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Plant-Based Plume-Scale Mapping of Tritium Contamination in Desert Soils

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ABSTRACT

Plant-based techniques were tested for field-scale evaluation of tritium contamination adjacent to a low-level radioactive waste (LLRW) facility in the Amargosa Desert, Nevada. Objectives were to (i) characterize and map the spatial variability of tritium in plant water, (ii) develop empirical relations to predict and map subsurface contamination from plant-water concentrations, and (iii) gain insight into tritium migration pathways and processes. Plant sampling [creosote bush, *Larrea tridentata* (Sessé & Moc. ex DC.) Coville] required one-fifth the time of soil water vapor sampling. Plant concentrations were spatially correlated to a separation distance of 380 m; measurement uncertainty accounted for <0.1% of the total variability in the data. Regression equations based on plant tritium explained 96 and 90% of the variation in root-zone and sub-root-zone soil water vapor concentrations, respectively. The equations were combined with kriged plant-water concentrations to map subsurface contamination. Mapping showed preferential lateral movement of tritium through a dry, coarse-textured layer beneath the root zone, with concurrent upward movement through the root zone. Analysis of subsurface fluxes along a transect perpendicular to the LLRW facility showed that upward diffusive-vapor transport dominates other transport modes beneath native vegetation. Downward advective-liquid transport dominates at one endpoint of the transect, beneath a devegetated road immediately adjacent to the facility. To our knowledge, this study is the first to document large-scale subsurface vapor-phase tritium migration from a LLRW facility. Plant-based methods provide a noninvasive, cost-effective approach to mapping subsurface tritium migration in desert areas.

The release of radionuclides from disposal sites is of concern because of the potential effects of exposure on human health and the environment. Questions concerning radionuclide migration include the spatial extent of contamination, the concentration as a function of distance from the source, and the rate at which contamination spreads. Tritium, the radioactive isotope of hydrogen, has been released into the environment from human activities since the 1940s. A principal waste from nuclear-power generation, tritium comprises a large portion of the total activity interred at radioactive-waste disposal sites. Because tritiated water (^3HHO) and nontritiated water (H_2O) have virtually identical chemical behaviors, tritiated water is an excellent tracer for the movement of waterborne contamination in both the liquid and vapor phases. In the liquid phase, tritiated water serves as an indicator for the transport of other potentially dissolved radionuclides, such as ^{60}Co and ^{238}Pu.

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Subsurface monitoring helps us quantify and manage environmental risks. Traditional monitoring methods include sampling of bulk soil, soil water, soil gas, and groundwater (Faybishenko, 2000; Lindgren, 2000). While these methods provide detailed information on the presence of contaminants, the associated site disturbance and costs of equipment, installation, and maintenance usually limit the number of samples. Because traditional methods provide only point measurements, limited sampling makes it difficult to adequately assess potentially contaminated areas. Novel approaches are thus needed for detection and monitoring. Such approaches must be cost effective, sensitive enough to provide early warning of contaminant releases, and accurate and robust enough for routine use in assessments of containment and remediation strategies.

In the late 1980s, trees were found to be useful indicators of subsurface tritium movement from the Maxey Flats, KY LLRW disposal site (Rickard and Kirby, 1987; Kalisz et al., 1988). Water taken up by tree roots showed tritium to be migrating along the regolith–bedrock interface. Andraski et al. (2003) recently introduced an efficient method of collecting plant water for tritium analysis. That study also documented a high correlation between tritium levels in plant water and in root-zone soil-water vapor.

The present study builds on previous work to evaluate the applicability of plant-based methods for large-scale contaminant-plume mapping in an arid environment. Testing was done adjacent to a closed LLRW facility in the Amargosa Desert, Nevada. Specific objectives were to (i) characterize and map the spatial variability of tritium in plant water (creosote bush), (ii) develop empirical relations to predict and map subsurface tritium contamination from plant-water concentrations, and (iii) gain insight into tritium migration pathways and processes.

MATERIALS AND METHODS

Field Site

Plume-scale application of the simplified contamination-detection methods was evaluated at the Amargosa Desert Research Site (ADRS; USGS, 1998). The ADRS includes study areas adjacent to a waste-burial facility located 17 km south of Beatty, NV and 20 km east of Death Valley National Park. The main study area is within the 400-m buffer zone surrounding the waste facility. A second study area, which serves as an uncontaminated control, is located 3 km to the south. The waste facility has been used for the burial of LLRW (1962–92) and hazardous chemical waste (1970–present). The LLRW facility was the first commercially operated facility in the United States. The LLRW trenches range from 2 to 15 m deep and are unlined.

The ADRS is in the Mojave Desert ecosystem, one of the

Abbreviations: ADRS, Amargosa Desert Research Site; LLRW, low-level radioactive waste.

driest regions of the United States. Annual average precipitation (1981–2001) is 108 mm yr^{-1}. The volume-weighted tritium concentration in precipitation (November 1997–April 2001) averaged 1.1 Bq L^{-1}. Surface soils belong to the Yermo (loamy-skeletal, mixed, superactive, calcareous, thermic Typic Torriorthent)–Arizo (sandy-skeletal, mixed, thermic Typic Torriorthent) association. Underlying sediments are primarily fluvial deposits. Detailed information on soil properties is given in Andraski (1996). Depth to the water table ranges from 85 to 115 m below land surface.

Vegetation is sparse. Creosote bush, the most abundant shrub of the North American warm deserts, is the dominant species. Creosote bush forms nearly pure stands in many desert areas (Smith et al., 1997). At the ADRS, total shrub-species ground cover is 6.4% [based on April 2001 data collected using the line-transect method (Smith, 1974)]; ground cover by species is 4.0% creosote bush, 1.2% shadscale [or spiny saltbush, *Atriplex confertifolia* (Torr. & Frém.) S. Wats.], 0.8% burrobush [*Ambrosia dumosa* (Gray) Payne], and 0.4% wolfberry [*Lycium pallidum* Miers]. Observations indicate creosote-bush roots are horizontally extensive; literature values for the radial extent of creosote-bush roots exceed 4 m (Cannon, 1911; Gile et al., 1998). A 4-m rooting radius is about 10 times the measured creosote-bush canopy radius (0.43 m). The rooting depth of creosote bush generally corresponds to the maximum-annual penetration depth of precipitation, which is about 0.75 to 1 m at the ADRS (Andraski, 1997). The penetration depth of precipitation is limited by plant-water uptake and a laterally extensive gravelly layer (very gravelly sand, about 1 m thick) that underlies the surface soil and impedes downward percolation of liquid water under unsaturated conditions. Multiyear measurements have shown that, in vegetated parts of the study area, root-zone soil-water content varies temporally between 0.02 and 0.14 $m^3\ m^{-3}$ (Fischer, 1992; Andraski, 1997; Johnson et al., 2002). The gravelly sub-root-zone layer has a temporally invariant soil water content of approximately 0.05 $m^3\ m^{-3}$. In devegetated areas, soil moisture accumulates and penetrates below the root zone.

Sampling and Tritium Analysis

Creosote bush samples (n = 103) were collected within a 63-ha area adjacent to the waste facility. Creosote bush was selected for this study because of its dominance and drought-resistant evergreen character. Most plant samples were collected along transects that ran parallel to the perimeter of the waste facility. Spacing between adjacent samples usually ranged between about 50 and 100 m. Closer spacing was used nearer the facility to better allow for identification of potentially localized areas of contamination. The ultimate combination of sample number and locations provided reasonable coverage of the study area and allowed all plant samples to be collected in 1 d. Soil water vapor samples were collected at selected locations to develop empirical relations between plant and subsurface tritium concentrations. Root-zone soil-gas tubes (n = 10) were installed to a nominal depth of 0.5 m. Sub-root-zone soil-gas tubes (n = 17) were installed into the underlying gravelly layer, to a nominal depth of 1.5 m. Each soil-gas tube was located 0.5 to 5 m from the center of a sampled plant. Canopy air samples were collected 0.5 m above land surface along a transect perpendicular to the LLRW facility. Background tritium concentrations in plant water, soil water vapor, and air were determined at the control site.

Andraski et al. (2003) detailed field and laboratory procedures used in the collection, preparation, and analysis of samples. Briefly, the plant-water method involved hand-stripping of foliage (170 g on average) from randomly selected branches, solar distillation in plastic bags, collection of distillate (23 mL on average) by pipet, and extraction of scintillation-interfering constituents by filtration and adsorption on a graphite-based medium before tritium analysis. Foliage samples were weighed before distillation, pipet volumes were recorded, and foliage samples were reweighed after pipeting. These data indicated that, on average, about 2 to 3 g of liquid was lost during the field distillation and sample transfer process. Soil water vapor and canopy water vapor were collected by pulling air through a dry-ice freeze trap using a downstream pump. Water vapor collected as ice in the trap. Tritium analyses were done according to the direct liquid-scintillation counting method described by Thatcher et al. (1977) at the USGS tritium laboratory in Menlo Park, CA. Scintillation counting uncertainty (±one sigma) for canopy air, plant water, and soil water vapor samples averaged 1, 7, and 10%, respectively.

Data and Spatial Analyses

Univariate statistics on tritium concentrations in plant water were used to summarize the data and determine whether transformation was needed before further statistical analysis. Geostatistical techniques (Journel and Huijbregts, 1978; Isaaks and Srivastava, 1989) were used to evaluate spatial correlation in the data and to generate a complete map of tritium concentrations in plant water. The semivariogram was fitted with a Gaussian model:

$$\gamma(h) = C_n + C_0\lfloor 1 - \exp(-h^2/a^2)\rfloor \qquad [1]$$

where γ is the semivariogram of plant-water tritium, h is separation distance, C_n is nugget variance, C_0 is structural variance, $C_n + C_0$ is sill variance, and a is correlation length. Equation [1] describes the asymptotic approach to a sill; the effective range (r_e) is the distance at which the semivariogram reaches 95% of the sill ($r_e \approx 3^{1/2}a$). Parameters for the model semivariogram were optimized using nonlinear regression procedures. The modeled semivariogram was used for ordinary-kriging estimation and mapping of plant-water tritium concentrations throughout the study area. Statistical analyses were done using SAS software (SAS Institute, 2001).[1]

Data from collocated plant-water and soil water vapor sampling sites were analyzed using linear regression procedures. The resulting empirical relations were used to predict subsurface tritium concentrations from the more abundant (and more easily determined) plant-water concentrations. Root-zone and sub-root-zone tritium were mapped by combining the kriged plant-water concentrations with the appropriate regression equation.

RESULTS AND DISCUSSION

Tritium in Plant Water

Locations of sampled plants and corresponding contours of plant-water tritium concentrations are shown in Fig. 1. The disturbed area north of the LLRW area had no plants because it was used to stockpile sediments excavated from waste trenches. Background values for tritium in plant water and soil water vapor averaged 2.5 ± 0.4 Bq L^{-1}. The most distant plant with a greater-than-background concentration was >400 m from the LLRW area (6.0 Bq L^{-1} at easting 528 039 m, northing 4 068 456 m) (36.76328° N, 116.68585° E; NAD 1927).

[1] The use of trade names is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

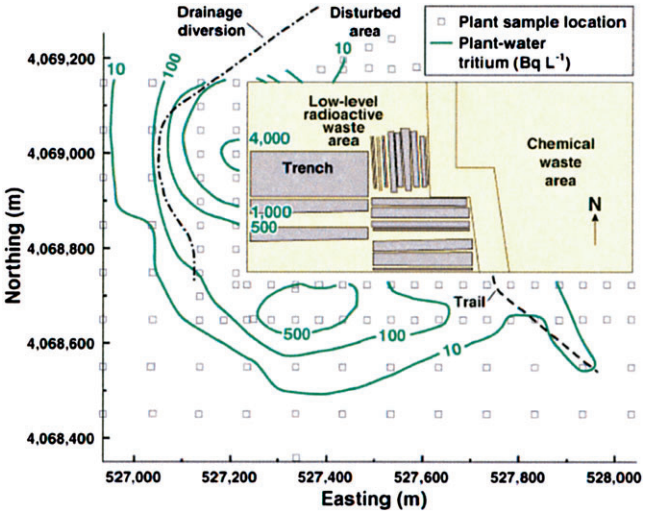

Fig. 1. Plant sample locations and contours of measured plant-water tritium concentrations.

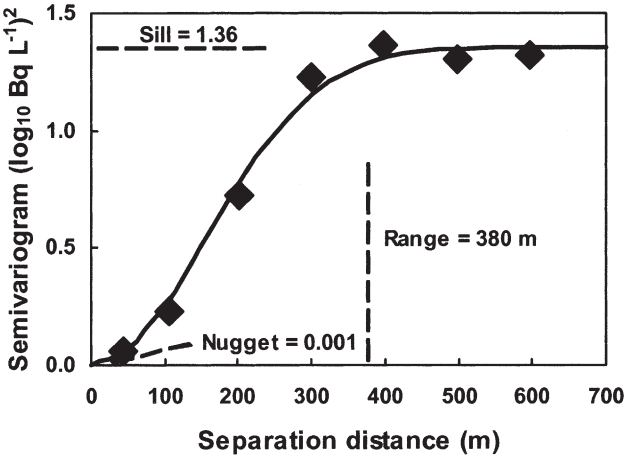

Fig. 2. Sample (symbols) and model (solid line) semivariograms for plant-water tritium concentrations. Nugget variance (C_n), sill variance ($C_n + C_0$), and effective range (r_e) associated with the Gaussian-model semivariogram (Eq. [1]) also are shown.

The contours of plant-water tritium concentrations indicate two hot spots (areas of high concentration), one to the south and one to the west of the LLRW area (Fig. 1). The maximum measured plant-water concentration within the southern and western hot spot was 941 and 4890 Bq L^{-1}, respectively. These data confirm earlier work that outlined part of the southern hot spot through soil water vapor sampling (Striegl et al., 1998; Healy et al., 1999). The greatest concentrations in the earlier studies were along the eastern edge of a 250 by 250 m sampling area (near Fig. 1 *x*–*y* coordinate 527 335 m–4 068 700 m). Plant samples delineated the complete hot spot south of the waste facility and identified the previously unrecognized hot spot west of the waste facility. Plant-water sampling provides a relatively simple, inexpensive tool to screen for hot spots and delineate contamination.

Statistical Analyses and Mapping Plant and Soil Tritium Distributions

Univariate statistics for the contoured plant-water tritium concentrations (Fig. 1) are given in Table 1. The mean tritium concentration for nontransformed values is 352 Bq L^{-1}. Individual concentrations are highly variable, with minimum and maximum values spanning four orders of magnitude. The large positive skewness of the nontransformed values reflects the asymmetric distribution caused by a small number of very high values. Applying a $\log_{10}$ transformation to the data improves the normality of the distribution. Relative to nontransformed values, the difference between mean and median values is decreased and the skewness is reduced (Table 1). Thus, $\log_{10}$ transformed values were used for subsequent statistical analyses.

Geostatistical procedures were used to quantify the spatial correlation structure of $\log_{10}$ plant-water tritium concentrations. Sample and model semivariograms are shown in Fig. 2. For all lags, the sample semivariance was calculated from a minimum of 39 sample pairs. The sample semivariogram was limited to a maximum separation distance of 650 m. This cutoff, about one-half the total distance sampled, was used to avoid edge effects in the semivariance. The *a* parameter in the Gaussian model semivariogram (Eq. [1]) was 220 m. The associated effective range value showed that the plant-water tritium concentrations were spatially correlated to a separation distance of 380 m (Fig. 2). In addition, the nugget/sill variance ratio $[C_n/(C_n + C_0)]$ indicated that measurement uncertainties accounted for <0.1% of the total variability in the data. An additional semivariogram analysis on a subset of plant data showed that a less intensive sampling (n = 68; ≈75–100 m between adjacent samples) would give results similar to those shown in Fig. 2. For example, model-semivariogram parameters for the subset-data analysis were C_n = 0.0 and C_0 = 1.29 in units of $(\log_{10}$ Bq $L^{-1})^2$; a = 225 m, giving an effective range of 390 m.

Using the fitted model-semivariogram parameters (C_n, C_0, and a) for the full data set, we performed ordinary kriging to generate a complete map of the estimated plant-water tritium concentrations and the associated prediction errors across the study area (Fig. 3a and 3b, respectively). The kriging standard errors were small throughout the mapped area (typically <0.2 $\log_{10}$ Bq L^{-1}). The slight increases in standard errors near the northern and southern extremes of the map (Fig. 3b) reflect areas where fewer plant data were available for the kriging calculation (Fig. 1). Unlike the simple contour-map approach (Fig. 1), kriging allowed estimation of plant-

Table 1. Univariate statistics for nontransformed and log-transformed plant-water tritium concentrations.

Variable (n = 103)	Mean	SD	Min.	Max.	Median	CV	Skewness
						%	
Tritium, Bq L^{-1}	352	813	0.5	4890	20.0	231	3.52
Tritium, $\log_{10}$ Bq L^{-1}	1.52	1.04	−0.32	3.69	1.30	68.4	0.38

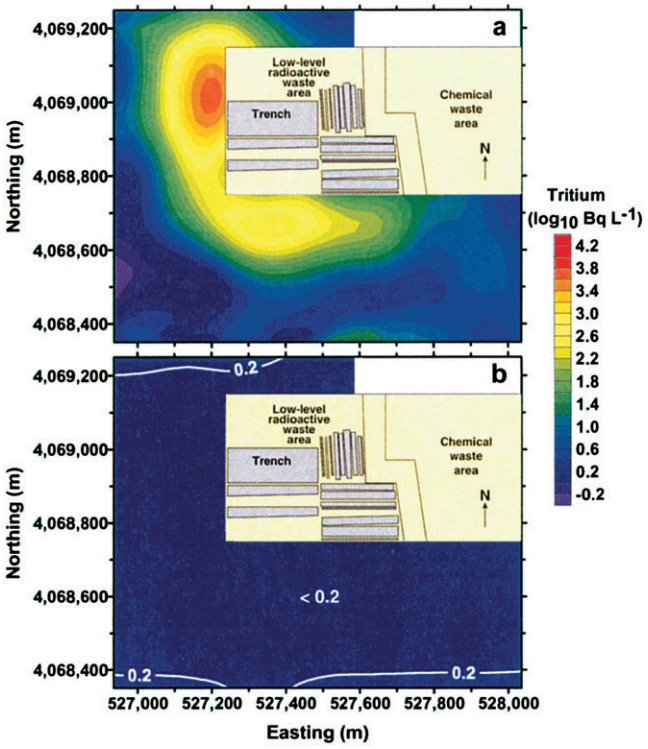

Fig. 3. Maps of (a) kriged plant-water tritium concentrations and (b) associated kriging standard errors.

water concentrations where measured values were not available. For example, kriged concentrations indicated the western hot spot extended northward into the disturbed area that had no plants; the northernmost kriged concentrations reached values of 1.65 $\log_{10}$ Bq L^{-1} (45 Bq L^{-1}) (Fig. 3a).

The kriged map (Fig. 3a) shows that structure in the plant-water tritium concentrations is consistent with the simple contour map (Fig. 1). Western and southern hot spots are readily apparent. The presence of hot spots violates the intrinsic hypothesis in that the plant data have a nonstationary expectation. In reality, there is no physical reason for the mean to be stationary. Tritium concentrations are undoubtedly affected by the distribution and integrity of containers in the waste-burial area. In addition, the southern hot spot may be associated with a documented 1978 spill of liquid radioactive waste (1890 L) that occurred inside the LLRW area and flowed about 175 m to a location near the Fig. 1 *x*–*y* coordinate 527 330 m–4 068 750 m (ERM Program Management Co., written communication, 1996). To account for the nonstationarity (drift) in the data, small search neighborhoods equal to the effective range (380 m) were used to krige the plant-water tritium concentrations. Thus, for each grid point, only data values within the neighborhood were used in the estimation procedure that produced the maps shown in Fig. 3. This satisfied the stationarity assumption within the limited range of separation distances, producing a condition known as quasi-stationarity (Journel and Huijbregts, 1978).

Andraski et al. (2003) found a good correlation between tritium in plant water and root-zone soil water vapor. Thus, we developed empirical relations to predict

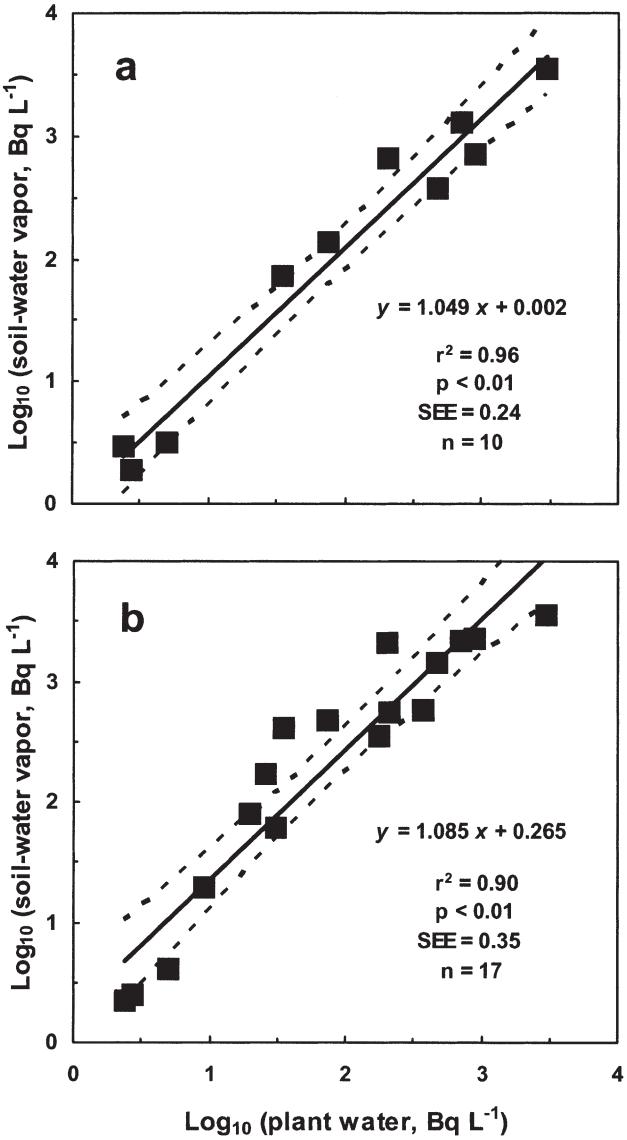

Fig. 4. Relation between tritium concentrations in (a) plant water and root-zone soil water vapor and (b) plant water and sub-root-zone soil water vapor. The 95% confidence limits for each regression line are indicated by dashed lines.

root-zone and sub-root-zone tritium concentrations from the more easily determined plant-water concentrations. These results are shown in Fig. 4a and 4b, respectively. In both cases, the regression relation between plant- and subsurface-tritium concentrations is highly significant ($p < 0.01$). Correlation coefficients (r^2) showed that the empirical regressions explained 96% of the variation in the root-zone data and 90% of the variation in the sub-root-zone data. The decrease in the r^2 value for the sub-root zone prediction reflects the lack of direct contact between plant roots and soil water in that zone. Nevertheless, these results show that plant-water data can be used to predict specific tritium concentrations in both root-zone and sub-root-zone soil water vapor.

The spatial distribution of subsurface tritium contamination was estimated by combining the kriged plant concentrations (Fig. 3a) with the appropriate regression equation (Fig. 4). Resulting maps of regressed soil water

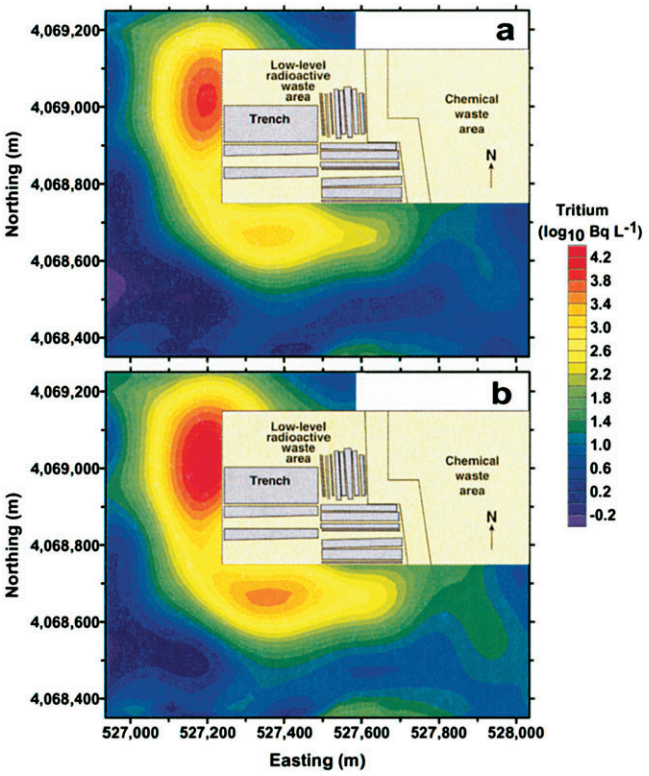

Fig. 5. Maps of soil-water-vapor tritium concentrations in the (a) root zone and (b) sub-root zone. Maps were based on combining kriged plant-water concentrations shown in Fig. 3a with the appropriate regression equation given in Fig. 4.

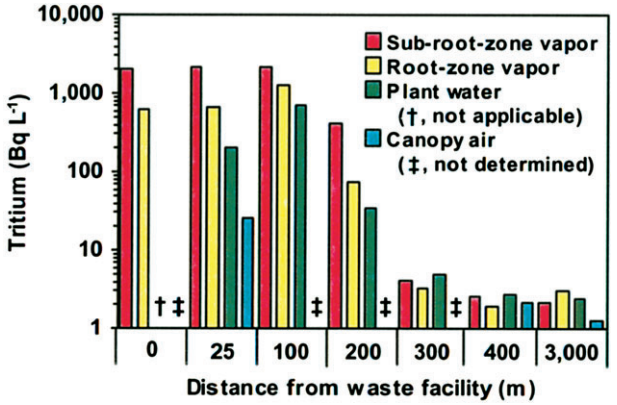

Fig. 6. Measured tritium concentrations on a north-south transect that started at the perimeter of the low-level radioactive waste area and passed through the southern hot spot shown in Fig. 1 (easting ≈527 335 m), along with background data collected about 3000 m south of the waste-disposal facility. No plants were present at the 0-m distance location.

vapor tritium concentrations in the root zone and in the sub-root zone are shown in Fig. 5a and 5b, respectively. As noted above, the extent of the southern hot spot and the presence of the western hotspot were previously unknown. The "bulls-eye" appearance of both hot spots (Fig. 1, 3a, and 5) may be due to localized dilution of tritium concentrations that was caused by soil moisture accumulation beneath the dirt access road along the perimeter of the waste facility. Moisture accumulation would result from incident precipitation, dust-control watering, and lack of transpiration. In addition to hot spots, plant-based mapping indicated details of the contaminant distribution—notably, the finger-like projection near the trail directly south of the chemical waste area (Fig. 1, 3a, and 5).

A comparison of tritium concentrations shown in Fig. 3a, 5a, and 5b indicates that, for any given location within the contaminant plume, concentrations are greatest in the sub-root-zone gravel layer. This trend is further illustrated in Fig. 6, which shows measured tritium concentrations along a transect through the southern hot spot (easting ≈527 335 m), along with background data collected 3 km south of the waste facility. At distances of 0, 25, 100, and 200 m from the perimeter of the facility, the sub-root-zone tritium concentration exceeded the root-zone concentration by a factor of two to six. At a distance of 300 m, all measured concentrations were about twice background levels, but differences among soil and plant samples were not readily apparent (compared with the one-sigma scintillation counting errors of ± 0.6 Bq L^{-1} for this location). At a distance of 400 m, all tritium concentrations were statistically equivalent to those measured at the background site.

The concentration of tritium in canopy air was 25 Bq L^{-1} at 25 m from the facility. This is more than 10 times the 400-m and background-site concentrations (Fig. 6), but well below regulatory limits. Soil-water vapor tritium concentrations for the 0-m location likely were affected by dilution because the site had no plants and was subject to soil moisture accumulation from both incident precipitation and watering of the roadway. A minimum estimate of soil moisture accumulation at this location can be based on measurements made under precipitation-only conditions at a nearby devegetated study site, where soil water content of the sub-root-zone gravel layer increased from 0.05 to 0.08 m^3 m^{-3} (60%) during a 13-yr period (Andraski, 1997; Johnson et al., 2002). Assuming a soil water content increase of 60%, the minimum undiluted tritium concentration for the sub-root-zone gravel layer at the 0-m location would be 5100 Bq L^{-1}.

Soil water vapor sampling was limited in the western hot spot, but nevertheless showed a vertical concentration gradient like that observed in the southern hot spot. For example, concentrations approximately 25 m west of the LLRW area (easting 527 208 m, northing 4 068 945 m) decreased as follows: sub-root zone (3623 Bq L^{-1}), root zone (3505 Bq L^{-1}), and plant water (2960 Bq L^{-1}).

The results show that plant sampling in combination with a limited number of in situ soil water vapor samples is useful for plume-scale mapping of subsurface tritium contamination. The plant sampling method is cost effective. Collection and preparation of plant samples for tritium analysis required only one-fifth the time of soil water vapor samples. Plant sampling is relatively noninvasive with respect to plants and completely noninvasive with respect to the soil. Plant water provides a volume-integrated (versus point) sample that reflects the relatively large soil volume exploited by the active root system. A survey of more than 200 species indicates many plants can develop

far-reaching root systems in the absence of restrictive subsoil characteristics (Stone and Kalisz, 1991). This underscores the potential for other plants to act as volume-integrated samplers of subsurface contamination.

The greatest source of uncertainty in plant-based plume-scale mapping stems from the empirical relations between plant- and subsurface-tritium concentrations. Other, but relatively minor, sources of uncertainty are those associated with the solar-distillation and solid-phase extraction of plant water, and scintillation counting (Andraski et al., 2003). Future work must establish the presumably species- and environment-specific relation between plant- and soil water contamination. Nevertheless, our approach is likely transferable to additional species and environments. Note that site-specific testing will be needed to establish solid-phase-extraction requirements for the plant water of interest and to establish empirical relations between plant and subsurface contaminant concentrations. Depending on the objectives and results of such testing, the end-user may have the option to use a plant-based method as a general indicator or a quantitative predictor of subsurface tritium contamination. In addition, the resultant tritium data may serve as a proxy for constraining the migration patterns of other liquid-phase or gas-phase (e.g., mercury) contaminants that can be associated with buried LLRW.

Transport Pathways and Processes

The distribution of tritium in relation to site features provides insight into field-scale transport. Data collected as part of this study, together with data from deep unsaturated-zone boreholes (Mayers, 2003; Stonestrom et al., 2004), show that tritium moves preferentially away from the waste source through dry, coarse-textured layers beneath the root zone, with subsequent upward release to the surface through the root zone. Near the southern hot spot at Borehole UZB-3 (≈30 m south of LLRW area; easting 527 336 m, northing 4 068 713 m), the tritium concentration in the shallow sub-root-zone gravel layer (2248 Bq L^{-1} at 1.5-m depth) exceeded values at the 0.50-m depth (710 Bq L^{-1}) and 4.95-m depth (335 Bq L^{-1}) by factors of 3 and 7, respectively. Likewise, at Borehole UZB-2 (≈100 m south of LLRW area; easting 527 257 m, northing 4 068 645 m), the tritium concentration in the shallow sub-root-zone gravel layer (1429 Bq L^{-1} at 1.5-m depth) exceeded values at the 0.50-m depth (375 Bq L^{-1}) and 5.5-m depth (85 Bq L^{-1}) by factors of 4 and 17, respectively. Earlier work postulated subsurface liquid transport along preferential flow paths as a mechanism for tritium contamination observed at the UZB-2 borehole (Striegl et al., 1996). However, multiple-year soil moisture measurements (water content and water potential—Fischer, 1992; Andraski, 1997; Johnson et al., 2002) and electromagnetic surveys (B.R. Scanlon, B.J. Andraski, and D.A. Stonestrom, unpublished data, 1999) showed no evidence of elevated soil moisture in the vicinity of the southern hot spot. Thus, the mapped contamination (Fig. 3a and 5) appears to be primarily the result of subsurface vapor-phase transport.

Liquid and vapor transport are coupled processes, requiring integrated analysis for accurate work (Thorstenson and Pollock, 1989). For purposes of initial data evaluation, a single-phase independent-process approach was used to estimate the relative magnitudes of vertical, diffusive and advective fluxes of tritiated water in the liquid and vapor phases. Flux estimates were based on measured root-zone and sub-root-zone soil water vapor tritium concentrations at distances of 0, 25, 100, and 200 m from the perimeter of the LLRW area (Fig. 6). Tritium concentrations in the liquid phase were calculated assuming isotopic equilibrium between water vapor and liquid water and using a fractionation factor of 1.108 (Ferronsky and Polyakov, 1982).

Diffusive fluxes of tritiated water were estimated using (Pruess et al., 1999):

$$J_{d\beta} = -\phi\tau_o\tau_\beta\rho_\beta D_{d\beta}\nabla X_\beta \quad [2]$$

where $J_{d\beta}$ is diffusive flux in phase β (liquid, "l", or gas, "g"), ϕ is porosity, $\tau_o\tau_\beta$ is a tortuosity factor ($\tau_o\tau_\beta = \phi^{1/3} S_\beta^{10/3}$), S_β is phase saturation, ρ_β is phase density, $D_{d\beta}$ is diffusion coefficient of tritiated water in phase β, and X_β is mass fraction in phase β. We used $\phi = 0.25$, the average total porosity for root-zone and sub-root-zone soil measurements. For the 25-, 100-, and 200-m locations, calculated S_l and S_g values were based on an average measured soil water content of 0.05 $m^3\ m^{-3}$. For the 0-m (bare soil) location, S_l and S_g values were based on a soil water content of 0.08 $m^3\ m^{-3}$ reported for devegetated soil (Johnson et al., 2002). Values used for the other parameters were based on published information: $\rho_l = 997.9\ kg\ m^{-3}$, $\rho_g = 1.077\ kg\ m^{-3}$, $D_l = 2.05 \times 10^{-9}\ m^2\ s^{-1}$, and $D_g = 2.60 \times 10^{-5}\ m^2\ s^{-1}$. Kinetic fractionation effects during sample collection were assumed to produce small errors relative to the range of absolute tritium concentrations.

The advective liquid-phase flux of tritiated water, J_{al}, was estimated using

$$J_{al} = J_w\overline{X_l} \quad [3]$$

where J_w is liquid water flux and $\overline{X_l}$ is depth-averaged mass fraction in the liquid phase. For the 25-, 100-, and 200-m locations, J_w was based on the average value beneath native vegetation ($1.2 \times 10^{-13}\ kg\ m^{-2}\ s^{-1}$) reported by Andraski (1997). For the 0-m location, J_w ($-4.3 \times 10^{-5}\ kg\ m^{-2}\ s^{-1}$) was based on Darcy's Law using average measured water-potential gradients beneath devegetated soil (Andraski, 1997) and the estimated unsaturated hydraulic conductivity for sub-root-zone-gravel at a soil-water content of 0.08 $m^3\ m^{-3}$ (Andraski, 1996).

The advective vapor-phase flux of tritiated water due to barometric "pumping" (a dispersive flux) was estimated using (Parker, 2003)

$$J_{ag} = -D_{ag}\nabla X_g \quad [4]$$

where J_{ag} is advective vapor-phase flux, D_{ag} is dispersion coefficient associated with barometric-pressure fluctuations, and X_g is mass fraction in the gas phase. The dispersion coefficient was calculated by $D_{ag} = (\phi_a \Delta P d r v)/(P_o t)$ where ϕ_a is air-filled porosity, ΔP is average diurnal barometric forcing, d is depth of barometric pressure

Table 2. Estimated vertical fluxes of tritiated liquid- and vapor-phase water calculated using concentrations measured in the root zone (0.5-m depth) and sub-root zone (1.5-m depth) for four locations within 200 m of the low-level radioactive-waste area.

Distance from waste facility†	Diffusive fluxes		Advective fluxes		Total flux
	Liquid phase	Vapor phase	Liquid phase	Vapor phase	
m	g m^{-2} yr^{-1}				
0	7×10^{-12}‡	2×10^{-11}	-4×10^{-8}	3×10^{-13}	-4×10^{-8}
25	1×10^{-12}	3×10^{-11}	1×10^{-16}	3×10^{-13}	3×10^{-11}
100	9×10^{-13}	2×10^{-11}	1×10^{-16}	2×10^{-13}	2×10^{-11}
200	3×10^{-13}	7×10^{-12}	2×10^{-17}	7×10^{-14}	7×10^{-12}

† Locations correspond with the 0-, 25-, 100-, and 200-m sample locations shown in Fig. 6. The 0-m location had no plants; the other three locations were vegetated.
‡ Sign convention is that upward fluxes are positive.

propagation, r is dispersivity to travel distance ratio, v is vertical travel distance to top of contaminant zone, P_o is mean barometric pressure, and t is period We used $v = 1$ m (distance to the top of the sub-root-zone gravel); $d = 108$ m (depth of capillary fringe); and $t = 1$ d, $\Delta P = 0.4$ kPa, and $P_o = 92$ kPa, based on data from Smith et al. (1999). Following Parker (2003) we assumed $r = 0.02$.

Estimated diffusive and advective fluxes of tritiated water calculated using Eq. [2] through [4] are given in Table 2. For the 0-m location, water accumulation beneath devegetated soil produces a downward-directed, advective-liquid flux more than 10^3 times greater than the other fluxes. In contrast, fluxes beneath vegetation at distances of 25, 100, and 200 m are upward and dominated by vapor-phase diffusion (Table 2). The diffusive vapor-phase fluxes are one to five orders of magnitude greater than other fluxes in vegetated areas. The diffusion coefficient of tritiated water in vapor is about 10^4 times greater than that for tritiated water in liquid; this more than offsets differences in tritiated water mass fraction between soil gas and liquid soil water. The diffusive/advective vapor flux ratio is approximately 67 at the 0-m location and about 100 elsewhere. Consistent with results of Parker (2003), relative to advective vapor transport, diffusive vapor transport is more important at the shallow depths considered here and at sites with lower soil water contents. Under present climatic conditions, the efficiency of root-zone water depletion by native plants (Andraski, 1997) and the associated transpiration of tritiated-liquid water will likely support relatively continuous expulsion of tritiated water vapor from the sub-root zone.

Data from this study, paired with data from the deep unsaturated zone in contaminated areas (Striegl et al., 1996; Prudic et al., 1997; Prudic et al., 1999; Mayers, 2003) and uncontaminated areas (Prudic, 1994; Scanlon et al., 2003; Walvoord et al., 2004, 2005), indicate that tritium migration from the LLRW area is superimposed on an upward-directed natural flow field (Stonestrom et al., 2004). Tritium contamination (Fig. 1, 3, and 5) originates from two possible sources, buried waste and surface spills. As described above, the southern hot spot may be associated with a surface spill. A spill of sufficient volume could have overcome the capillary-break effect of fine-grained over coarse-grained soil, resulting in penetration of tritiated liquid into the sub-root-zone gravel. This tritiated liquid could then serve as a source for subsequent vapor-phase movement. Borehole data collected at the time of this study (Mayers, 2003) show deeper, secondary peak concentrations in the UZB-3 profile (948 Bq L^{-1} at 23.8 m) and the UZB-2 profile (742 Bq L^{-1} at 47.9 m). These secondary peaks are associated with deep gravel layers, indicating a tritium source at depth (Prudic et al., 2000; Stonestrom et al., 2004).

Evaluation of the western hot spot is speculative, as no deep data are available. As shown, near-surface vertical tritium-concentration gradients are similar to those in the southern hot spot. The drainage diversion ditch (Fig. 1), excavated during 1987–1988, cut through the near-surface gravel layer. The fact that the plant and shallow-subsurface tritium distributions do not reflect the discontinuity (Fig. 1, 3a, and 5) suggests that (i) the leading edge of a shallow plume migrated beyond the ditch before 1987-88 or (ii) the primary path of lateral migration is through gravel layers at depth. Recognizing the upward migration of tritium from sub-root-zone to root-zone soil layers documented in this study, as well as the importance of upward flow processes in deep unsaturated zones, it is plausible that tritium contamination from a subsurface source well below the root zone could move upward and be detected in near-surface soils and in plants. Insight into the historic record and rate of plume advancement might be gained by tritium analysis of plant-growth rings (Love et al., 2002).

Although vapor-phase transport appears to be the primary mechanism of near-surface tritium migration from the waste area, the correspondence between the finger-like projection in the 10 Bq L^{-1} contour line and the trail south of the chemical waste area (Fig. 1) suggests an off-site surface spill may have contributed to elevated concentrations in this area. Increased subsurface concentrations in the finger area (Fig. 5) are reasonable if a surface spill caused focused infiltration and percolation of tritiated water.

To our knowledge, this study is the first to document extensive lateral, subsurface vapor-phase transport of tritium from a LLRW area. The observed extent of tritium transport, to distances >300 m, is inconsistent with predictions from process-based numerical models (e.g., Striegl et al., 1996; Mayers et al., 2005). Results of this study will help test and refine models of tritium transport. Better understanding of the relevant processes will aid containment and monitoring efforts at contaminated sites.

The strong relation between tritium in plant water and tritium in sub-root-zone soil water vapor demonstrates the role of desert vegetation in the upward migration of waterborne contaminants from beneath the root zone. This has implications beyond monitoring. Phyto-

remediation is often assumed to be limited to material that is in direct contact with plant roots (Rock, 1997). The present study shows that the remedial effects of desert vegetation on tritium contamination can extend beneath the root zone.

CONCLUSIONS

We documented plume-scale testing of a plant-based method to determine subsurface tritium contamination. Testing was done at the USGS Amargosa Desert Research Site, adjacent to a closed low-level radioactive waste (LLRW) facility near Beatty, NV. The approach includes a recently developed plant-sampling technique that involves solar distillation and solid-phase extraction to collect and prepare plant water for tritium analysis. Creosote bush was used as the test plant because of its ubiquity in North American warm deserts and its drought-resistant evergreen character. Plant sampling yields volume-integrated samples that reflect the entire soil volume exploited by the plant's active root system. It requires little field equipment and is noninvasive to the subsurface. Collection and preparation of plant water for tritium analysis is fast, requiring one-fifth the time of soil water vapor samples collected in a freeze trap.

Plant data revealed hot spots and other trends in the distribution of tritium contamination. Geostatistical analysis showed that plant tritium was spatially correlated to a separation distance of 380 m. Measurement uncertainty accounted for <0.1% of the total variability in the data. Kriging produced full-coverage maps of estimated plant contamination. Kriging standard errors were small, typically <0.2 $\log_{10}$ Bq L^{-1}. Results provided a synoptic view of the plant tritium distributions. The method is simple and robust enough for repeat sampling to determine evolution of a plume.

Tritium concentrations in plant water accurately reflected those in root-zone and sub-root-zone soil water vapor. The linear regression relations between measured plant and subsurface tritium concentrations were highly significant ($p < 0.01$). Regression equations explained 96 and 90% of the variation in root-zone and sub-root-zone data, respectively. The empirical extrapolation from plant tritium to subsurface tritium represents the greatest source of uncertainty in the plant-based approach to subsurface contaminant mapping. Other relatively minor sources of uncertainty include those associated with collection and preparation of plant water for tritium analysis.

Preliminary analysis of results in relation to site features provided insight into tritium transport pathways and processes. Tritiated water vapor is inferred to be moving preferentially from the waste source through a coarse-textured layer beneath the root zone. To our knowledge, this study is the first to document large-scale subsurface vapor-phase tritium migration from a LLRW disposal area. Transport beneath native vegetation is upward from the sub-root-zone gravel to the root zone, where diffusive vapor-phase fluxes exceed the advective vapor-phase fluxes by a factor of about 100 and liquid-phase (diffusive and advective) fluxes by a factor of about 20 to 10^5. Plants can play an important role in the detection, movement, and potential remediation of tritium contamination in desert areas.

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