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A Division of Southwest Research Institute
6220 Culebra Road • San Antonio, Texas, U.S.A. 78228-5166
(210) 522-5160 • Fax (210) 522-5155

January 21, 2000
Contract No. NRC-02-97-009
Account No. 20.01402.871

U.S. Nuclear Regulatory Commission
ATTN: Dr. John W. Bradbury
Division of Waste Management
Two White Flint North
Mail Stop 7F-13
Washington, DC 20555

Subject: Transmittal of the deliverable "An Archaeological Site at Akrotiri, Greece, as a Natural Analog for Radionuclide Transport: Implications for Validity of Performance Assessments" (IM 1402.871.040).

Dear Dr. Bradbury:

This letter transmits Intermediate Milestone "An Archaeological Site at Akrotiri, Greece, as a Natural Analog for Radionuclide Transport: Implications for Validity of Performance Assessments" (IM 01402.871.040). This deliverable will be submitted for publication in the proceedings volume for the Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management XXIII.

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Washington Office • Twinbrook Metro Plaza #210
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

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If you have any questions regarding this deliverable, please call me at (210) 522-5540 or Dr. Debra Hughson at (210) 522-3805.

Sincerely yours,

English C. Pearcy, Manager
Geohydrology and Geochemistry

/ph

cc: J. Linehan
D. DeMarco
B. Stiltenpole
B. Meehan
J. Greeves
J. Holonich
W. Reamer
K. Stablein
D. Brooks
B. Leslie
J. Ciocco
D. Esh
W. Dam
N. Coleman
T. McCartin
R. Codell
C. Lui
W. Patrick
CNWRA Directors
CNWRA Element Managers
T. Nagy (SwRI Contracts)
P. Maldonado

AN ARCHEOLOGICAL SITE AT AKROTIRI, GREECE, AS A NATURAL ANALOG FOR RADIONUCLIDE TRANSPORT: IMPLICATIONS FOR VALIDITY OF PERFORMANCE ASSESSMENTS

D.L. HUGHSON, L. BROWNING, W.M. MURPHY, R.T. GREEN
Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX 78238-5166, dhughson@swri.org

ABSTRACT

Natural analog studies provide a means to test assumptions in performance assessment models. Data on the spatial distribution of metals derived from archeological artifacts at Akrotiri, Greece, were used to evaluate performance assessment model assumptions of radionuclide transport through unsaturated volcanic tuffs hosting the proposed repository at Yucca Mountain, Nevada. Processes controlling transport of trace elements from 3600 year old metallic artifacts at Akrotiri are analogous to processes controlling radionuclide transport at Yucca Mountain. Archeological information temporally and spatially constrains the source and chemistry of these trace elements, providing a comparison basis for model validation efforts. Despite these constraints and characterization of the Akrotiri site, the data are open to different interpretations as the extent of the plume emanating from the Minoan artifacts, transport pathways, heterogeneities in parameters, and boundary conditions are uncertain. Rather than validating a conceptual model of flow and transport, the Akrotiri site data indicate that 1-D models of aqueous phase transport in the unsaturated zone are conservative. Different conceptual models, apparently matching site data, produce different predictions illustrating that predictive flow and transport modeling is uncertain due to under-determined parameters and boundary conditions.

INTRODUCTION

The Akrotiri archeological site on the island of Santorini, Greece, was selected as a natural analog for supporting performance assessment modeling of the proposed high-level nuclear waste (HLW) repository at Yucca Mountain, Nevada, due to the presence of a well-constrained source of trace metals over a several thousand year time period and similarities in climate and geology. Both sites are in oxidizing, unsaturated, silicic volcanic rock in relatively arid climates. Around 1600 BC the Minoan eruption buried Akrotiri under several meters of ash. Bronze utensils on a ground floor subsequently became a temporally and spatially well-constrained source of trace metal contaminants. Sampling and testing activities at the Akrotiri archeological site were conducted to characterize its hydrological and geochemical features and to look for evidence of a plume of trace metals emanating from the artifacts [1,2]. These data showed subtle evidence for a plume of Cu, Pb, and Zn.

The approach taken in modeling trace metal transport at the Akrotiri archeological site [2] was patterned after that typically employed in performance assessments. Site characterization information, such as permeability and moisture retention measurements, and reasonable estimates (e.g., infiltration rate, solubility, and sorption coefficient) were used in a numerical model of flow and transport through porous media to predict concentration distributions of trace metal species over time. Input parameters were varied to investigate effects of uncertainty and to attempt to bound estimates. Model results predicted steady state concentration profiles from source to water table in less than the 3600 yr time frame, contrary to the field data which indicated an apparent concentration transient. This discrepancy persisted over parameter intervals of, for example, a factor of 36 for saturated hydraulic conductivity and 66% increase or reduction in infiltration flux. Some qualitative agreement between model results and observations was noted, however the discrepancy between model results and the data regarding trace metal distribution was not reconciled.

In this study we employ alternative hypotheses in an attempt to explain the distribution of trace metals observed near the location where the artifacts were removed. This modeling effort should be viewed as heuristic in contrast to the previous, predictive modeling work. We examine two alternatives suggested previously [2], variations in infiltration flux and spatial heterogeneity in model parameters. Effects of boundary flux assumptions are modeled in 1-D and potential effects of 3-D geological and anthropogenic features are simplified to 2-D with variable boundary flux assumptions. Natural analog sites, such as the archeological excavation at Akrotiri, offer opportunities for ascertaining performance model predictive reliability that are

otherwise unavailable. Successful modeling of the natural analog would help to increase confidence in the model predictions. Likewise failure in modeling the natural analog site may lead to iterative model improvements and quantitative assessment of model prediction uncertainties.

MODELING STUDY

Recap of Previous Work

Rock and soil samples were collected from 8 boreholes to a depth of approximately 0.5 m, all within approximately 1 m of the artifacts' location, and analyzed for Cu, Pb, Ag, Co, and Zn by selective extraction. A contour plot of total Cu, extracted sequentially from cation-exchangeable sites, associated with carbonates, and with reducible Fe and Mn oxides is shown in Figure 1. Borehole, sample, and artifact locations are shown schematically in these plots. The contour plot indicates lateral spreading of the Cu plume away from the artifact location in a southerly direction with minimal vertical transport apparent except near borehole VII which is adjacent to a discrete vertical fracture. Parameters treated as constant in this study are given in Table 1. Saturation is noted as S, α and n are parameters of the van Genuchten moisture retention function, and k is permeability.

The model domain tested [2] was a 1-D column consisting of 1.5 m of Minoan ash overlying a 4 cm packed earth layer overlying 22.5 m of Cape Riva tuff to the water table. With a flux boundary condition at the top representing estimated infiltration of 15 cm/yr [2], the hydrologic properties given in Table 1, and no sorption to the solid phase, the dissolved aqueous species derived from the artifacts are predicted to achieve a steady state profile within 30 yr. Including equilibrium sorption onto solids by means of a linear model with estimated [2] distribution coefficients $K_d = 0.45$ m^3/kg for packed earth and $K_d = 0.0027$ m^3/kg for Cape Riva tuff and a bulk density for the Cape Riva tuff of $\rho_b = 1.74E+6$ g/m^3, the plume takes over 1000 years to reach a uniform distribution to the water table. This corresponds to a retardation coefficient of about 30, as calculated from the relationship

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad (1)$$

where K_d is the distribution coefficient, ρ_b is bulk density, and θ is moisture content.

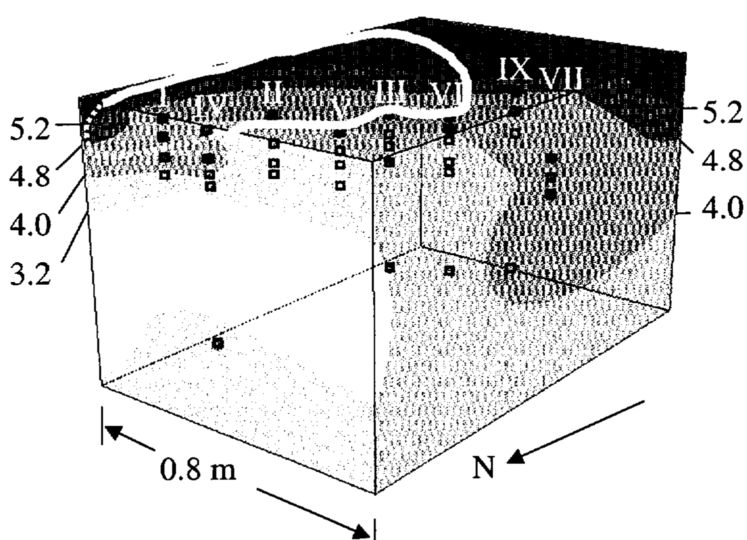

Figure 1. 3D perspective of sample locations (small squares), boreholes (Roman numerals), and Cu concentration contours. Numbers on the sides indicate ppm Cu associated with solids. Sides and top are 2D slices through solid contours. White line shows the approximate location of the base of the artifacts, dotted where extending beyond plotted range.

Alternative Hypotheses

1. Precipitation and Infiltration

Murphy et al. [2] estimated runoff using U.S. Bureau of Reclamation methods and applied a mean net infiltration of 15 cm/yr varying sinusoidally from 20 cm infiltration in the winter to 5 cm evapotranspiration in the summer. Data from the Hellenic National Meteorological Service (Figure 2) show the average monthly precipitation over the period 1974-1991. The average rainfall over this period is 32 cm/yr. However potential evapotranspiration, estimated using the empirical method of Hamon [3], is exceeded by precipitation only 4 months out of the year, keeping the soil surface dry during summer months. Steady state flow in the 1-D model, using properties

Table 1. Model parameters from [2] treated in this study as constants.

Material	Porosity	VG n	VG α (Pa^{-1})	k (m^2)	Residual S
Minoan ash	0.60	1.4	5.01×10^{-5}	1.945×10^{-11}	0.02
Packed Earth	0.30	1.13	2.76×10^{-4}	1.144×10^{-14}	0.10
Cape Riva	0.25	1.7	7.02×10^{-5}	1.716×10^{-11}	0.02

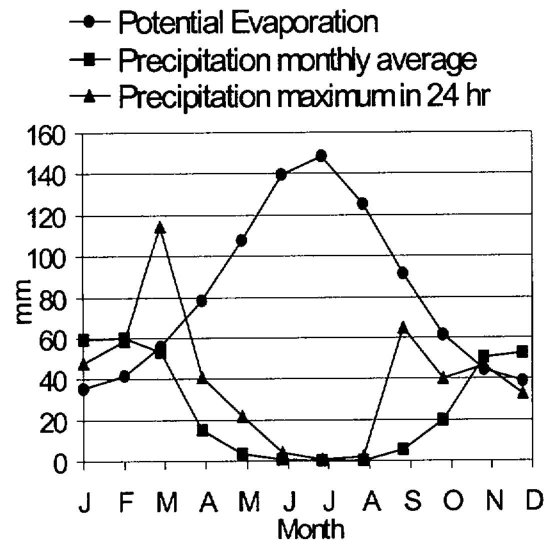

Figure 2. Precipitation data in mm for Latitude 36.25^0 N, Longitude 25.26^0 E, averaged over the period 1974-1991.

given in Table 1 and a prescribed boundary condition at the surface of S = 0.1, results in an upward flux of water from the water table of about 4 mm/yr, assuming a constant temperature of 20°C.

Redistribution of moisture from precipitation infiltration is complicated by evapotranspiration and soil heterogeneity. A low permeability packed earth layer on the floor of room Δ3 at the Akrotiri archeological site may have been part of a more extensive low permeability horizon compacted by human activity or may have been limited to the area of the Δ3 room, possibly diverting infiltration and creating a dry shadow below the artifacts. Remnants of the flagstone floor of the collapsed building may also have diverted infiltration above, creating a dry shadow surrounding the artifacts. Figure 3 illustrates the temporal effect of an areally extensive low permeability layer on moisture redistribution during and following a hypothetical storm. The model is a 1-D soil column of 1.5 m Minoan tuff overlying 0.04 m of packed earth overlying 22.46 m of Cape Riva tuff, with a water table boundary at the bottom and a constant flux boundary at the top, so the lateral extent of the low permeability layer is effectively infinite. The hypothetical storm lasts two days during which saturation at the surface is maintained at 0.85. Following the storm the soil surface dries out and is maintained at a saturation of 0.2. Initially the soil surface is at a saturation of 0.4 which is the hydrostatic condition.

This simulation suggests that, in the presence of a low permeability layer, an isolated 2 day precipitation event would contribute very little to percolation flux in the Cape Riva formation. Comparison of the average monthly precipitation with the average maximum precipitation in a 24 hour period during the month (Figure 2) suggests that such isolated storms are the norm at Akrotiri. Murphy et al. [2] performed sensitivity analyses reducing the flux boundary condition by 66% to 5.1 cm/year. However, referring to the discussion above, further sensitivity analyses with boundary flux reduced by a factor of 10 or more seem warranted. For the conservative solute, reducing flux by a factor of 10 scales the time required to reach a uniform concentration distribution to the water table from approximately 30 to 300 yr. However, the reduced infiltration results in a lower moisture content, except near the water table, which increases the retardation factor. Thus, as shown in Figure 4, the retarded plume, with 1.5 cm/yr infiltration flux and sorption to the solid phase as described by the distribution coefficients given above, has not reached the water table in 3600 yr.

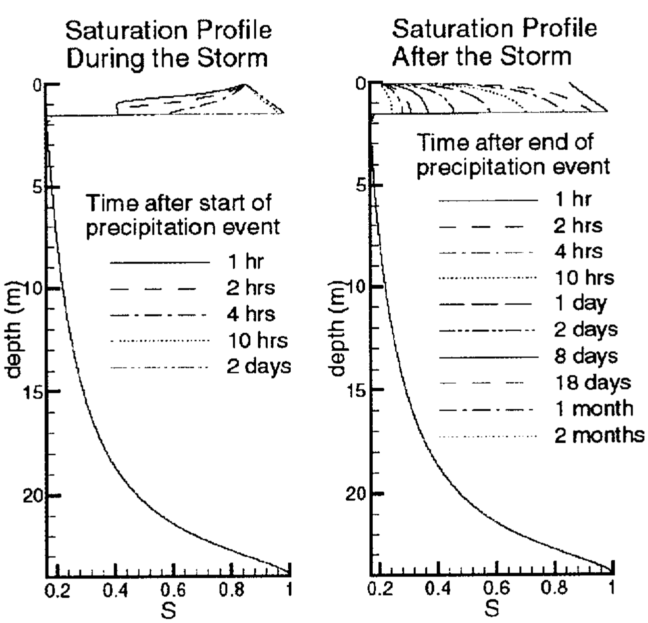

Figure 3. Saturation as a function of depth and time during a simulated storm.

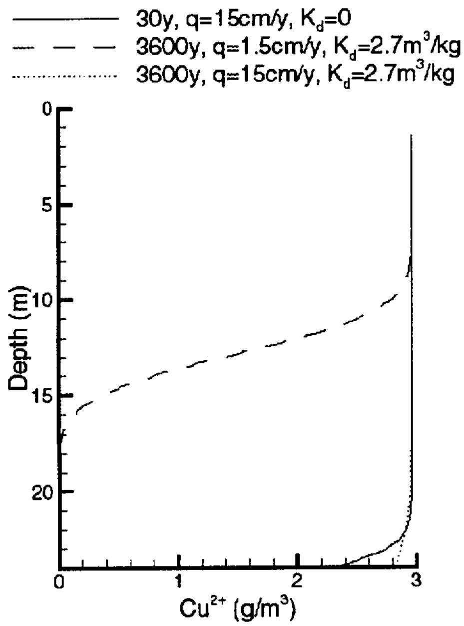

Figure 4. 1-D simulations illustrating the combined effects of plume retardation and low infiltration.

2. Heterogeneity

Parameters such as permeability commonly vary over several orders of magnitude in geological formations. Large discrete vertical fractures were observed in the Cape Riva formation within the vicinity of the artifacts' location. Borehole VII was located specifically to sample one such feature. Cu analyses of samples from borehole VII appear to indicate that more vertical transport occurred near this feature (Figure 1) than was observed from the other borehole data. The hydrological properties of the packed earth floor were not characterized. It was observed to be compacted and to have a high clay content suggesting low permeability. The floor was not level but dipped approximately 10 degrees in a southerly direction. Figure 5 shows the development of an aqueous phase Cu^{2+} plume from an atacamite ($Cu_2Cl(OH)_3$) source located above a thin low permeability layer extending laterally for 1.4 m. The entire model geometry of Figure 5 dips 10 degrees to the right with respect to gravity so the plume is asymmetric. A uniform infiltration flux of 1.5 cm/yr is applied along the top boundary and the resulting streamlines are shown in Figure 5. Infiltration flux diverges above the packed earth layer due to its low permeability and converges below due to capillarity in the Cape Riva formation. Sorption to the solid phase was not considered in this simulation so solute advection corresponds to water velocity. A molecular diffusion coefficient of 7.5E-6 cm^2/s was assumed. Model simulated saturation in the Minoan ash layer surrounding the source term is about 0.3 with 1.5 cm/yr infiltration. The umbrella effect of the low permeability layer, however, creates a dry zone in the Cape Riva formation immediately beneath the artifact location where flux vectors are less than 1 mm/yr and saturation is reduced to the range of 0.06 to 0.09. This corresponds to a moisture content in the range of 0.03 to 0.05 and a corresponding retardation factor of 95 to 158, assuming a distribution coefficient of $K_d = 0.0027$ m^3/kg. Distribution coefficients in [2] were determined from isotherm data for sorption of Cu on quartz [4] and kaolinite [5] to represent values for tuff and packed earth, respectively, using a water chemistry model [2]. We calculated 4.67E-5 molar concentration of Cu^{2+} in equilibrium with acatamite at pH = 6 using the geochemical speciation code EQ3. Taking an approximate average of 3 ppm of Cu sorbed to the solid phase from the data of Murphy et al. [2] gives an estimate of K_d =0.001 m^3/kg which reduces these retardation coefficients to the range of 36 to 59. At the high end of the K_d estimate, however, we have a plausible conceptual model for the observed Cu distribution. Lower infiltration flux due to evapotranspiration and a low permeability layer results in smaller flux velocities, lower moisture content, and increased retardation. Less solute transport may have occurred through the packed earth due to its clay content and possibly larger distribution coefficient. Assuming a distribution coefficient

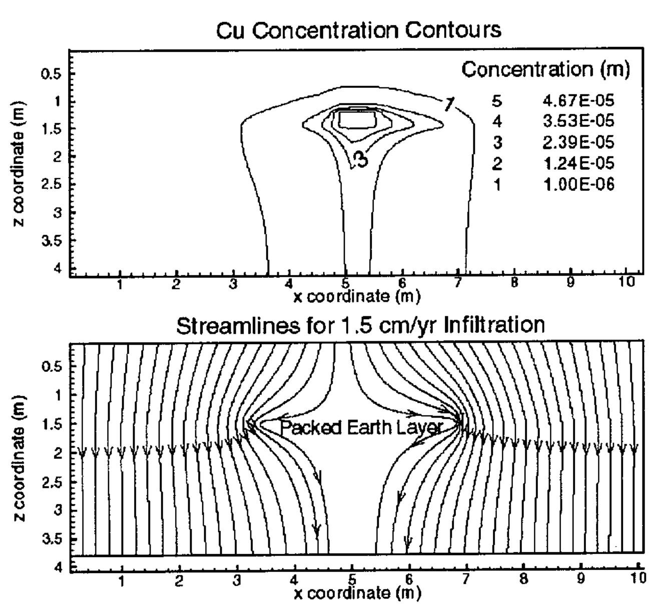

Figure 5. Distribution of aqueous phase Cu^{2+} at 3600 yr and infiltration flux of 1.5 cm/yr (without sorption) resulting from the presence of a low permeability layer underneath the source.

$K_d = 0.45\ m^3/kg$ in the packed earth layer and a bulk density of 1300 kg/m^3 gives retardation coefficients in the range of 975 to 1085.

The effect of the large discrete vertical fracture intersecting borehole VII on unsaturated flow and transport is difficult to evaluate because it may act as a barrier to unsaturated flow under low infiltration flux and as a conduit for flow during a precipitation event. This transition is not easily handled using a porous media continuum model. The fracture was simulated by increasing the permeability five orders of magnitude over the permeability of the Cape Riva tuff in a column of elements in the grid. This may exaggerate the tendency of the fracture to act as a conduit for flow because moisture retention properties were the same as the surrounding Cape Riva tuff. The effect of a hypothetical high permeability vertical feature located at the downslope end of the packed earth layer at 3600 yr is shown in Figure 6 for 1.5 cm/yr infiltration and in Figure 7 for 15 cm/yr infiltration. The more widespread concentration distribution of aqueous Cu^{2+} at 1.5 cm/yr infiltration than at 15 cm/yr infiltration can be explained by mixing and dilution. The streamlines in Figure 6 show the path of advective transport below the packed earth layer. Transport through the packed earth layer is primarily by diffusion. With 1.5 cm/yr of infiltration the liquid velocities are low enough to allow for diffusive spreading of the plume. At 15 cm/yr, though, advection dominated flow below the packed earth layer sweeps the solute into the fracture where it is diluted by flux converging on this highly permeable zone and is transported out the bottom boundary of the model. Even though the plume is more widespread at 1.5 cm/yr infiltration, significantly more mass has been transported to the water table with 15 cm/yr infiltration flux. With 1.5 cm/yr infiltration 44 g of the mineral atacamite source term has been dissolved by 3600 yr (nominal width of the 2-D model is 0.2 m). Increasing the infiltration rate to 15 cm/yr resulted in 341 g of atacamite dissolved in 3600 yr, although the resulting contamination plume was less widespread.

These simulations did not include sorption. Considering a retardation coefficient for the packed earth layer as above in the transport model with 1.5 cm/yr infiltration would result in a sorbed phase concentration distribution in the rock similar to that observed from borehole data (Figure 1). These simulation results tend to support the hypothesis that infiltration is low as the artifacts removed were observed to be only slightly corroded with surface ornamentation of the bronze pieces essentially intact [2].

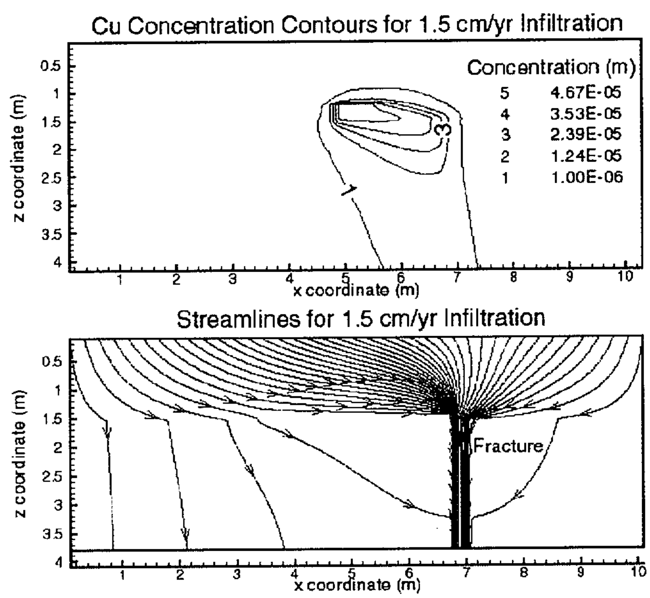

Figure 6. Distribution of aqueous phase Cu^{2+} at 3600 yr (without sorption) resulting from the presence of both a low permeability layer underneath the source and a vertical high permeability zone representing a fracture.

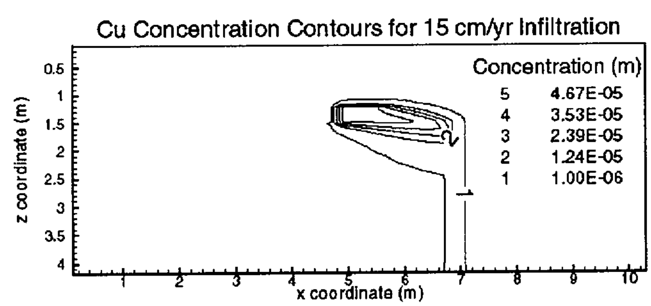

Figure 7. Identical model geometry as that shown in Figure 6 but with the higher 15 cm/yr infiltration rate.

Implications for Performance Assessments

Problems inherent in validation of groundwater flow and solute transport models, particularly verification of model predictions as bases for public policy decisions, are widely recognized [6]. The uncertainty in model predictions due to model non uniqueness is illustrated here by showing the effect of two alternative conceptualizations on solute transport predictions. Alternative models,

apparently matching field data, yield different predictions for long-term release of trace metals to the water table by varying only infiltration flux and heterogeneity. Despite the good temporal and spatial constraints on the source term and the small size of the modeling domain, many degrees of freedom still exist. One goal of performance assessments is to bound the range of possibilities. Clearly the 1-D model with the higher flux rate of 15 cm/yr and no retardation predicts an early arrival of aqueous trace metal species at the water table. Mass flux from the vertical 1-D model is per unit horizontal area. For an area equivalent to the atacamite source term in the 2-D model (Figures 5, 6, and 7) the 1-D model with no retardation calculates 2 moles of Cu arriving at the water table in 3600 yr. This corresponds to dissolution of 427 g of atacamite which agrees reasonably well with the 341 g of atacamite dissolved in the 2-D model over the same time period. Including sorption to solids and assuming a lower flux rate of 1.5 cm/yr, however, results in a dramatically different prediction. In that case none of the dissolved Cu is transported to the water table within 3600 yr.

CONCLUSIONS

Two factors, spatially heterogeneous hydraulic properties and sorption to solids with reduced infiltration, could potentially explain the field data of Cu distribution at the Akrotiri archeological site. Transport models incorporating either of these factors, however, make divergent predictions within the 3600 yr time frame. In the case of heterogeneity and high infiltration, the plume arrived at the water table in about 30 yr and several hundred grams of the source mineral were removed by 3600 yr. In the case of low infiltration combined with sorption and retardation, no Cu reached the water table and little source mineral was removed by 3600 yr. Determining which of these models (if either) is more representative of transport processes at the site is difficult without more field work. Site characterization and modeling alone may result in unrealistic predictions. However, if more field work indicated that heterogeneity is a major factor affecting transport at the site but no evidence of an extensive plume was found, it would remain uncertain whether transport did not occur or if the sampling holes did not intersect the plume. So another conclusion is that the 1-D model with high infiltration and no retardation conservatively bounds the predictions. The non-conservative bound would be that very little transport has occurred.

ACKNOWLEDGMENTS

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A Division of Southwest Research Institute
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(210) 522-5160 • Fax (210) 522-5155

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Division of Waste Management
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English C. Pearcy, Manager
Geohydrology and Geochemistry

/ph

cc:	J. Linehan	B. Leslie	W. Patrick
	D. DeMarco	J. Ciocco	CNWRA Directors
	B. Stiltenpole	D. Esh	CNWRA Element Managers
	B. Meehan	W. Dam	T. Nagy (SwRI Contracts)
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D.L. HUGHSON, L. BROWNING, W.M. MURPHY, R.T. GREEN
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INTRODUCTION

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MODELING STUDY

Recap of Previous Work

Rock and soil samples were collected from 8 boreholes to a depth of approximately 0.5 m, all within approximately 1 m of the artifacts' location, and analyzed for Cu, Pb, Ag, Co, and Zn by selective extraction. A contour plot of total Cu, extracted sequentially from cation-exchangeable sites, associated with carbonates, and with reducible Fe and Mn oxides is shown in Figure 1. Borehole, sample, and artifact locations are shown schematically in these plots. The contour plot indicates lateral spreading of the Cu plume away from the artifact location in a southerly direction with minimal vertical transport apparent except near borehole VII which is adjacent to a discrete vertical fracture. Parameters treated as constant in this study are given in Table 1. Saturation is noted as S, α and n are parameters of the van Genuchten moisture retention function, and k is permeability.

The model domain tested [2] was a 1-D column consisting of 1.5 m of Minoan ash overlying a 4 cm packed earth layer overlying 22.5 m of Cape Riva tuff to the water table. With a flux boundary condition at the top representing estimated infiltration of 15 cm/yr [2], the hydrologic properties given in Table 1, and no sorption to the solid phase, the dissolved aqueous species derived from the artifacts are predicted to achieve a steady state profile within 30 yr. Including equilibrium sorption onto solids by means of a linear model with estimated [2] distribution coefficients $K_d = 0.45$ m^3/kg for packed earth and $K_d = 0.0027$ m^3/kg for Cape Riva tuff and a bulk density for the Cape Riva tuff of $\rho_b = 1.74E{+}6$ g/m^3, the plume takes over 1000 years to reach a uniform distribution to the water table. This corresponds to a retardation coefficient of about 30, as calculated from the relationship

$$R = 1 + \frac{\rho_b K_d}{\theta} \tag{1}$$

where K_d is the distribution coefficient, ρ_b is bulk density, and θ is moisture content.

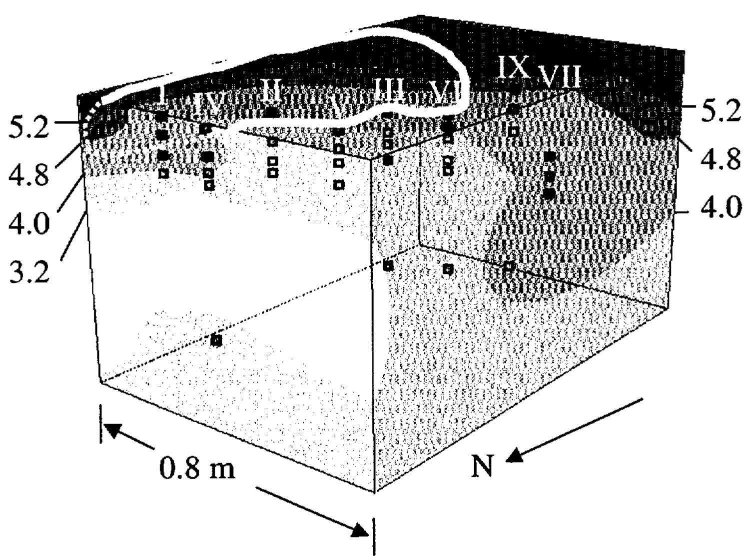

Figure 1. 3D perspective of sample locations (small squares), boreholes (Roman numerals), and Cu concentration contours. Numbers on the sides indicate ppm Cu associated with solids. Sides and top are 2D slices through solid contours. White line shows the approximate location of the base of the artifacts, dotted where extending beyond plotted range.

Alternative Hypotheses

1. Precipitation and Infiltration

Murphy et al. [2] estimated runoff using U.S. Bureau of Reclamation methods and applied a mean net infiltration of 15 cm/yr varying sinusoidally from 20 cm infiltration in the winter to 5 cm evapotranspiration in the summer. Data from the Hellenic National Meteorological Service (Figure 2) show the average monthly precipitation over the period 1974-1991. The average rainfall over this period is 32 cm/yr. However potential evapotranspiration, estimated using the empirical method of Hamon [3], is exceeded by precipitation only 4 months out of the year, keeping the soil surface dry during summer months. Steady state flow in the 1-D model, using properties

Table 1. Model parameters from [2] treated in this study as constants.

Material	Porosity	VG n	VG α (Pa^{-1})	k (m^2)	Residual S
Minoan ash	0.60	1.4	5.01×10^{-5}	1.945×10^{-11}	0.02
Packed Earth	0.30	1.13	2.76×10^{-4}	1.144×10^{-14}	0.10
Cape Riva	0.25	1.7	7.02×10^{-5}	1.716×10^{-11}	0.02

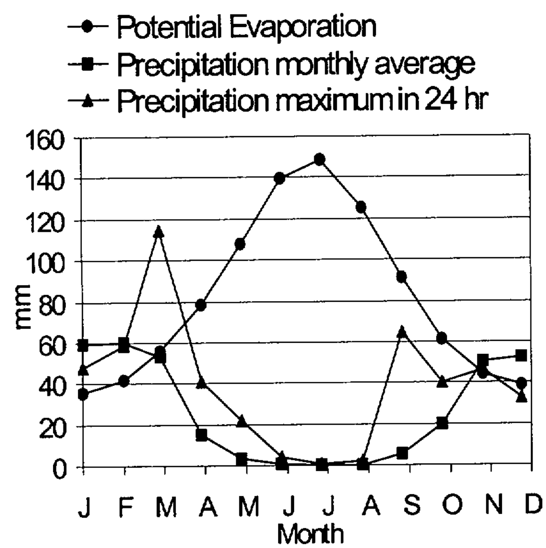

Figure 2. Precipitation data in mm for Latitude 36.25^0 N, Longitude 25.26^0 E, averaged over the period 1974-1991.

given in Table 1 and a prescribed boundary condition at the surface of S = 0.1, results in an upward flux of water from the water table of about 4 mm/yr, assuming a constant temperature of 20°C.

Redistribution of moisture from precipitation infiltration is complicated by evapotranspiration and soil heterogeneity. A low permeability packed earth layer on the floor of room Δ3 at the Akrotiri archeological site may have been part of a more extensive low permeability horizon compacted by human activity or may have been limited to the area of the Δ3 room, possibly diverting infiltration and creating a dry shadow below the artifacts. Remnants of the flagstone floor of the collapsed building may also have diverted infiltration above, creating a dry shadow surrounding the artifacts. Figure 3 illustrates the temporal effect of an areally extensive low permeability layer on moisture redistribution during and following a hypothetical storm. The model is a 1-D soil column of 1.5 m Minoan tuff overlying 0.04 m of packed earth overlying 22.46 m of Cape Riva tuff, with a water table boundary at the bottom and a constant flux boundary at the top, so the lateral extent of the low permeability layer is effectively infinite. The hypothetical storm lasts two days during which saturation at the surface is maintained at 0.85. Following the storm the soil surface dries out and is maintained at a saturation of 0.2. Initially the soil surface is at a saturation of 0.4 which is the hydrostatic condition.

This simulation suggests that, in the presence of a low permeability layer, an isolated 2 day precipitation event would contribute very little to percolation flux in the Cape Riva formation. Comparison of the average monthly precipitation with the average maximum precipitation in a 24 hour period during the month (Figure 2) suggests that such isolated storms are the norm at Akrotiri. Murphy et al. [2] performed sensitivity analyses reducing the flux boundary condition by 66% to 5.1 cm/year. However, referring to the discussion above, further sensitivity analyses with boundary flux reduced by a factor of 10 or more seem warranted. For the conservative solute, reducing flux by a factor of 10 scales the time required to reach a uniform concentration distribution to the water table from approximately 30 to 300 yr. However, the reduced infiltration results in a lower moisture content, except near the water table, which increases the retardation factor. Thus, as shown in Figure 4, the retarded plume, with 1.5 cm/yr infiltration flux and sorption to the solid phase as described by the distribution coefficients given above, has not reached the water table in 3600 yr.

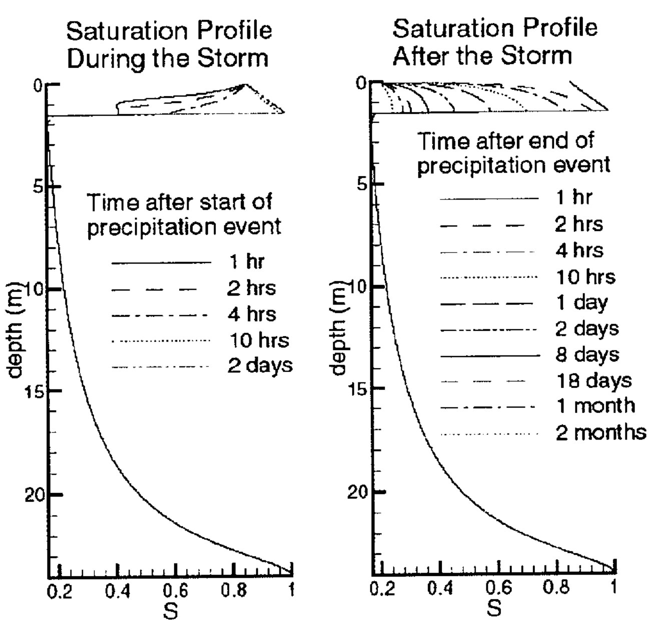

Figure 3. Saturation as a function of depth and time during a simulated storm.

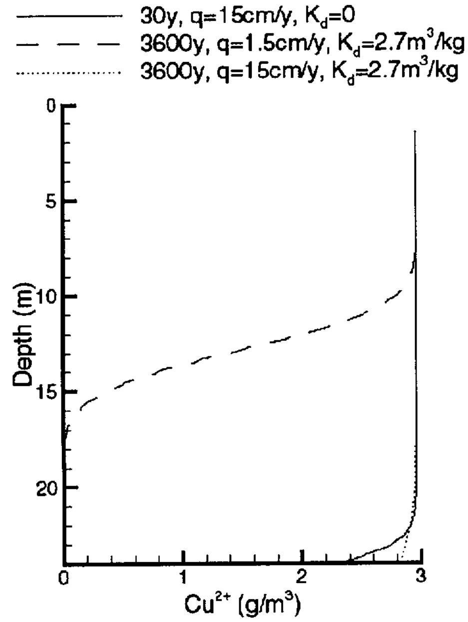

Figure 4. 1-D simulations illustrating the combined effects of plume retardation and low infiltration.

2. Heterogeneity

Parameters such as permeability commonly vary over several orders of magnitude in geological formations. Large discrete vertical fractures were observed in the Cape Riva formation within the vicinity of the artifacts' location. Borehole VII was located specifically to sample one such feature. Cu analyses of samples from borehole VII appear to indicate that more vertical transport occurred near this feature (Figure 1) than was observed from the other borehole data. The hydrological properties of the packed earth floor were not characterized. It was observed to be compacted and to have a high clay content suggesting low permeability. The floor was not level but dipped approximately 10 degrees in a southerly direction. Figure 5 shows the development of an aqueous phase Cu^{2+} plume from an atacamite ($Cu_2Cl(OH)_3$) source located above a thin low permeability layer extending laterally for 1.4 m. The entire model geometry of Figure 5 dips 10 degrees to the right with respect to gravity so the plume is asymmetric. A uniform infiltration flux of 1.5 cm/yr is applied along the top boundary and the resulting streamlines are shown in Figure 5. Infiltration flux diverges above the packed earth layer due to its low permeability and converges below due to capillarity in the Cape Riva formation. Sorption to the solid phase was not considered in this simulation so solute advection corresponds to water velocity. A molecular diffusion coefficient of 7.5E-6 cm^2/s was assumed. Model simulated saturation in the Minoan ash layer surrounding the source term is about 0.3 with 1.5 cm/yr infiltration. The umbrella effect of the low permeability layer, however, creates a dry zone in the Cape Riva formation immediately beneath the artifact location where flux vectors are less than 1 mm/yr and saturation is reduced to the range of 0.06 to 0.09. This corresponds to a moisture content in the range of 0.03 to 0.05 and a corresponding retardation factor of 95 to 158, assuming a distribution coefficient of $K_d = 0.0027$ m^3/kg. Distribution coefficients in [2] were determined from isotherm data for sorption of Cu on quartz [4] and kaolinite [5] to represent values for tuff and packed earth, respectively, using a water chemistry model [2]. We calculated 4.67E-5 molar concentration of Cu^{2+} in equilibrium with acatamite at pH = 6 using the geochemical speciation code EQ3. Taking an approximate average of 3 ppm of Cu sorbed to the solid phase from the data of Murphy et al. [2] gives an estimate of $K_d = 0.001$ m^3/kg which reduces these retardation coefficients to the range of 36 to 59. At the high end of the K_d estimate, however, we have a plausible conceptual model for the observed Cu distribution. Lower infiltration flux due to evapotranspiration and a low permeability layer results in smaller flux velocities, lower moisture content, and increased retardation. Less solute transport may have occurred through the packed earth due to its clay content and possibly larger distribution coefficient. Assuming a distribution coefficient

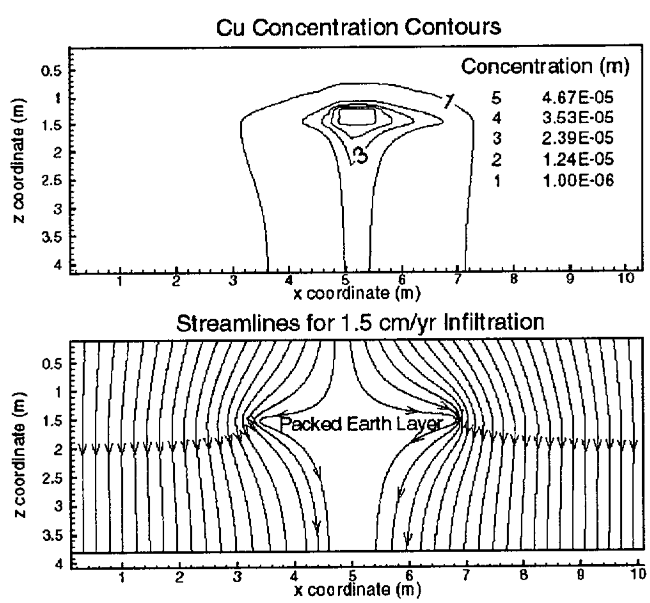

Figure 5. Distribution of aqueous phase Cu^{2+} at 3600 yr and infiltration flux of 1.5 cm/yr (without sorption) resulting from the presence of a low permeability layer underneath the source.

$K_d = 0.45\ m^3/kg$ in the packed earth layer and a bulk density of 1300 kg/m^3 gives retardation coefficients in the range of 975 to 1085.

The effect of the large discrete vertical fracture intersecting borehole VII on unsaturated flow and transport is difficult to evaluate because it may act as a barrier to unsaturated flow under low infiltration flux and as a conduit for flow during a precipitation event. This transition is not easily handled using a porous media continuum model. The fracture was simulated by increasing the permeability five orders of magnitude over the permeability of the Cape Riva tuff in a column of elements in the grid. This may exaggerate the tendency of the fracture to act as a conduit for flow because moisture retention properties were the same as the surrounding Cape Riva tuff. The effect of a hypothetical high permeability vertical feature located at the downslope end of the packed earth layer at 3600 yr is shown in Figure 6 for 1.5 cm/yr infiltration and in Figure 7 for 15 cm/yr infiltration. The more widespread concentration distribution of aqueous Cu^{2+} at 1.5 cm/yr infiltration than at 15 cm/yr infiltration can be explained by mixing and dilution. The streamlines in Figure 6 show the path of advective transport below the packed earth layer. Transport through the packed earth layer is primarily by diffusion. With 1.5 cm/yr of infiltration the liquid velocities are low enough to allow for diffusive spreading of the plume. At 15 cm/yr, though, advection dominated flow below the packed earth layer sweeps the solute into the fracture where it is diluted by flux converging on this highly permeable zone and is transported out the bottom boundary of the model. Even though the plume is more widespread at 1.5 cm/yr infiltration, significantly more mass has been transported to the water table with 15 cm/yr infiltration flux. With 1.5 cm/yr infiltration 44 g of the mineral atacamite source term has been dissolved by 3600 yr (nominal width of the 2-D model is 0.2 m). Increasing the infiltration rate to 15 cm/yr resulted in 341 g of atacamite dissolved in 3600 yr, although the resulting contamination plume was less widespread.

These simulations did not include sorption. Considering a retardation coefficient for the packed earth layer as above in the transport model with 1.5 cm/yr infiltration would result in a sorbed phase concentration distribution in the rock similar to that observed from borehole data (Figure 1). These simulation results tend to support the hypothesis that infiltration is low as the artifacts removed were observed to be only slightly corroded with surface ornamentation of the bronze pieces essentially intact [2].

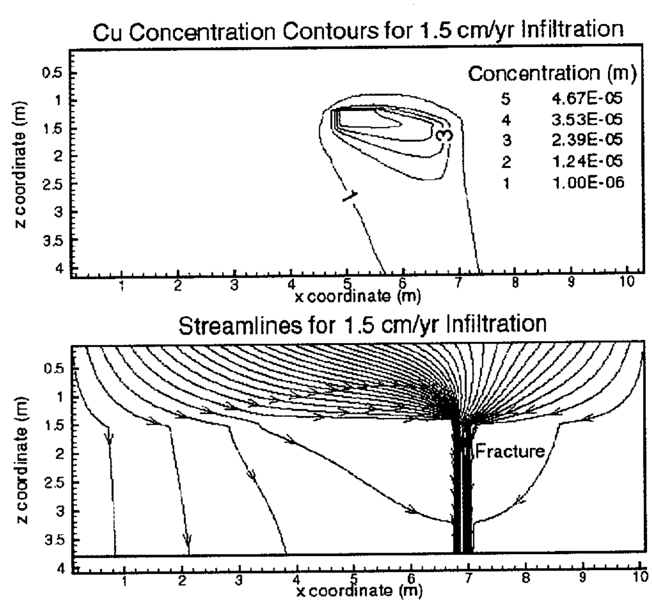

Figure 6. Distribution of aqueous phase Cu^{2+} at 3600 yr (without sorption) resulting from the presence of both a low permeability layer underneath the source and a vertical high permeability zone representing a fracture.

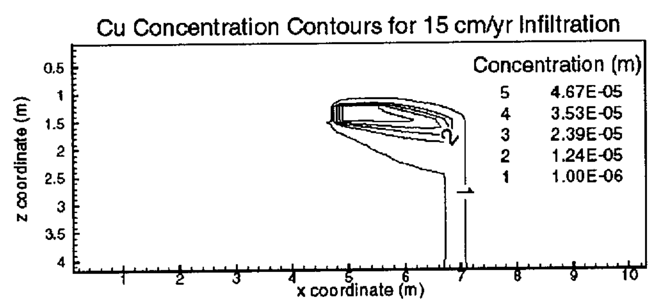

Figure 7. Identical model geometry as that shown in Figure 6 but with the higher 15 cm/yr infiltration rate.

Implications for Performance Assessments

Problems inherent in validation of groundwater flow and solute transport models, particularly verification of model predictions as bases for public policy decisions, are widely recognized [6]. The uncertainty in model predictions due to model non uniqueness is illustrated here by showing the effect of two alternative conceptualizations on solute transport predictions. Alternative models,

apparently matching field data, yield different predictions for long-term release of trace metals to the water table by varying only infiltration flux and heterogeneity. Despite the good temporal and spatial constraints on the source term and the small size of the modeling domain, many degrees of freedom still exist. One goal of performance assessments is to bound the range of possibilities. Clearly the 1-D model with the higher flux rate of 15 cm/yr and no retardation predicts an early arrival of aqueous trace metal species at the water table. Mass flux from the vertical 1-D model is per unit horizontal area. For an area equivalent to the atacamite source term in the 2-D model (Figures 5, 6, and 7) the 1-D model with no retardation calculates 2 moles of Cu arriving at the water table in 3600 yr. This corresponds to dissolution of 427 g of atacamite which agrees reasonably well with the 341 g of atacamite dissolved in the 2-D model over the same time period. Including sorption to solids and assuming a lower flux rate of 1.5 cm/yr, however, results in a dramatically different prediction. In that case none of the dissolved Cu is transported to the water table within 3600 yr.

CONCLUSIONS

Two factors, spatially heterogeneous hydraulic properties and sorption to solids with reduced infiltration, could potentially explain the field data of Cu distribution at the Akrotiri archeological site. Transport models incorporating either of these factors, however, make divergent predictions within the 3600 yr time frame. In the case of heterogeneity and high infiltration, the plume arrived at the water table in about 30 yr and several hundred grams of the source mineral were removed by 3600 yr. In the case of low infiltration combined with sorption and retardation, no Cu reached the water table and little source mineral was removed by 3600 yr. Determining which of these models (if either) is more representative of transport processes at the site is difficult without more field work. Site characterization and modeling alone may result in unrealistic predictions. However, if more field work indicated that heterogeneity is a major factor affecting transport at the site but no evidence of an extensive plume was found, it would remain uncertain whether transport did not occur or if the sampling holes did not intersect the plume. So another conclusion is that the 1-D model with high infiltration and no retardation conservatively bounds the predictions. The non-conservative bound would be that very little transport has occurred.

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