with those used in the repository study (1) with the exception of chloride, which was not considered. Moreover, because the onsite monitoring wells all show the presence of oxygen and the pH of the waters varies over a fairly narrow range (7.8–8.3; 22), there is no reason to suspect that anoxic conditions are present in the upper 100–200 m of the water table, which could lead to reducing conditions.

In the repository study, ^{129}I was presumed to be present as I^- . However, ^{129}I displays a complicated chemistry through nuclear fuel dissolution and reprocessing steps, appearing as reduced (I^-), oxidized (IO_3^-), uncharged (I_2), and organic species in gaseous effluents (23). It is possible therefore that, in addition to inorganic forms of ^{129}I , the liquid waste discharges from the ICPP also contained $^{129}\text{I}_2$ and $^{129}\text{I}_{2(\text{org})}$ species. Unfortunately, the long-term behavior and transformation rates of molecular and organic forms of iodine in the subsurface to inorganic forms are largely unknown, and we cannot entirely discount that some fraction of the retentive behavior of ^{129}I we observe in the SRP basalts is derived from such uncharged species. However, because of the strong oxidizing conditions that exist in the process stream (nitric acid), we think it more probable that $^{129}\text{I}_2$ and $^{129}\text{I}_{2(\text{org})}$ species are released as gaseous effluents due to their higher vapor pressures and that iodine species retained in the aqueous, nitric acid phase are ultimately transformed to inorganic forms of iodine. However, the exact chemical form of the iodine that leads to its retardation in the SRP basalts requires elucidation.

Radionuclide Concentrations and Drinking-Water Standards. Finally, in no case do the measured radioactivity levels reported here exceed Federal guidelines. The highest ^{99}Tc activity recorded, $2060 \pm 16 \text{ mBq L}^{-1}$ (uncertainties at 1σ) at well 50, represents 1.4% of the U.S. Environmental Protection Agency's (EPA) drinking-water standard (148 Bq L^{-1}) for this radionuclide as calculated using Department of Energy Order DOE 5400.5 (24). At the southern site boundary (well 108), the ^{99}Tc activity represents $\sim 0.0006\%$ of the EPA standard. In the case of ^{236}U , the concentration in well 123 (Table 4) represents 0.034% of the EPA standard (740 mBq L^{-1}) while near the southern site boundary (well 106) the percentage decreases to 0.000026. For ^{237}Np , the concentration at well 123 (Table 4) represents 0.25% of the EPA standard (111 mBq L^{-1}) and decreases to $< 0.00015\%$ at well 106.

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