Estimates of Vadose Zone Drainage From a Capped Seepage Basin, F Area, Savannah River Site

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Abstract Disposal of waste solutions into seepage basins has resulted in large contaminant plumes in groundwaters at many locations. At the F-Area within the Savannah River Site, plutonium was extracted from depleted uranium from 1955 to 1988, with contaminated waters disposed of in seepage basins. Basin 3 was the largest F-Area seepage basin, with the water table typically at about 20 m below the soil surface. The acidic solutions disposed in the basin contained radioactive components (including tritium, ^{129}I, and multiple isotopes of U, Pu, Sr, and Cs), elevated nitrate, and some metals. Contaminants transported into the groundwater are carried toward Fourmile Branch, a tributary to the Savannah River. We developed a two compartment mixing model and used 20 years of groundwater quality data to estimate the post-closure drainage of waste solutions through its vadose zone, into the unconfined aquifer. Tritium, nitrate, and specific conductance were used as tracers in the mixing model to estimate drainage rates. Our calculations indicate that early stages of post-closure waste drainage occurred with high water fluxes ($\approx$ 0.5 m y^{-1}), and quickly declined. However, even 20 years after basin closure, drainage continues at a low rate of several cm y^{-1}. While the magnitude of this late stage vadose zone drainage rate is low, its impact is large because of the high concentrations of contaminants it continues to supply to the groundwater. These estimated drainage fluxes can help constrain predictions on the waste plume behavior, especially with respect to its emerging trailing gradient and anticipated time scales suitable for monitored natural attenuation. The methodology presented here requires only groundwater monitoring data and a small number of well-constrained input quantities. Thus, this approach can be useful for gaining better understanding of contaminant dissipation at other locations as well, especially where the hydrogeological setting is relatively simple.

Introduction

Many mining and ore milling sites, and nuclear weapons production facilities have used large volumes of water, and consequently require discharge of similarly large volumes of contaminated wastewaters. In the case of ore milling, mill tailings were commonly discharged over large areas in slurry form, with waste solutions draining into underlying sediments and groundwaters (Fernandes et al., 1995; Narasimhan et al., 1986). Past practices used for disposal of some contaminated waters at nuclear weapons production facilities included discharge into soil, the vadose zone, and underlying groundwaters via permeable seepage basins (Arai et al., 2007; Denham and Vangelas, 2008; Kaplan et al., 1995; Shevenell et al., 1994). Whether groundwater at these sites is actively remediated to accelerate removal of contaminants, or untreated and subjected to monitored natural attenuation, it is important to determine the timescale over which contaminant concentrations in the trailing plume edge diminish below their regulatory levels (Denham and Vangelas, 2008). A key factor controlling the dynamics of the trailing plume edge is the timeframe for cessation of drainage from the contaminated vadose zone. This timeframe has two limiting conditions, depending on whether the upper boundary of the contaminated soil or sediments is sealed with a truly impermeable cap, or open to continued infiltration and drainage of rainfall or snowmelt. With respect to engineered surface seals, complete diversion of precipitation inputs will allow waste solutions to approach hydrostatic equilibrium in the vadose zone. However, net seepage beyond the perimeter of caps, combined with leaching of laterally distributed vadose zone contaminants can compromise the ideal behavior.

Although the importance of determining seepage rates from vadose zones contaminated by past waste disposal practices is recognized, it is often not attempted because of large uncertainties in (1) hydrologic properties and boundary conditions, (2) vadose zone geochemical processes and parameters, and (3) the history of waste composition and disposal volumes. Thus, a need exists for development of simple approaches that rely only on relatively well-constrained inputs to determining vadose zone drainage rates. In this study, we present such an approach based on representative concentrations of nonreactive components in waste solutions, upstream background groundwater, and downstream (contaminated) groundwater. In addition to these inputs, the only other parameters needed are waste basin dimensions, thickness of the sampled aquifer, and groundwater velocity. With these inputs, we developed a simple mixing model for relating downstream groundwater quality to fluxes from uncontaminated groundwater and waste basin drainage.

Site description

Beginning in the 1950's, materials used for nuclear weapons were produced at the Savannah River Site (South Carolina, USA). Within the F-Area of the Savannah River Site, waste process waters containing radioactive components (including tritium, ^{129}I, and multiple isotopes of U, Pu, Sr, and Cs), elevated nitrate, and some metals (Hg, Pb, Cd) were discharged into seepage basins from 1955 up to 1988 (Kaplan et al., 1995; Serkiz et al., 2007). An overview map of the F Area basins is shown in Figure 1. Basin 3, with an areal extent of 94 m by 219 m (long axis oriented north-south), a volume capacity of 8.3x10^{4} m^{3}, received the largest quantities of waste solutions in the F Area (Killian et al., 1987). The upper water table has an average depth about 20 m below the soil surface. The shallow unconfined aquifer has an average thickness of about 10 m within the Irwinton Sand member of the Eocene Dry Branch Formation (Denham, 1995), with measured hydraulic conductivities ranging from 0.1 to 10 m day^{-1} (Killian et al., 1987). Underlying this upper aquifer is the thin (2.5 m average thickness (Killian et al., 1987)), lower permeability Tan Clay (Twiggs Clay, also a member of the Dry Branch Formation). Estimated shallow aquifer (pore water) flow rates in the vicinity of Basin 3 have spanned a wide range, with earlier values as low as 29 m y^{-1} (Chase, 1995), and 41 to 61 m y^{-1} (Killian et al., 1987). More recent reports indicate that groundwater velocities are in the range of 104 to 143 m y^{-1} (Chase, 1999). The piezometric surface slopes to the south at Basin 3 (Chase, 1995; Killian et al., 1987), then is directed to the south-southeast, consistent with the measured tritium plume (Chase, 1995; Jean et al., 2004). Following cessation of waste disposal in August 1988, the F-Area basins were capped, and closure activities were completed in January 1991 (EPA, 1993). Groundwater samples have been regularly collected from an array of monitoring wells. We used groundwater chemistry data from Well FSB 95DR, located 21 m immediately down-gradient of Basin 3 (screened interval of 6.1 m), to represent the mixture of background and basin drainage waters. This well has been monitored from February 1991 (2.5 years after Basin 3 closure) to the present (Denham and Vangelas, 2008; SRNL, 2011).

Conceptual Model and Method

In order to estimate time trends in F Basin 3 seepage into the shallow aquifer, a two-source mixing model was developed and applied to groundwater chemical data immediately down-gradient from the basin (Figure 2). For simplicity, this model assumes constant background concentrations $C_{b,i}$ [M L^{-3}] of the i^{th} nonreactive chemical species in the up-gradient groundwater flowing at a constant volumetric flow rate of $V_{b,w}$ [L^3 t^{-1}] into the region underlying Basin 3 (here, M, L, and t denote dimensions of mass, length, and time, respectively). The resultant mixture of pristine and contaminated waters has been characterized through periodic sampling and analyses of well FSB 95DR waters. The nonreactive components selected for this study are tritium (^{3}H, decay-corrected), nitrate, and specific conductance (EC). Christensen et al. (Christensen et al., 2010) reported isotopic analyses indicating that denitrification is insignificant within the F-Area waste plume groundwaters. Lack of significant denitrification is also suggested by its well-correlated behavior with ^{3}H concentrations observed in the F-Area plume. Thus, nitrate appears to be a suitable nonreactive tracer. Use of specific conductance as an inert tracer assumes that precipitation-dissolution reactions impart negligible changes to the solution ionic strength.

For a hydraulic head gradient aligned with the long (north-south) axis of Basin 3, the volumetric flow rate of background waters affecting the monitoring well samples, $V_{b,w}$, is equal to the product $W_w B_w J_b$, where W_w and B_w are the horizontal and vertical cross-section dimensions of the flow tube within the unconfined shallow aquifer, and J_b [L t^{-1}] is the constant Darcy velocity of the groundwater. The flow tube height B_w is equated with the vertical distance spanned by the FSB 95DR well screen. The flow tube width W_w is somewhat arbitrary because it cancels out in later calculations. Note that the flow tube cross-section $W_w B_w$ samples the mixing of drainage and background waters within this fixed cross-section, but does not necessarily contain the whole vertical extent of the plume exiting Basin 3. The likelihood that the vertical extent of the plume is captured within B_w is discussed later. The constant mass transport rate of the i^{th} chemical species entering with the background groundwater destined for the FSB 95DR sampling zone is thus $C_{b,i} V_{b,w} = C_{b,i} J_b W_w B_w$.

Similar approximations are employed for characterizing the average downward flux of waste solutions through the vadose zone, with the exception that this seepage rate is time-dependent. Thus, the volumetric flow of waste solutions destined for the shallow aquifer sampling zone is represented as $V_{o,w}(t) = W_w L J_o(t)$, where L is the basin length (≈ 219 m), and

$J_o(t)$ [L t^{-1}] is the area-averaged, time-dependent seepage velocity. We further assume that suitable values of representative source zone concentrations of the i^{th} nonreactive chemical species $C_{o,i}$ can be identified based on historical records. Selecting values of representative $C_{o,i}$ is difficult because of the complex, highly variable composition of the waste solutions. Nevertheless, approximate values for $C_{o,i}$ are available from reports on waste stream chemistry (Killian et al., 1987; Ryan, 1984). It is worth noting here that at the Savannah River Site, rainfall dilution and evaporative concentration of solutes in open waste basins is relatively insignificant on an annual basis because evaporation from large water surfaces is nearly balanced by precipitation (Flach, 2002). Thus, with these approximations, the transport rate of the i^{th} chemical species from Basin 3 into the shallow aquifer sampled by well FSB 95DR is $C_{o,i}V_{o,w}(t) = C_{o,i}J_o(t)W_wL$. The volumetric flux immediately downstream from Basin 3 in the FSB 95DR flow tube is $V_\Sigma(t)$, equal to $V_{b,w}$ plus the path-weighted (over distance L) volumetric basin seepage. In other words, waters sampled at the downstream monitoring well at any given time are affected by basin fluxes entering the groundwater over the time interval required for groundwater to traverse under the basin. The pore water velocity in the shallow aquifer is $v_p = J_b/n_e$, where n_e is the effective porosity of the aquifer. Thus, the basin flux contributing to $V_\Sigma(t)$ is characteristic of drainage entering the shallow aquifer over a range of earlier times, with the oldest input associated with seepage from the basin's upstream edge, entering about L/v_p before time t. The time-integrated basin flux is approximated as $V_{o,w}(t\text{-}\Delta t)$, with Δt equated to half the groundwater travel time required to traverse the distance L. Thus, $\Delta t \approx 0.5n_eL/J_b = 0.5L/v_p$, which is about 0.9 year for $v_p \approx 124$ m y^{-1}. Given mass conservation of nonreactive solute tracers in the basin-affected flow tube (negligible exchanges with laterally adjacent groundwater), the concentration of the i^{th} nonreactive species in the immediately down-gradient groundwater, $C_{\Sigma,i}(t)$, and the down-gradient volumetric flow rate $V_{\Sigma}(t)$, are related to the background and basin values through

$$C_{b,i}V_{b,w} + C_{o,i}V_{o,w}(t-\Delta t) = C_{\Sigma,i}(t)V_{\Sigma}(t) \tag{1a}$$

and

$$C_{b,i}V_{b,w} + C_{o,i}V_{o,w}(t-\Delta t) = C_{\Sigma,i}(t)\left[V_{b,w} + V_{o,w}(t-\Delta t)\right] \tag{1b}$$

It should be noted that $C_{\Sigma,i}(t)$ are average concentrations resulting from flow-weighted contributions of pore waters entering along the vertical extent of the monitoring well. Groundwater chemical compositions within the plume are actually vertically stratified, as reflected in analyses of core samples (Johnson, 1995; Wan et al., 2012). Such stratification is consistent with the sediment depositional structure and small values (ca. 10^{-2} m) associated with transverse dispersivities (Gelhar et al., 1992). It should be noted that well FSB 95DR traverses only the upper 61% of the aquifer's thickness, hence the representativeness of $C_{\Sigma,i}(t)$ values needs to be considered. Other studies of the F Area upper aquifer plume (Johnson, 1995; Wan et al., 2012) indicate that concentrations of contaminants are maximum at intermediate depths, and trend to lower concentrations toward the water table and toward the Tan Clay. However, at FSB-95DR highest concentrations of some contaminants are generally observed near the top of the saturated zone. Therefore, $C_{\Sigma,i}(t)$ values measured in well FSB 95DR represent the upper 6.1 m of the aquifer immediately downstream of Basin 3, and also probably capture characteristic concentrations of contaminants in the aquifer at this location. Consideration of hydraulic properties described later also indicates that well samples reflect suitable mixtures of basin drainage and background groundwater. In particular, capture of the mixing of basin drainage and background groundwater by well FSB-95DR is supported by the fact that product of the maximum drainage rate times L, divided by the background aquifer Darcy velocity is less than B_w. Rearranging equation 1 gives $F(t)$, the fraction of basin seepage flux contributing to the groundwater flux observed at the downstream boundary of the basin

$$F(t) = \frac{V_{o,w}(t - \Delta t)}{V_\Sigma(t)} = \frac{C_{\Sigma,i}(t) - C_{b,i}}{C_{0,i} - C_{b,i}} \tag{2a}$$

When $C_{o,i} > C_{\Sigma,i}(t) >> C_{b,i}$, as is usually the case for contaminants,

$$F(t) = \frac{C_{\Sigma,i}(t)}{C_{0,i}} \tag{2b}$$

Equation 2b is useful for determining how small the basin's fractional volumetric flux $F(t)$ must be before regulatory goals are achievable for nonreactive contaminants originally present at very high $C_{o,i}$. When $C_{o,i}$ is X times greater than a Maximum Contaminant Level (MCL), the MCL is reached only when $F(t) \leq F^* = X^{-1}$, where F^* denotes the threshold fractional basin flux at which the MCL is attained. When X is very large (e.g. > 100), drainage in the contaminated vadose zone must diminish to extremely low rates (e.g. to $F^* < 0.01$) before the MCL is reached.

Converting volumetric fluxes to flow per unit area gives the estimated time-dependent drainage flux density

$$J_0(t - \Delta t) = \frac{B_w}{L} n_e v_p \left[\frac{C_{\Sigma,i}(t) - C_{b,i}}{C_{0,i} - C_{\Sigma,i}(t)} \right] \tag{3}$$

Note that the calculated basin drainage rate depends directly on the product $n_e v_p$ (i.e., the upstream Darcy flux), and that uncertainties are associated with both porosity and velocity. For the calculations to be presented, n_e is set to 0.25, a value used in some Savannah River Sites groundwater flow modeling (Flach and Harris, 1997). Using known dimensions B_w (6.1 m) and L (219 m), estimated n_e (0.25), estimated v_p (124 m y^{-1}, the midpoint value within the range reported by Chase, 1999), known chemical composition of the background groundwater, representative concentrations for Basin 3 waste solutions, and measured chemical compositions over time in shallow groundwater immediately downstream of Basin 3 (SRNL, 2011), estimates of drainage fluxes can be obtained with equation 3 for any waste species that exhibit negligible reactivity. Thus, (decay-corrected) tritium concentrations, NO_3^- concentrations, and salinity (EC) measured on FSB 95DR groundwater samples collected over 20 years (Figure 3) will be used to independently generate $J_o(t)$. It should be noted that some fluctuations in trends shown in Figure 3 may be related to past pump-and-treat activities conducted slightly upstream of Basin 3. These activities did not significantly change subsurface inventories of ^3H and nitrate, and appear to have had little impact on overall trends of declining contaminant concentrations.

Input parameters for seepage basin influent and background groundwater concentrations are listed in Table 1. Values for $C_{o,i}$ for tritium and nitrate in Table 1 were obtained from Killian et al. (Killian et al., 1987). It is unclear whether the 1,220 mg L^{-1} value for average nitrate in Table 1 of Killian's report refers to NO_3^- or only N of nitrate. Therefore, nitrate values of 20 mM and 87 mM are listed here. As shown later, the interpretation as N of nitrate yields results in very good agreement with tritium-based calculations. For the case of C_o for specific conductance (EC), no reported values were located. Therefore, the average waste solution EC was estimated with a linear regression of the EC of $NaNO_3$ solutions, 110 µS cm^{-1} per mM, scaled up by 5% to reflect the presence of minor contributions from other ions. Thus, the estimated EC for the representative waste solution in Table 1 were obtained by multiplying nitrate values by 115.5 µS cm^{-1} per mM. Measurements of Na^+ in waste solutions and groundwaters appear to have been obtained much less frequently, and therefore were not used in our calculations. Nevertheless, the estimated average waste solution of Na^+ concentration of 34 mM provided by Killian is included here to support later arguments that the overall ionic strength of these waste solutions was likely significantly greater than 20 mM. It should be noted that with respect to the analyses reported on the FSB 95DR groundwater data, nitrate was clearly reported as N of nitrate, and EC values were directly measured. Also shown in Table 1 are MCLs for ^{3}H and NO_3^-, and the F^* required to reach these goals. Note that these F^* are on the order of 10^{-2} and less, indicating that vadose zone drainage fluxes will have to diminish to < 1% of upper aquifer fluxes in order to reach water quality goals for ^{3}H and NO_3^-. Although radioactive decay of ^{3}H helps reach its MCL more quickly than through dilution alone, it still will require a long time for attenuation because its concentrations in the waste waters were initially extremely elevated.

Finite drainage volume constraint

Mass (volume) balance of water drained from the vadose zone provides a useful constraint on drainage rates calculated using equation 3. If the capping of Basin 3 resulted in an effectively impermeable upper boundary, then integration of the drainage flux (equation 3) over time should not exceed the drainable volume at hydrostatic equilibrium with the underlying water table. On a per unit horizontal area basis, the drainable column of water from the vadose zone is

$$H = \int_0^d \left[\theta_s - \theta(z)\right] dz \qquad (4)$$

where $\theta(z)$ is the local volumetric water content [$L^3\ L^{-3}$] at hydrostatic equilibrium, θ_s is its value at saturation, z is the vertical distance relative to the water table, and d is the extent of the contaminated vadose zone. While equation 4 could be formulated with respect to matric head (ψ) instead of elevation above the water table, likely heterogeneity in $\theta(\psi)$ will prevent simple integration of a single function. Although vadose zone hydraulic properties are not available for the F-Area, some measurements have been obtained for sediment cores collected from the nearby E-Area of the Savannah River Site (Phifer et al., 2006). A wide range of drainage characteristics was reported, but for purposes of estimating an upper limit in possible vadose zone drainage, properties of the sandier sediments are more useful. Moisture characteristics for these coarser media exhibit average saturations of about 45% over the interval -20 m $< \psi < 0$ m. Thus, drainage of 55% of the total porosity (0.39) within a 20 m vadose zone amounts to 4.3 m of water per unit area. It should be noted that seepage through the cap and net infiltration just beyond the perimeter of the basin cap will contribute to displacement of some contaminated vadose zone waters. These effects and simple molecular diffusion will deplete tracer constituents from the vadose zone in the extremely long time limit. Nevertheless, the estimated hydrostatic equilibrium drainage volume serves as an independent check on the reasonableness of tracer-based calculated results. These calculated drainage amounts are obtained by integrating (summing) incremental drainage steps determined from equation 3.

An estimate of the initial drainage during the 2.5 years between basin closure and FSB-95DR sampling needs to be added to this monitoring well-based time-integrated drainage. This initial flux can be calculated as simply the product of a representative saturated hydraulic conductivity K_{sat} times the 2.5 year interval, because saturated unit gradient (gravity) drainage dominates within the thick “vadose” zone during the early stage. Based on their measurements on upper vadose zone cores from the E-Area, Phifer et al. obtained global estimated K_{sat} values of 0.44 and 0.82 m y^{-1} (Phifer et al., 2006). Using these values leads to estimates of 1.1 and 2.1 m of vadose zone drainage during the 2.5 years prior to initial monitoring at FSB 95DR.

The elapsed time required to reach hydrostatic drainage equilibrium can be estimated following DiCarlo (DiCarlo, 2003), using these global K_{sat} values and van Genuchten parameters for E Area vadose zone sediments (Millings et al., 2011). The full range of van Genuchten parameters included in Table 4 of that report yields a wide range of possible equilibration times when combined with DiCarlo's analysis (years to centuries). However, recognizing that the tabulated values reflect layered heterogeneity of the sediment deposition, drainage equilibrium times of several decades appear quite likely. Step-wise integration (summation) of equation 3 mentioned previously will also be compared for consistency with this time scale.

Results and Discussion

Applying the previously described input parameters and the continuous record of groundwater composition at well FSB 95DR to equation 2 yields time trends of *F(t),* the estimated fractional volumetric contributions of basin drainage to the overall flux immediately downstream of the basin. These results are shown in Figure 4a and 4b, for *F(t)* calculations assuming the basin nitrate concentrations reported in Killian et al. (Killian et al., 1987) represented mg L^{-1} of NO_3 and NO_3-N, respectively. Note that the tritium (^3H) *F(t)* curves are identical in both plots, and predict that basin drainage contributed about 33% to the downstream groundwater flow during initial monitoring (2.5 years since basin closure), and currently contributes less than 3%. The nitrate and EC *F(t)* trends are internally consistent because of the assumption that the original waste solutions were primarily nitrate salts, and because nitrate remains the dominant anion in the waste plume. It should be noted that EC is treated as being linearly related to ionic strength in these analyses, whereas this approximation is better suited to the lower concentration range of measurements. The shaded region of the Figure 4a graph outlines calculated *F(t)* > 1, which are not physically possible. These anomalous calculations indicate that the nitrate concentrations representative of the Basin 3 waste stream must have been significantly higher than 20 mM. Recall that estimated average Na^+ concentration reported for the waste stream was 34 mM, indicating that the nitrate concentration was probably at least this high. Estimates based on the alternative interpretation of the representative waste nitrate concentration being that of nitrogen only, i.e. NO_3-N, are shown in Figure 4b (smaller y-axis range). With this interpretation, no anomalously high initial fractional contributions from basin drainage are obtained. Furthermore, values for *F(t)* based on these basin nitrate and EC values are in fairly good agreement with the tritium-based calculations. Note that although fractional contributions of vadose zone waste solution drainage at later stages are low (typically < 10%), their impact remains high (Figure 3) because contaminant concentrations in source solutions are many orders of magnitude greater than their background levels (Table 1). Recall that equation 2b shows *F(t)* is about equal to $C_{\Sigma,i} / C_{o,i}$., and that this must diminish to very low values of F^* in order to reach MCLs of ^3H and NO_3^-.

Calculated time trends of Basin 3 seepage rates entering the shallow aquifer based on equation 3 are shown in Figure 5, using tritium data and the two interpretations of average basin nitrate concentration. The tritium-based estimates indicate that early stage drainage fluxes are about 0.46 m y^{-1}, and have declined to less than 0.05 m y^{-1}. In contrast, the calculations based on 20 mM nitrate are again anomalous (Figure 5a). The shaded area at early times corresponds to fractional fluxes greater than unity, resulting in negative values of calculated basin drainage fluxes. This initial interval is followed by very high drainage fluxes on the order of 10 m y^{-1}, which later declines to about 0.8 m y^{-1}. The unrealistically large magnitude of such drainage fluxes is evident from the fact that the Basin 3 vadose zone is only about 20 m thick, and that its K_{sat} is < 1 m y^{-1}. When the characteristic nitrate concentration in the waste stream is assumed to be 87 mM, much more reasonable drainage fluxes are obtained (Figure 5b). This interpretation also leads to values in better agreement with those obtained based on the tritium data. Thus, the higher value for average Basin 3 nitrate concentration is supported by fractional flux and drainage flux calculations, and by consistency with similar tritium-based estimates. Overall, these calculations indicate that contaminants from the vadose zone are continuing to drain into the aquifer, even 20 years after closure of the seepage basin.

The cumulative estimated drainage fluxes based on the tritium, nitrate (with source nitrate concentration of 87 mM), and EC are shown in Figure 6, with the time scale extended back to -2.5 years, the approximate time of Basin closure. Cumulative drainage predictions using 20 mM as the characteristic basin nitrate concentration could not be obtained because of the anomalous values at early times, leading to negative drainage fluxes. The two steady flow rates equivalent to the vadose zone K_{sat} values of 0.44 and 0.82 m y^{-1} were used for the earliest time interval, as described previously. The fair continuity of slopes in the vicinity of groundwater monitoring time zero (2-24-91) indicate that these assumed profile-averaged K_{sat} values predict early stage fluxes that are consistent with those calculated from tracer concentrations. Note that the lower K_{sat} value of 0.44 m y^{-1} is practically identical with our estimated early stage drainage flow rate of 0.46 m y^{-1}, hence displays the more continuous slope at time zero in Figure 6. The horizontal strip at y = 4.3 m represents the predicted cumulative drainage for hydrostatic equilibrium. Note that the tritium-based curves are leveling off (diminishing flow rates) near this predicted limit, with the use of the higher initial flux slightly exceeding the estimated drainable flux, while the lower initial flux is still approaching this predicted value. In contrast to the later stage tritium trends, the nitrate-based results indicate more gradual decreases in drainage rates, averaging about 0.05 m y^{-1} over the most recent 5 years. Uncertainties in the assumed nitrate concentrations for the basin and for the background groundwater probably contribute to this result, because the measurements do show a general decline in nitrate concentrations over time (Figure 3). More reliable drainage estimates are made when $C_{o,i}$ and $C_{b,i}$ of tracer species have very different magnitudes. As seen from values in Table 1, $C_{o,i}/C_{b,i}$ for ^{3}H (4.3×10^4) are much larger than that of nitrate (1.0×10^3). Incomplete diversion of rainfall infiltration may also contribute to advection of waste solutions to a greater extent than predicted from hydrostatic equilibrium (Albright et al., 2006). Based on the recent 5 years nitrate-based drainage, an upper limit on cap leakage would be about 0.05 m y^{-1}. Additional inputs of more concentrated nitrate solutions from deeper groundwaters might also influence the FSB 95DR samples, although this was not indicated by the tritium trends. Overall, the calculations of cumulative drainage indicate that most of the drainable (to hydrostatic equilibrium) contaminated pore waters have already entered the upper aquifer, but a small fraction currently remains and will continue to discharge at progressively slower rates. The asymptotic approach to apparent drainage equilibrium within the time frame of decades is consistent with predictions based on DiCarlo's method described earlier.

Conclusions

We developed an approach for estimating drainage rates from a contaminated vadose zone into underlying groundwater, based on tracer concentrations measured in a downstream monitoring well and representative tracer concentrations in the original waste water and background groundwater. The methodology was applied to the contaminant plume originating from Seepage Basin 3 in the F-Area of the Savannah River Site. Tritium in Basin waste solutions served as the most suitable tracer for this approach, while uncertainties in representative waste solution nitrate concentration and specific conductance made these components less reliable.

Calculations indicate that even 20 years after closure of the seepage basin, vadose zone drainage still contributes a small fraction of the local aquifer flow. This small fraction continues to have a large impact on groundwater quality because its contaminant concentrations are orders of magnitude greater than background levels. Simple hydraulic estimates of initial (pre-monitoring) vadose zone drainage volumes and equilibrium drainage volumes were found to be reasonably consistent with calculations based on tracer concentrations. These results show that drainage from deep contaminated vadose zones can continue to compromise groundwater quality for decades after cessation of waste discharge. Further investigations can lead to a clearer understand on the trailing edge of this plume. Measurements of Basin 3 vadose zone hydraulic and geochemical properties could contribute to improved understanding of the system, especially when appropriately utilized in reactive transport modeling. Nevertheless, the magnitude of long-term vadose zone drainage is evident from the analysis presented here. The general understanding developed from this work is that highly contaminated, thick vadose zones provide large and very long-term sources for post-closure contaminant transport into underlying aquifers. In a related study (Wan et al., 2012), calculations are presented showing that nitrate and tritium concentrations in F-Area groundwaters near Basin 3 are likely to remain above their MCLs for decades into the future.

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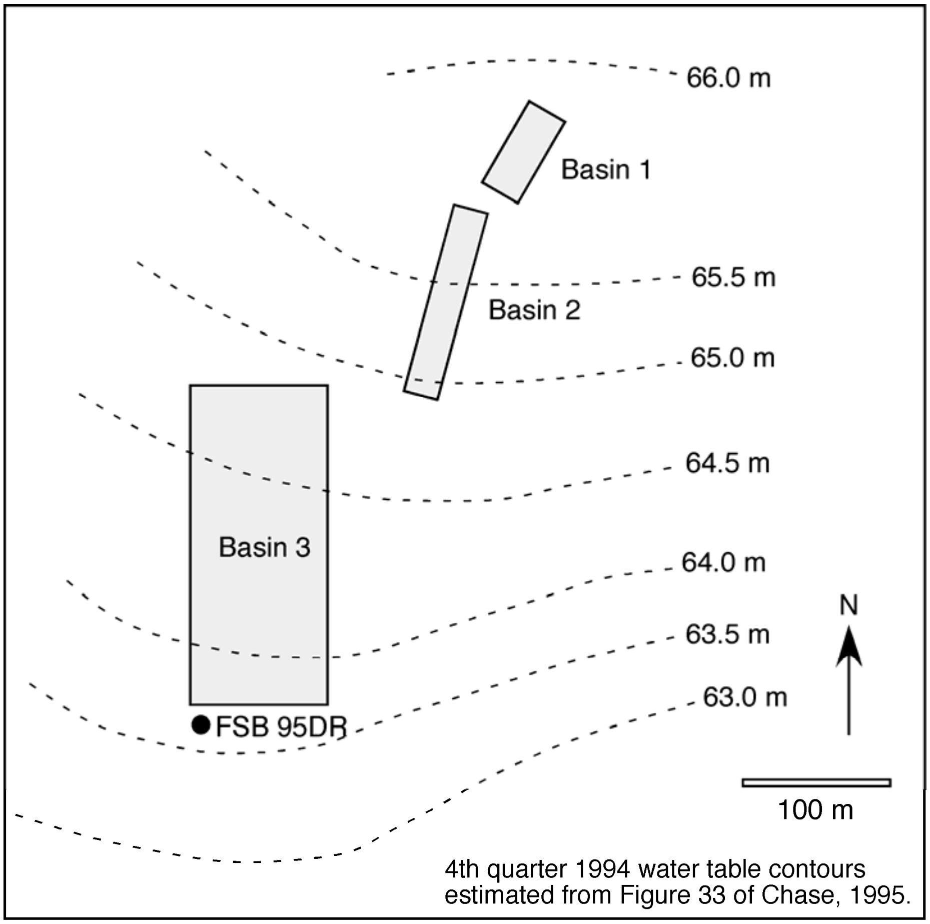
Table 1. Characteristic concentrations of solutes in basin waste stream and in background groundwater. The $C_{b,i}$ values were taken from Serkiz et al. (Serkiz et al., 2007). The tritium activity in the waste solution is from Killian et al. (Killian et al., 1987), of 101,609 nCi L^{-1}, decay-corrected to the date of the first groundwater sample analysis from FSB 95DR on 2-24-91. F^* represent the critical F at which the regulatory goal (MCL) is met. [a]Note that this F^* does not include radioactive decay of ^3H. Nitrate and Na^+ concentrations in the waste solution were based on the estimated average values in Killian et al.

constituent	$C_{b,i}$	$C_{o,i}$	**MCL**	F^*
Tritium, nCi L^{-1}	2	85,800	20 (4 mrem y^{-1})	0.0002[a]
Nitrate, mg L^{-1}	1.2	1,220	10	0.008
Nitrate, mM	0.02	20 or 87	0.71	0.04 or 0.008
Specific conductance, μS cm^{-1}	5	2,310 or 10,050		
Sodium, mM		34		



4th quarter 1994 water table contours
estimated from Figure 33 of Chase, 1995.

Figure 1. Map of Savannah River Site, F Area seepage basins and piezometric surface, from Chase (1995).

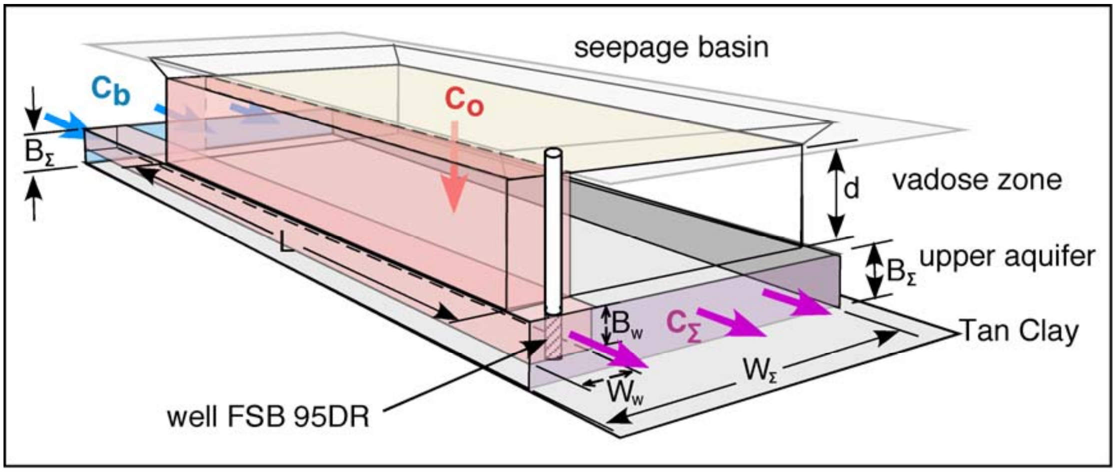


Figure 2. Conceptual model of Basin 3 (length *L*, total width W_Σ) interactions with shallow groundwater (total thickness B_Σ). The background shallow groundwater provides a steady influx of solutes at concentration C_b. The Basin 3 vadose zone drains contaminants at concentration C_o, in a time-dependent manner. The tracer concentrations at the down-gradient well FSB 95DR are assumed to reflect complete mixing of basin drainage and background groundwaters within the well's screened thickness B_w and a transverse width W_w.

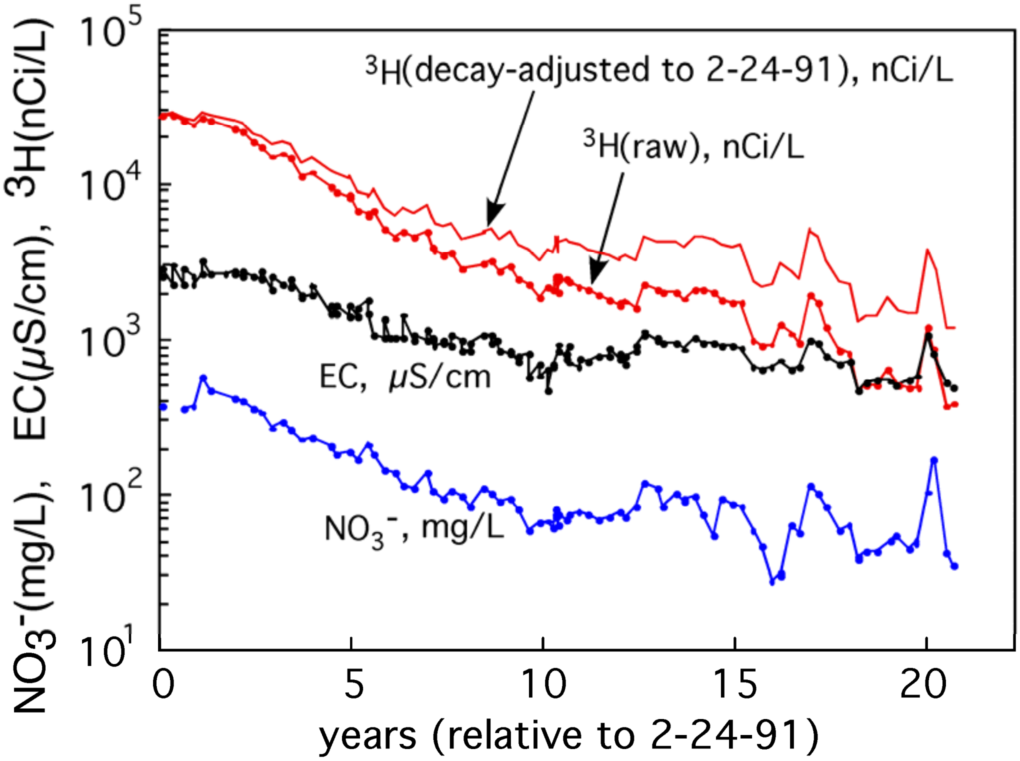


Figure 3. Time trend in Well FSB 95DR components used as tracers for calculating drainage rates. The raw tritium activities were converted to equivalent activities referenced to monitoring time-zero (2-24-91) with the tritium half-life of 12.3 years. Data are from (SRNL, 2011).

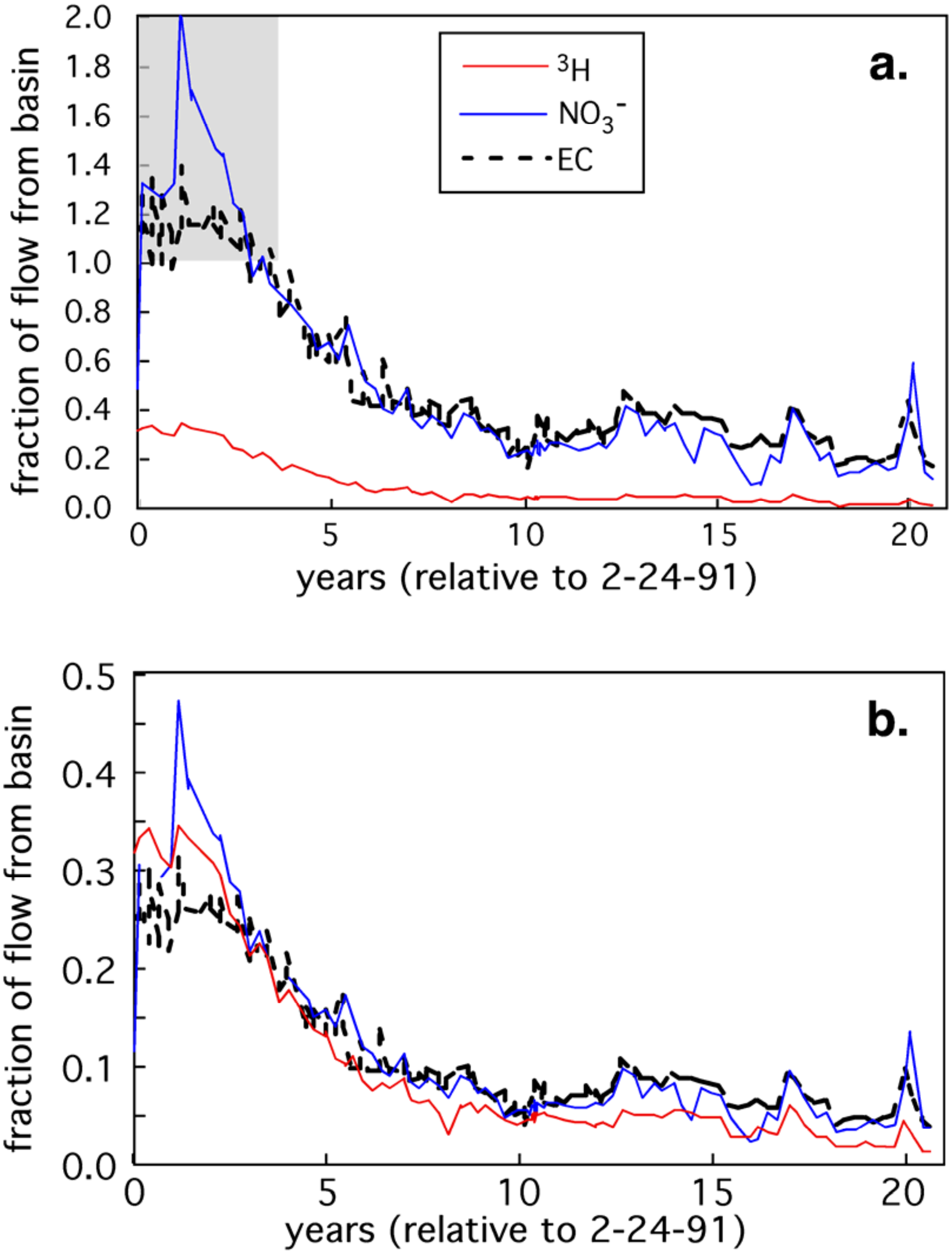


Figure 4. Calculated *F(t)*, volume fraction of downstream flow attributed to Basin 3 seepage, based on an average waste nitrate concentration of **a.** 20 mM, and **b.** 87 mM.

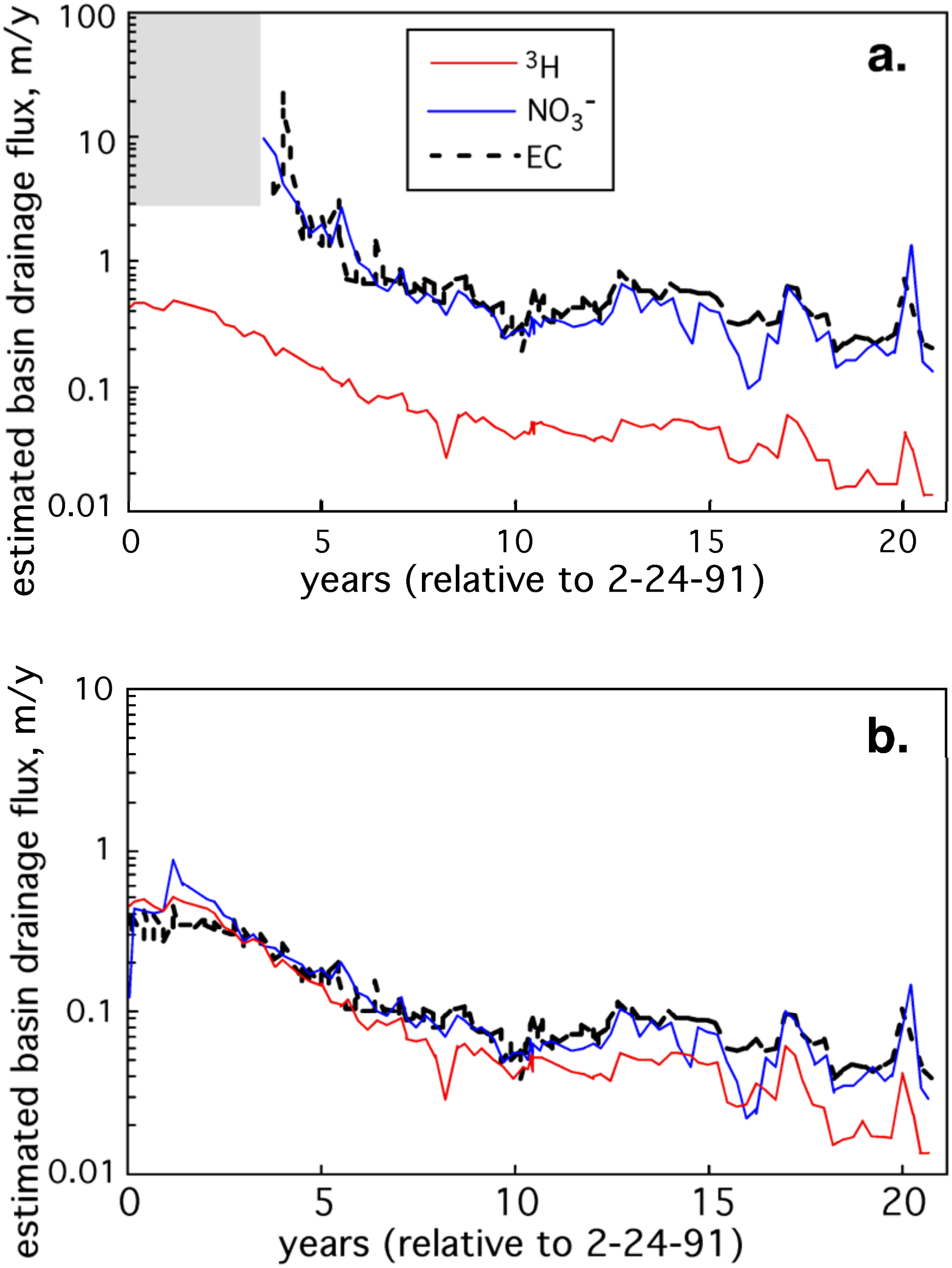


Figure 5. Estimated Basin 3 seepage fluxes into water table, based on an average waste nitrate concentration of **a.** 20 mM, and **b.** 87 mM.

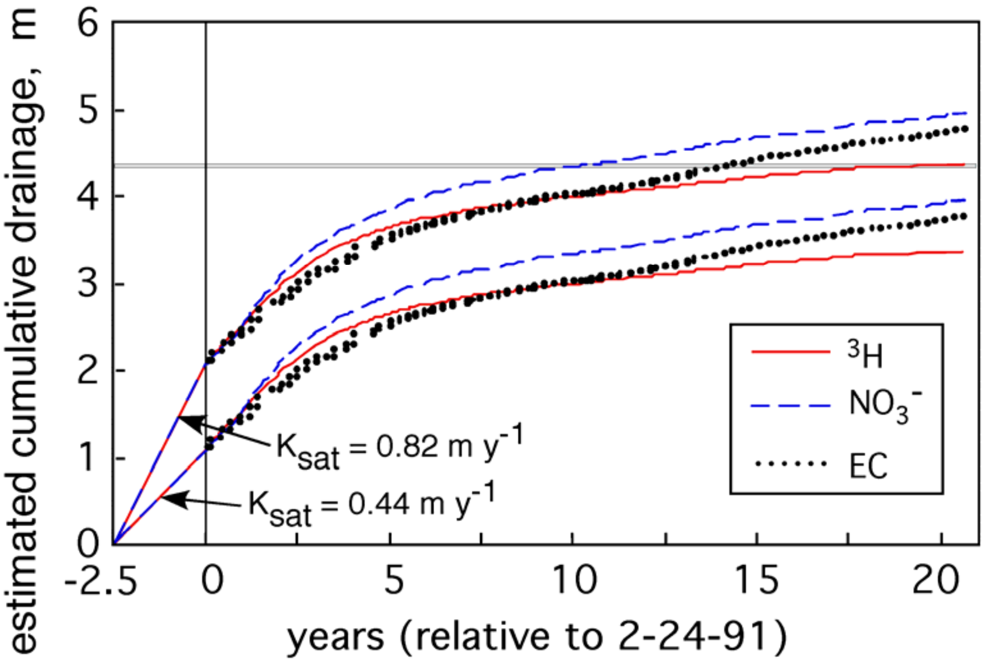


Figure 6. Time trends in estimated cumulative drainage from Basin 3, based on summation of equation 3 using the tritium and nitrate (87 mM source) results presented in Figure 5b, and assumed steady drainage based on two different average K_{sat}.