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Simplified Method for Detecting Tritium Contamination in Plants and Soil

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ABSTRACT

Cost-effective methods are needed to identify the presence and distribution of tritium near radioactive waste disposal and other contaminated sites. The objectives of this study were to (i) develop a simplified sample preparation method for determining tritium contamination in plants and (ii) determine if plant data could be used as an indicator of soil contamination. The method entailed collection and solar distillation of plant water from foliage, followed by filtration and adsorption of scintillation-interfering constituents on a graphite-based solid phase extraction (SPE) column. The method was evaluated using samples of creosote bush [*Larrea tridentata* (Sessé & Moc. ex DC.) Coville], an evergreen shrub, near a radioactive disposal area in the Mojave Desert. Laboratory tests showed that a 2-g SPE column was necessary and sufficient for accurate determination of known tritium concentrations in plant water. Comparisons of tritium concentrations in plant water determined with the solar distillation–SPE method and the standard (and more laborious) toluene-extraction method showed no significant difference between methods. Tritium concentrations in plant water and in water vapor of root-zone soil also showed no significant difference between methods. Thus, the solar distillation–SPE method provides a simple and cost-effective way to identify plant and soil contamination. The method is of sufficient accuracy to facilitate collection of plume-scale data and optimize placement of more sophisticated (and costly) monitoring equipment at contaminated sites. Although work to date has focused on one desert plant, the approach may be transferable to other species and environments after site-specific experiments.

LOW-LEVEL RADIOACTIVE and mixed wastes are disposed primarily by shallow land burial in trenches that are filled with waste and previously excavated soil. The hazard to public health following burial is considered to exist for 500 yr (United States Nuclear Regulatory Commission, 1989). Thus, there is ongoing concern about the release and fate of radionuclides in the environment near contaminated sites. In humid environments, transport by ground water is considered the main radionuclide migration pathway and, in arid environments, transport by soil water and vapor is considered the main migration pathway (Siefken et al., 1982). Tritium, the only radioactive isotope of hydrogen, is one of the most common radionuclides disposed at waste burial sites. Water (H_2O) and tritiated water (^3HHO)

behave nearly identically in the subsurface and can move in both the liquid and vapor phases (Phillips, 1994).

Ground water and soil water monitoring can provide detailed information needed to assess risks associated with waterborne radionuclides in the subsurface, but the high costs of equipment, installation, and maintenance of these monitoring systems limits the number of sampling locations. Thus, cost-effective methods are needed to identify the presence and distribution of contamination. Such methods should be capable of providing an early warning of contaminant releases. In addition, the methods should be of sufficient accuracy to facilitate collection of plume-scale data and optimized placement of more sophisticated monitoring equipment at contaminated sites.

Previous studies at a humid site (Maxey Flats, Kentucky; precipitation 1000 mm yr^{-1}) showed that trees could serve as indicators of subsurface tritium flows away from a radioactive waste site (Rickard and Kirby, 1987; Kalisz et al., 1988). Trees at the Kentucky site were rooted in shallow colluvium on steeply sloping hillsides, and sandstone bedrock limited the vertical penetration of roots and water to a depth of about 1 to 4 m. Subsurface flow was reported to primarily occur as water movement along the top of the sandstone and through horizontal fractures in the sandstone. Rickard and Kirby (1987) sampled trees by collecting sap from maple (*Acer* spp.) and by collecting and solar-distilling water from foliage of oak (*Quercus* spp.) and hickory (*Carya* spp.). Kalisz et al. (1988) sampled trees by collecting and microwave-distilling water from leaves. In both studies, the collected liquid then was distilled in the laboratory to remove constituents that can interfere with tritium analysis by liquid scintillation counting. Distillation was selected as the interference removal method because it is a common laboratory technique. When sample volumes are large (e.g., 20–100 mL), the laboratory distillation is relatively simple (W.H. Rickard, personal communication, 2001). However, when sample volumes are small (5–10 mL), microdistillation equipment is required and the need for more rigorous handling and cleaning procedures can greatly slow the sample preparation process, especially when the number of samples is large (J.A. Volpe, personal communication, 2001).

Recent research in an arid environment (Amargosa Desert near Beatty, Nevada; precipitation 108 mm yr^{-1}) indicates that tritium movement away from the waste

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Abbreviations: SPE, graphite-based solid phase extraction.

source primarily occurs in the gas phase with preferential transport through coarse-textured sediment layers in the 110-m-deep unsaturated zone (Prudic et al., 2000). Models for movement of tritiated water vapor at the site, however, fail to predict the extent of transport indicated by field measurements (Striegl et al., 1996). The work reported here was driven by the need for cost-effective methods to gather plume-scale data for use in the development and testing of tritium transport models. Our preliminary efforts focused on two plant water collection methods: solar distillation of bagged, live branches (Lewis and Burgy, 1964) and vacuum distillation of foliage (Amano and Garten, 1991). Both of these methods were found to be too laborious for use with large numbers of samples. In addition, organic compounds that were transferred with the plant sample water interfered with liquid scintillation counting, causing tritium analyses to be unreliable. These results underscored the need for the development of improved methods. To our knowledge, the work reported here is the first to evaluate a simplified method for detecting tritium contamination in desert shrubs and soil. The results demonstrate that a solar distillation and graphite-based solid phase extraction (SPE) approach provides a simple and effective way to collect and prepare plant water for tritium analysis. In addition, we show that tritium concentrations of plant water collected with the distillation–SPE method compare favorably with those of plant water collected with the standard toluene-extraction method and soil water vapor collected with gas sampling methods.

MATERIALS AND METHODS

Study Area

Plant and soil water vapor samples were collected at the Amargosa Desert Research Site (United States Geological Survey, 1998). The site includes two study areas located near a waste burial facility that is 17 km south of Beatty, NV and 20 km east of Death Valley National Park. One study area is within the 0.4-km buffer zone that surrounds the waste burial facility, and the second study area, hereafter referred to as the distant study area, is located 3 km south of the waste facility. The waste facility has been used for the burial of low-level radioactive waste (1962–1992) and hazardous chemical waste (1970 to present). The study site is in the Mojave Desert ecosystem, one of the most arid regions of the United States. Annual precipitation averages 108 mm. The volume-weighted average tritium concentration in precipitation at the site, based on data from November 1997 to April 2001, is 1.1 Bq L^{-1}. Vegetation in the area is sparse; creosote bush, an evergreen shrub, is the dominant species. Creosote bush is the most abundant shrub of the North American warm deserts, and forms nearly pure stands in many areas (Smith et al., 1997). Surface soils are mapped as the Yermo (loamy-skeletal, mixed, superactive, calcareous, thermic Typic Torriorthent)–Arizo (sandy-skeletal, mixed, thermic Typic Torriorthent) association. The underlying sediments are primarily fluvial deposits. Detailed information on soil and sediment properties is given by Andraski (1996). Depth to the water table ranges from 85 to 115 m below land surface.

The rooting depth of creosote bush generally corresponds with the penetration depth of precipitation, which at the Amargosa Desert site is about 0.75 to 1 m (Andraski, 1997). The penetration depth of precipitation is limited by plant water uptake and a gravelly sand layer (approximately 1 m thick) that underlies the surface soil and impedes downward percolation of liquid water under unsaturated conditions. Root-zone soil water content typically ranges between 0.02 and 0.12 m^3 m^{-3}. Soil water content of the gravelly sand layer is temporally invariant and averages about 0.04 m^3 m^{-3}. In some areas, the dry, gravelly sand layer contains elevated levels of tritium and may be a preferential pathway for tritium movement away from the waste source (Striegl et al., 1998).

Laboratory Tests

Three sample preparation methods and four test waters were used to evaluate the efficacy of the SPE approach for removing constituents that can interfere with tritium analysis. The three sample preparation methods were: (i) none or filter only, (ii) filter plus a 0.5-g SPE column, and (iii) filter plus a 2-g SPE column. The filter prevents clogging of the SPE column and the column removes organic compounds and color. The four test waters were: (i) tritium-free water, (ii) tritium-spiked water, (iii) solar-distilled creosote bush water, and (iv) tritium-spiked solar-distilled creosote bush water. The tritium-free water was from a deep ground water well in southern California. The tritium-spiked water had a concentration of 476 Bq L^{-1} ($\pm$3.6 Bq L^{-1} one-sigma counting uncertainty). The spiked creosote bush water was made by combining equal volumes of tritium-spiked water and solar-distilled creosote bush water. Creosote bush water for these tests was collected in February 2001 from the distant study area where tritium concentrations are at background levels. Thirty plants were sampled by hand-stripping about 200 g of foliage from randomly selected branches. Foliage from each plant was placed into the innermost of two clear, 3.78-L plastic freezer-slider bags (Pactiv Corp., Hefty Products, Del Rio, TX[1]), excess air was pushed out of the bags, and the bags were closed. Sample bags were set on top of a black plastic or plywood sheet and solar-distilled in direct sunlight for about 8 h. Water vapor released from the foliage condensed on the inside surface of the innermost bag. Each bag was spun overhead to force the condensate into one corner, and the condensate (about 15 mL) was transferred to a composite sample bottle by disposable, plastic pipet. The plant water sample was kept in the dark and stored cool (first in an iced cooler, then in a refrigerator) until laboratory tests were run.

Test waters that were filtered before analysis were passed through 47-mm-diameter GF/F glass-fiber filters (0.7-μm nominal pore diameter; Whatman, Maidstone, UK) under vacuum, and the filtrate was collected in 1-L glass bottles. The disposable SPE columns consist of a tube that holds a granular, graphite-based, nonporous-carbon absorbent between two 20-μm polyethylene frits (Supelclean ENVI-Carb; Supelco, Bellefonte, PA). The absorbent has a surface area of 100 m^2 g^{-1} and a particle size of 120 to 140 mesh. Two SPE column sizes were included in the laboratory tests: (i) 0.5 g of sorbent in a 6-mL tube and (ii) 2 g of sorbent in a 12-mL tube. Aliquots of filtered test water were added to each tube until a total of 15 mL had been added. The 15 mL volume was selected because it represents the typical water volume obtained from an individual solar-distilled creosote bush sample. A syringe fitted with a rubber stopper was used to slowly inject air into the top of the SPE tube to move water into and start gravity flow through the sorbent. Water that passed through each

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

column was collected in a 15-mL polysealed glass bottle and stored at 4°C until analyzed. Residual water held in the column following gravity drainage was not collected.

All laboratory tests were run in duplicate. Tritium analyses were done, according to the direct liquid scintillation counting method described by Thatcher et al. (1977), at the USGS Isotope Laboratory in Menlo Park, CA. Samples were counted for 800 min with a liquid scintillation analyzer (Model 2200CA; Packard Instrument Company, Meriden, CT). Organic carbon analyses were done according to the wet oxidation method described by Wershaw et al. (1987) with a carbon analyzer (Model 524B; Oceanography International Corp., College Station, TX). Solar-distilled creosote bush waters collected in March and September 2001 were used to evaluate the effects of preparation method on ultraviolet (UV) absorption. Measurements of UV-absorbing organic constituents were made at 254 nm according to the method described by Eaton et al. (1995) with a UV-visible spectrophotometer (Model 8453; Agilent Technologies, Palo Alto, CA). The organic carbon and UV absorption analyses were done at the USGS National Water Quality Laboratory in Lakewood, CO.

Data were analyzed with one-way analysis of variance (ANOVA) procedures (SAS Institute, 1999) and means were compared with Fisher's least significant difference test (Steel and Torrie, 1980). Before applying ANOVA procedures, residual analyses were used to test assumptions of normally distributed and homogeneous errors, and to determine the need for data transformation. The Shapiro–Wilk W statistic was used to test the assumption of normally distributed experimental errors and residual plots were used to test error homogeneity.

Field Tests

In April 2001, samples of plant water and soil water vapor were collected to compare (i) the tritium concentrations in solar-distilled, solid phase–extracted creosote bush water and toluene-extracted creosote bush water and (ii) the tritium concentrations in solar-distilled, solid phase–extracted creosote bush water and soil water vapor. Results from previous sampling of soil water vapor were used to select field sites anticipated to cover a wide range of plant and soil tritium concentrations. Within individual plants, all foliage samples were collected from randomly selected branches.

Eighteen plants were sampled for solar distillation of foliage according to the procedures described in the previous section. Plant water condensate from each sample was transferred to a 30-mL polysealed glass bottle and refrigerated. Field measurements were made to document the range of ambient and inside-bag air temperatures during the solar distillation process. Ambient air temperatures were measured at the study site weather station. Temperatures inside test-sample bags placed at two different locations on the solar distillation board were measured with small data loggers (TidbiT Model TB132; Onset, Pocasset, MA). One bag was placed adjacent to the outer edge of the board and surrounded on the remaining three sides by other samples; the second bag was placed in the middle of the board and surrounded on all four sides by other samples.

Solar-distilled creosote bush water samples were prepared for tritium analysis with the batch filtration column apparatus shown in Fig. 1. The batch procedure follows the basic filter plus 2-g SPE column method described above, but each individual sample is passed through its own disposable, syringeless filter (Autovial 35; Whatman). The filtering device consists of a stack of three GF/F filters, each with a 0.7-μm nominal pore diameter. The filter–plunger compression board shown in Fig. 1 is advanced downward by simultaneously turning nuts on the two threaded guide rods. Removal of the upper filtration assembly allows access to the SPE columns and sample bottles that are held in the lower column–bottle assembly. When processing 15-mL plant water samples, the volume of residual water held in the 2-g SPE columns following gravity drainage averaged 4.72 ± 0.13 mL ($n = 18$).

Samples for toluene extraction of creosote bush water were collected by hand-stripping foliage from the same 18 plants used for solar distillation. For each plant, about 15 g of foliage was placed into a 60-mL polysealed glass bottle and stored cool (first in an iced cooler, then in a refrigerator). Extraction was done with the toluene distillation method described by Revesz and Woods (1990), but the glassware was modified to allow the sample bottle to be placed directly into the distillation apparatus. Thus, fractionation of the sample was avoided and all plant water contained in the bottle, including that
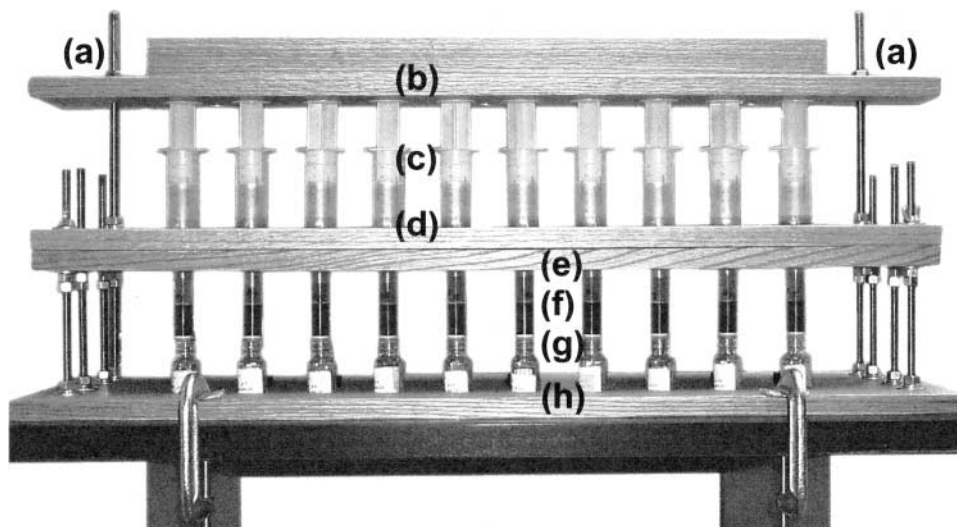

Fig. 1. Apparatus for batch filtration and solid phase extraction. The removable upper filtration assembly (*a–d*) includes: advancement nut and threaded guide rod (*a*), filter–plunger compression board (*b*), syringeless filters (*c*), and base (*d*). The lower column–bottle assembly (*e–h*) includes: column suspension board (*e*), solid phase extraction column (*f*), sample collection bottle (*g*), and base (*h*).

Table 1. Preparation method effects on tritium concentration in four test waters.†

Method	Tritium concentration			
	Tritium-free water	Tritium-spiked water	Creosote bush water	Tritium-spiked creosote bush water
	Bq L^{-1}			
None	0.1a‡ (0.0)	476a (1.7)	12.0a (0.4)	18.8c (6.5)
Filter + 0.5-g SPE§	−0.1a (0.3)	481a (3.4)	2.1b (0.5)	221b (5.0)
Filter + 2-g SPE	0.4a (0.6)	474a (3.4)	2.4b (0.8)	240a (0.8)
	Analysis of variance			
$P > F$¶	0.483	0.186	0.0008	<0.0001

† Mean and standard deviation (in parentheses) calculated from two replications.
‡ Column values followed by the same letter are not significantly different at the 0.05 probability level, as determined by Fisher's least significant difference test.
§ Graphite-based solid phase extraction column.
¶ Denotes the probability that no significant differences exist within a column.

condensed on the walls, was collected in the distillation. Toluene extraction was done at the USGS Isotope Laboratory in Menlo Park, CA.

Samples for foliage water content determination were collected by hand-stripping foliage from the same 18 plants used for solar distillation and toluene extraction. For each plant, about 15 g of foliage was placed into a 60-mL, wide-mouth, polysealed glass bottle and stored cool (first in an iced cooler, then in a refrigerator). Foliage water content was calculated from the difference between fresh weight and oven-dry weight (70°C for 48 h) (Pallardy et al., 1991).

Samples of soil water vapor were collected at 10 sites that were located about 0.5 to 5 m from the center of a sampled plant. Steel gas-sampling tubes (10.3-mm o.d., 5.5-mm i.d.) fitted with removable drive-point inserts (duplex-head nail; 7.4-mm-diameter head, 4.2-mm-diameter shaft cut to 25.4 mm long) were hand-driven to a depth of 0.55 m. The tube then was retracted 0.05 m to remove the drive-point and leave an open space at the bottom of the tube through which soil air was drawn. Soil air was pulled from the steel tube, through Bev-a-line IV tubing (9.6-mm o.d., 6.4-mm i.d.; Thermoplastic Processes, Stirling, NJ), and through a glass freeze trap with a peristaltic pump (Masterflex 07533-40; Cole-Parmer Instrument Co., Vernon Hills, IL) powered by a 12-V deep-cycle battery. The freeze trap was placed in a Dewar flask and chilled in a slurry of solid carbon dioxide (dry ice) and isopropyl alcohol. Air was cooled in the freeze trap, and water vapor was frozen as ice that accumulated on the inside of the freeze trap (Striegl, 1988). The pump was set to a flow rate of 0.8 L min^{-1} and the sample-collection system was frequently serviced to add dry ice and verify the flow rate. On completion of the sample collection, the accumulated ice was thawed and the sample was transferred to a 15-mL polysealed glass bottle.

Sample collection times and water volumes averaged about 22 h and 15 mL, respectively.

Samples of creosote bush water and soil water vapor were analyzed for tritium according to the procedures described in the previous section. The field test data were analyzed with correlation procedures (SAS Institute, 1999) and paired *t* tests (Steel and Torrie, 1980).

RESULTS AND DISCUSSION
Laboratory Tests of the Solid Phase Extraction Method

The ANOVA results and means comparisons for evaluating the effects of laboratory preparation method on tritium concentration of the four test waters are summarized in Table 1. For the tritium-free water and the tritium-spiked water, no significant differences were observed among the three preparation methods. For the spiked creosote bush water, differences among the three preparation methods all were significant, and tritium concentrations increased in the order: no preparation < 0.5-g SPE < 2-g SPE. For the unspiked creosote bush water, however, this trend was not observed because the no-preparation method had an apparent tritium concentration that was erroneously high (12.0 Bq L^{-1}). The liquid scintillation counter is calibrated with clean water, but the magnitude of organics present in the creosote bush water with no SPE preparation (see Table 2) shifted the spectrum and produced spurious counts that raised the apparent tritium concentration to a value

Table 2. Preparation method effects on dissolved organic carbon concentration in four test waters.†

Method	Dissolved organic carbon concentration			
	Tritium-free water	Tritium-spiked water	Creosote bush water‡	Tritium-spiked creosote bush water‡
	mg L^{-1}			
Filter	1.2a§ (1.1)	18a (0.3)	2700a	1600a
Filter + 0.5-g SPE¶	3.1a (0.9)	11b (1.5)	1800b	840b
Filter + 2-g SPE	3.5a (1.0)	3.4c (1.1)	990c	640b
	Analysis of variance			
$P > F$#	0.199	0.0023	0.0001	0.0163

† Mean and standard deviation (in parentheses) calculated from two replications.
‡ Transformed (log$_{10}$) data were used in the analysis of variance because of variance heterogeneity. Resultant means were transformed back to the original scale for presentation in the table; however, resultant standard deviations are not presented because it is not appropriate to transform these values back to the original scale.
§ Column values followed by the same letter are not significantly different at the 0.05 probability level, as determined by Fisher's least significant difference test.
¶ Graphite-based solid phase extraction column.
# Denotes the probability that no significant differences exist within a column.

about five times the actual background concentration indicated by the 2-g SPE value (2.4 Bq L^{-1}; Table 1).

A spike recovery test (Clesceri et al., 1998) was done for each of the three preparation methods. Spike recovery values were calculated using:

$$R = 100(C_s - C_u)/C_e \qquad [1]$$

where R is spike recovery (%), C_s is measured concentration of spiked creosote bush water (Bq L^{-1}), C_u is measured concentration of unspiked creosote bush water (Bq L^{-1}), and C_e is expected concentration of spiked creosote bush water (Bq L^{-1}). The C_s and C_u values are given in Table 1 and the C_e value was calculated as:

$$C_e = (C_{std}V_{std})/V_s \qquad [2]$$

where C_{std} and V_{std} are concentration (476 Bq L^{-1}) and volume (0.1 L), respectively, of tritium standard used to spike the creosote bush water, and V_s is total volume of spiked creosote bush water (0.2 L). Spike recovery for the three methods increased in the order: no preparation (3%) < 0.5-g SPE (92%) < 2-g SPE (100%). It is noted that a spike recovery solution with less dilution would be desirable. However, our supply of creosote bush test water was limited; therefore, the tritium standard was used to produce a total spiked creosote bush water volume that would accommodate all of the planned laboratory tests.

Results show that the filtration plus 2-g SPE column treatment had no effect on measured tritium concentrations for the tritium-free water and the tritium-spiked water. Results also show that a 2-g column was necessary and sufficient for accurate determination of known tritium concentrations in creosote bush water.

The ANOVA results and means comparisons for evaluating the effects of laboratory preparation method on the dissolved organic carbon concentration of the four test waters are summarized in Table 2. For the tritium-free water, no significant differences were observed among the three preparation methods. For the tritium-spiked, creosote bush, and spiked creosote bush waters, the organic carbon concentrations all decreased with increasing SPE. Relative to the filter-only preparation, passage through a 2-g SPE column reduced the creosote bush and spiked creosote bush water organic carbon concentrations by 63 and 60%, respectively. For

the spiked creosote bush water, however, the magnitude of the within-method variability was such that the difference between the two SPE columns was not significant.

The exact mechanisms that interfere with liquid scintillation counting are not completely understood. In addition to spurious counts and quenching caused by dissolved organic constituents, colored substances can quench the scintillations and reduce the tritium count rates by interfering with the energy transfer process (including light absorption). Visual comparisons of the February 2001 creosote bush and spiked creosote bush test samples documented that the 0.5-g SPE column removed some color and the 2-g column appeared to remove all color. Additional creosote bush water was collected in March and September 2001 to further evaluate the effects of preparation method on organic carbon concentration and light absorption; results are summarized in Table 3. We were unable to statistically compare the effects of preparation method on UV absorption because the filter-only and 0.5-g SPE readings exceeded the upper limit of measurement (0.9 cm^{-1}) and sufficient sample was not available to rerun the analyses. Nonetheless, the results demonstrate a substantial removal of UV absorbing material by the 2-g SPE column. The source of the UV absorbing material may be the leaf surface resin of creosote bush, which is composed of lignin- and flavonoid-based compounds that absorb strongly in the UV region (Rhoades, 1977). Within dates, the organic carbon concentrations decreased with increasing SPE, but differences between the two SPE columns were not always significant. The relative magnitude of organic carbon reduction by the SPE columns also varied from date to date. For example, the 2-g SPE column removed 24% of the organic carbon from the March sample, and removed 62% of the organic carbon from the September sample.

The reason for the difference in organic carbon removal between dates is not clear, but it may be due to (i) aging of the sample during storage or (ii) differences in the source chemical composition of the creosote bush samples. First, the March sample was stored for 7 mo and the September sample was stored for 1 mo before being prepared for analysis. If the original source chemicals were the same, sample aging—condensation and

Table 3. Preparation method effects on creosote bush water dissolved organic carbon concentration and ultraviolet (UV) absorption at 254 nm for two sample collection dates in 2001.†

| Method | Dissolved organic carbon concentration | | UV absorption | |
	March	September	March	September
	——— mg L^{-1} ———		——— cm^{-1} ———	
Filter	5000a‡ (67)	5200a (290)	>0.9§ (ND¶)	>0.9 (ND)
Filter + 0.5-g SPE#	4100b (150)	3700b (35)	>0.9 (ND)	>0.9 (ND)
Filter + 2-g SPE	3800b (220)	2000c (87)	0.096 (0.008)	0.262 (0.097)
	Analysis of variance			
$P > F$††	0.0095	0.0009	ND	ND

† Mean and standard deviation (in parentheses) calculated from two replications.
‡ Column values followed by the same letter are not significantly different at the 0.05 probability level, as determined by Fisher's least significant difference test.
§ UV absorption reading exceeded the upper limit of measurement (0.9 cm^{-1}) and sufficient sample was not available to rerun the analyses.
¶ Not determined.
# Graphite-based solid phase extraction column.
†† Denotes the probability that no significant differences exist within a column.

oxidation reactions—during storage might have led to differences in chemical composition and structure of the two samples at the time they were prepared for analysis. This might cause an aged sample to interact less with the carbon in the SPE column and, in turn, reduce the amount of organic carbon removed. Second, creosote bush foliage is coated with large quantities of phenolic resins, and the resin content is greater for immature leaves (26% of dry mass) than for mature leaves (11% of dry mass) (Rhoades and Cates, 1976). If the quantity of a particular source chemical (e.g., polyphenols) varied with sampling date, this may have affected the interference removal efficiency of the SPE column. Further experiments are needed to improve quantitative understanding of the exact mechanisms that interfere with liquid scintillation counting. Until such work is completed, a combination of multiple interference removal tests (e.g., dissolved organic carbon, light absorption, and color) and spike recovery tests can be used to aid selection of a SPE column that is most appropriate for use with the plant species of interest.

Field Tests of the Solar Distillation and Solid Phase Extraction Method

Based on our laboratory test results, the 2-g carbon column was selected for further testing of the solar distillation–SPE method. Data for comparing the tritium concentrations in solar distilled, solid phase–extracted creosote bush water and toluene-extracted creosote bush water collected in April 2001 are shown in Fig. 2. The minimum value (2.4 Bq L^{-1}) was measured for distilled SPE water from a plant at the distant study area where tritium concentrations are at background levels. This value is the same as that for the February 2001 creosote bush laboratory test water that was passed through a filter and a 2-g SPE column (Table 1). The
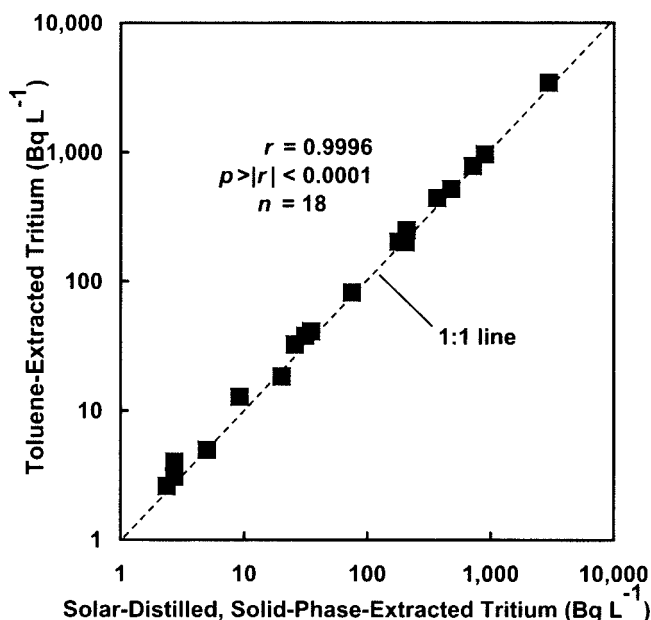

Fig. 2. Relation between tritium concentrations in solar-distilled, solid phase–extracted creosote bush water and toluene-extracted creosote bush water collected in April 2001.

maximum value (3457 Bq L^{-1}) was measured for toluene-extracted creosote bush water collected from a plant near the waste burial facility. Correlation analysis showed a significant, positive relation between tritium concentrations determined by the distillation–SPE method and the toluene-extraction method (Fig. 2). A paired t test showed that the difference between methods was not significant (mean difference = 48.1 ± 116 Bq L^{-1}; $P > |t| = 0.096$). Three of the 18 solar-distilled samples yielded sufficient plant water for duplicate filter + SPE processing and tritium analysis. Mean concentration ± standard deviation (and coefficient of variation), respectively, for each of the replicate tests were: 9.1 ± 0.0 Bq L^{-1} (0%), 34.7 ± 0.2 Bq L^{-1} (0.6%), and 208 ± 1.7 Bq L^{-1} (0.8%). Although the number of replicate tests was limited, the results show that the SPE results were reproducible to within 1%.

The magnitude of the scintillation counting uncertainty (one sigma) varied with tritium concentration. For concentrations > 25 Bq L^{-1}, the uncertainties for both plant water methods averaged ±2% about the measured value. For concentrations < 25 Bq L^{-1}, the average uncertainty was greater for the toluene-extraction method (±25%) than that for the distillation–SPE method (±15%).

Water yield for the solar-distilled samples averaged 0.14 g of water per gram of foliage, whereas water yield for the toluene-extracted samples averaged 0.52 g of water per gram of foliage. The toluene-extraction yield was significantly greater than that for solar distillation ($P > |t| = <0.0001$) and was equal to that for oven drying. The toluene-extraction method relies on the formation of a toluene–water azeotrope to completely remove all water, without isotopic fractionation. The azeotrope boiling temperature remains at 84.1°C until the water is depleted and then the temperature of the solution rises to the toluene boiling temperature of 110°C. In contrast, field measurements made during the solar distillation period showed that ambient air temperature averaged 26°C and reached a maximum of 31°C; average inside-bag temperatures ranged from 49 to 56°C and maximum inside-bag temperatures ranged from 58 to 66°C. Greater inside-bag temperatures were measured for the test sample that was surrounded on all four sides by other foliage samples.

The incomplete removal of foliage water during solar distillation suggests that isotopic fractionation is a source of uncertainty in the distillation–SPE method. Because tritium (^3H) has a lower vapor pressure than protium (^1H), isotopic fractionation will result in the heavier tritium isotope becoming disproportionately concentrated in the liquid water that remains during the evaporation process. The degree of isotopic fractionation is temperature dependent. For example, the α fractionation factor for tritium in liquid and vapor ranges from 1.030 at 100°C to 1.125 at 10°C; at temperatures similar to those measured during solar distillation, the factor ranges from 1.049 at 70°C to 1.065 at 50°C (Ferronsky and Polyakov, 1982). These factors indicate that isotopic fractionation during solar distillation will cause a slight reduction in the measured tritium concen-

trations. Although there was no statistical difference between the two plant water methods, an arithmetic comparison of paired field test data did imply a tendency toward decreased tritium concentrations for the solar-distilled samples. For example, percent difference calculations showed that solar-distilled concentrations were on average 12% less than the toluene-extracted concentrations. The individual percent differences, however, were highly variable and showed that the solar-distilled concentrations ranged from 32% less to 10% greater than the toluene-extracted concentrations. Additional work is needed to evaluate the potential effects of isotopic fractionation on solar-distilled tritium concentrations.

Data for comparing the tritium concentrations in samples of solar-distilled, solid phase–extracted creosote bush water and soil water vapor collected in April 2001 are shown in Fig. 3. Correlation analysis showed a significant, positive relation between plant and soil tritium concentrations (Fig. 3). A paired t test showed that the difference between methods was not significant (mean difference = 139 ± 275 Bq L^{-1}; $P > |t| = 0.146$). For comparison, the toluene-extracted creosote bush water concentrations also correlated closely with soil water values ($r = 0.9757$; $p > |r| < 0.0001$; data not shown) and the difference between methods was not significant (mean difference = 68.3 ± 237 Bq L^{-1}; $P > |t| = 0.386$). Scintillation counting uncertainties (one sigma) for soil water vapor were similar to those for plant water. For soil water concentrations > 25 Bq L^{-1}, the counting uncertainty averaged ±1.5% about the measured value; for concentrations < 25 Bq L^{-1}, the counting uncertainty averaged ±23%.

The solar distillation–SPE method provided a relatively quick and reliable means of collecting and preparing samples for tritium analysis. For example, we have used the distillation–SPE method to collect and prepare more than 100 creosote bush water samples in 7 d (1 d to collect, 1 d to distill, and 5 d to prepare samples using the apparatus shown in Fig. 1). In contrast, the collection and toluene extraction of 100 plant water samples using our available laboratory equipment would require 26 d (1 d to collect and 25 d to extract). Field test results showed that the distillation–SPE method could be used as a reliable indicator of tritium contamination in creosote bush foliage and in root-zone soil water. The significant correlations between distillation–SPE values and toluene-extraction values, and between distillation–SPE values and soil water vapor values, also indicate that empirical relations could be developed to predict plant and soil concentrations from the more simply determined distillation–SPE concentrations.

CONCLUSIONS

This paper reported on the development of a simplified method for detecting tritium contamination in plant foliage and in root-zone soil water in a desert environment. The method entailed collection and solar distillation of plant water from foliage, followed by filtration and adsorption of scintillation-interfering constituents on a graphite-based solid phase extraction (SPE) column. Columns of different size were tested for their interference removal efficiency using measurements of dissolved organic carbon and ultraviolet absorption, and for their effects on recovery of known tritium concentrations. A 2-g SPE column was found to be necessary and sufficient for accurate determination of known tritium concentrations in creosote bush water. Field tests showed that tritium concentrations in plant water determined with the distillation–SPE method did not differ significantly from those determined with the standard, and more laborious, toluene-extraction method or from concentrations in soil water vapor collected using gas sampling methods. Results also indicated that empirical relations could be developed to predict plant and soil concentrations from the more simply determined distillation–SPE concentrations. Thus, the solar distillation–SPE method provides a simple and cost-effective way to identify plant and soil contamination. The method is of sufficient accuracy to facilitate plume-scale mapping and optimize placement of more sophisticated (and costly) monitoring equipment at contaminated sites. Two main sources of uncertainty that can affect the accuracy of the distillation–SPE method and warrant further study are: (i) the exact mechanisms that interfere with liquid scintillation counting and (ii) the effects of isotopic fractionation on solar-distilled tritium concentrations.

Work to date has focused on one desert plant, but the solar distillation–SPE approach may be transferable to other species and environments after site-specific experiments. Tests like those described in this paper can be used to select an appropriate SPE column and determine the accuracy of the method for the species and soil of interest. Depending on the objective and results of such tests, the end-user may have options to use

$r = 0.9758$
$p > |r| < 0.0001$
$n = 10$

1:1 line

Soil-Water-Vapor Tritium (Bq L^{-1})

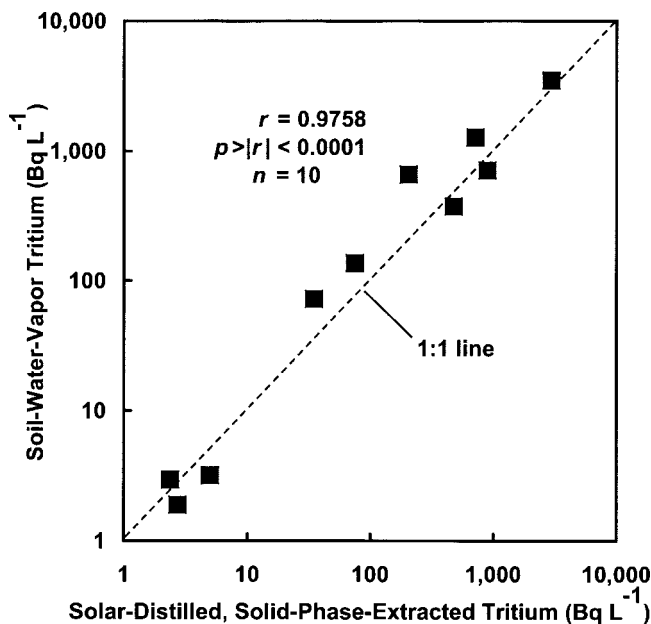Solar-Distilled, Solid-Phase-Extracted Tritium (Bq L^{-1})

Fig. 3. Relation between tritium concentrations in solar-distilled, solid phase–extracted creosote bush water and soil water vapor collected in April 2001.

the method as an indicator or as a predictor of tritium contamination in plants or soil.

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