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Savannah River Site

**Groundwater Model Update for Chemicals, Metals, and Pesticides (CMP)
Pits Operable Unit (OU) (U)**

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LIST OF ACRONYMS AND ABBREVIATIONS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cfs	cubic feet per second
CMP	chemicals, metals, and pesticides
COI	constituent of interest
DRN	Drain
EMR	Effectiveness Monitoring Report
ft	feet
ft ³	cubic feet
F _{oc}	fractional organic content
HCM	hydrogeologic conceptual model
K _d	sorption coefficient
kg	kilogram
K _{oc}	partition coefficient
L	liter
LAZ	lower aquifer zone
lb	pound
µg/L	microgram per liter
MAE	mean-absolute error
MAZ	middle aquifer zone
MCL	maximum contaminant level
mg	milligram
mg/kg	milligram per kilogram
MNA	monitored natural attenuation
ρ _b	bulk density
PCE	tetrachloroethylene
PCB	polychlorinated biphenyls
R	retardation factor
RCRA	Resource Conservation and Recovery Act
RMSE	root-mean-square error
RSL	Regional Screening Level
SRNS	Savannah River Nuclear Solutions LLC
SRS	Savannah River Site
SWAT	Soil & Water Assessment Tool
TCCZ	Tan Clay Confining Zone
TCLC	Tan Clay Lower Clay
TCE	trichloroethylene
TZ	transmissive zone
UTRA	Upper Three Runs aquifer
VOC	volatile organic compound
WSRC	Westinghouse Savannah River Company LLC (before October 2005)
WSRC	Washington Savannah River Company LLC (October 2005- July 2008)

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1.0 INTRODUCTION

The Chemical, Metals, and Pesticides (CMP) Pits are located about 1 mile north of L Area, in the central part of the Savannah River Site (SRS) (Figure 1). There, two rows of unlined pits, marked as CMP Pits, that received non-radioactive waste between 1971 and 1979. The waste included organic chemicals, metals, pesticides, and lighting ballasts containing polychlorinated biphenyls (PCBs). Several early environmental sampling studies identified the CMP Pits as a source of soil and groundwater contamination. In 1984, the pits were excavated, fill was added to 4 feet (ft) below grade, a liner was placed, and additional fill was added to grade. However, residual soil contamination remained in the 90-ft thick vadose zone beneath the excavated area. The CMP Pits site is a regulated waste unit under the combined Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) program for SRS.

For this study, the fate and transport in the groundwater of four constituents of interest (COIs): tetrachloroethylene (PCE), trichloroethylene (TCE), 1-4 dioxane, and lindane, are modeled. These COIs are observed in groundwater at concentrations above their respective maximum contaminant levels (MCLs) or regional screening levels (RSLs). Other identified contaminants at the CMP Pits (e.g., PCBs) are primarily surface soil contaminants, and are not likely to lead to future groundwater contamination. Three of the COI's considered here – PCE, TCE, and 1-4 dioxane – are volatile organic compounds (VOCs) whereas lindane is a pesticide.

This model update is based on the prior groundwater flow and transport model that was developed in 2002 (GeoTrans, 2002a) and updated in 2017 (Tetra Tech, 2017). Since the previous modeling effort, additional surface water and groundwater data have been obtained. The collected data shows that while concentrations have generally stabilized or reduced in major portions of the study area some concentrations have increased in areas near the CMP Pits. The current study updates the previously reported 2017 model using new groundwater data and soil boring data from around the pits source area to the year 2022 (SRNS 2022). The result is a recalibrated flow model and updated predictive simulations of future solute transport of the four COI's. The elevated concentrations observed in recent years were included in the model to update the estimated (model predicted) long-term impact at surface water bodies including the large wetlands area and Pen Branch.

2.0 HYDROGEOLOGICAL CONCEPTUAL MODEL

The general site hydrogeologic conceptual model (HCM) has been retained from the previous modeling efforts. This includes the site hydrostratigraphy, groundwater flow and solute transport processes. A basic overview is provided in this section along with the updated elements of the HCM. More details about the HCM can be obtained from the previous modeling reports (GeoTrans, 2002, Tetra Tech, 2017).

Figure 3 illustrates the HCM for the CMP Pits. The original source material and surrounding soil were removed by excavation in 1984 and a Soil Vapor Extraction (SVE) and Electrical Resistance Heating (ERH) systems, which operated in 2008-2009, have removed much of the contamination beneath the pits. The remaining contaminant source is the soil beneath the remediation systems and around the former pits outside the effective area of the former remediation systems. In general, the COIs at the site have moved downward through the vadose zone to the water table located in the Upper Three Runs Aquifer (UTRA). Once the contamination reaches the water table, it mixes with the saturated groundwater and moves northward toward Pen Branch. The saturated groundwater plume is subject to processes of dispersion, sorption, and biological degradation. In addition to spreading horizontally toward Pen Branch, the contamination has spread vertically throughout much of the UTRA.

Semi-continuous clay layers divide the UTRA into three different aquifer zones referred to as (from top) the transmissive zone (TZ), the middle aquifer zone (MAZ), and the lower aquifer zone (LAZ). The tan clay confining zone (TCCZ) and tan clay lower clay (TCLC) separate these aquifer zones. The confining zones, (TCCZ and TCLC) are hummocky, vary in thickness, and discontinuous or leaky in areas (SRNS 2017). The contaminant plumes reside in all three aquifer zones of the UTRA. The CMP Pits HCM is consistent with the SRS hydrostratigraphy presented in Figure 4.

Groundwater flow directions in the study area are similar to those estimated in the previous modeling effort (Tetra Tech, 2017). Near the CMP Pits source area, flow in the TZ is generally toward the north-northwest. There is a significant downward component to flow from the TZ to the MAZ through the TCCZ; and from the MAZ to the LAZ through the TCLC. The flow direction is to the north-northwest in the MAZ and towards the northwest in LAZ. All three aquifer zones discharge to Pen Branch or the unnamed tributary feeding Pen Branch from the southeast including the wetlands.

Water level measurements from the updated average of the total period of record (1984-2022) are used as targets for model calibration. This updated period of record average was chosen due to an increase in the number of wells and measurements since the previous modeling effort. The water levels used as targets in this modeling update are very similar to the previous modeling effort showing good correlation with the data. The spatial average water level from the previous modeling effort was 202.9 ft, while the spatial average of the current water level data is 201.9 ft. Table 1 shows the average, high, low and range for water levels in the previous modeling effort, the current model update, and the difference between the two sets. It is evident that the average water levels have not changed significantly since the previous modeling effort. Recalibration exercise was conducted to duly update the model and no significant changes were identified.

3.0 GROUNDWATER FLOW MODEL RECALIBRATION

The groundwater flow model was recalibrated and checked for calibration using pre-set metrics. The underlying numerical model including the modeling code (MODFLOW-2000) and model discretization was not modified. More details on the development of the numerical modeling code and model discretization can be obtained from the previous modeling report (Tetra Tech 2017). The data used in the recalibration process was discussed in the previous section on the updated HCM. Basic information about the model construction and discretization is provided here.

The horizontal domain of the CMP Pits numerical model has remained unchanged from the previous modeling effort and is presented in Figure 5. The model domain includes the contaminant plumes and extends to natural groundwater boundaries in the downstream discharge areas (surface water bodies). The surface water bodies include the large wetlands areas and the streams. Pen Branch and its tributary are the natural streams and groundwater boundaries to the north and east. Natural boundaries are not within a reasonable distance in the upstream areas of the CMP Pits contaminant plumes. Therefore, specified-head boundary conditions (MODFLOW- CHD package) were employed on the southern edge of the model based on the estimated potentiometric surfaces (Hiergesell, 1998 and GeoTrans, 2002). The western edge of the model was selected to approximate a groundwater flow line. The southern and western model edges are relatively distant (several hundred feet) from, and upgradient of, the CMP Pits contaminant plumes, reducing the possibility of simulation errors due to inexact specification of boundary conditions. The surface water bodies and wetlands are simulated using the

head-dependent flux boundary condition using the Drain (DRN) package within MODFLOW which allows groundwater discharge to these areas. The drain package can simulate the discharge of groundwater to surface water but cannot simulate the reverse flow of surface water into groundwater. The drain package was selected due to its ease of numerical convergence compared to other more complex packages available within MODFLOW such as the Stream Flow Routing (SFR) package which can cause numerical issues.

The CMP Pits model has a uniform horizontal grid spacing of 25 ft by 25 ft (Figure 5) and the model has 202 rows and 146 columns. Grid cells to the north of Pen Branch and its tributary are inactive (outside the modeled domain), as are grid cells outside the other chosen model boundaries. The lower left (southernmost) corner of the model has coordinates of 53,575 E and 48,887 N in the SRS plant coordinate system. The model extends 3,650 ft and 5,050 ft in the x and y directions, respectively. The grid is rotated 35° west of SRS north. The relatively fine 25-foot grid spacing is used throughout the model so that the resolution of transport results is increased and so that the error in the calculation of the concentration gradient ($\partial c/\partial x_i$) is decreased. This spacing (Δd) results in a Peclet number (P_e) of 2 or less for a characteristic dispersivity (α) of 12.5 ft or greater. Maintaining a Peclet number of 2 or less helps to ensure stability of the numerical solution and to minimize numerical dispersion (Huyakorn and Pinder, 1983).

Nine model layers are used – two for the TZ, one for the TCCZ, one for the MAZ, one for the TCLC, and four for the LAZ (Figure 6). The first four layers are convertible between confined and unconfined layers whereas the remaining layers are confined (MODFLOW type 0). The aquifer properties such as storage and transmissivity are employed differently for confined and unconfined layers. Since the potentiometric surface is below the top surface of a model layer in an unconfined aquifer – transmissivity gets reduced as the potentiometric surface falls reducing the effective thickness of the aquifer. The storage property also changes as the compressible storage portion no longer exists in an unconfined aquifer. The TZ is divided into two layers. This split includes a very thin (one half foot thick) layer and a second layer representing the remainder of the TZ. This was done to prevent numerical non-convergence issues.

Steady-state groundwater flow conditions are assumed for the flow model indicating that average conditions over the entire period of record till the end of the year 2022 are being simulated. This

assumption leads to a more robust model as historically long-term average conditions tend to provide a better estimate of future conditions for predictive purposes. The main hydraulic properties in the steady-state groundwater flow model are the values of hydraulic conductivity and recharge. In this study, the calibrated model parameters from the previous model (Tetra Tech, 2017) were used as initial values. Initial head conditions were also kept the same. As noted earlier, since the long-term average values have not changed significantly, no numerical issues were anticipated using these initial conditions for the calibration of the updated model.

A no-flow condition (specified flux of zero) is used on the western edge of the model to represent an inferred groundwater flow line in all aquifers. The confining units (layers 3 and 5) have no-flow boundary conditions for all edges of the active area, except in locations where the creek intersects, and a head-dependent flux (drain boundary condition) is defined. Figure 7 provides an overview of the active and inactive areas employed in the model. It should be noted that some areas in layers 1 and 2 have been forced to start off as dry and therefore initiated as inactive to match field conditions as a qualitative or soft calibration target as explained later.

Model hydraulic conductivity specifications and flow-model boundary conditions are treated as calibration parameters in the model. As stated earlier the initial model parameterization was taken from the final calibrated groundwater model from the previous modeling exercise (Tetra Tech, 2017). Table 2 lists the initial parameter values used in the current groundwater flow model.

The CMP Pits groundwater flow model was recalibrated to increase model reliability. It involved a trial-and-error approach along with the use of a simple zone-based parameter estimation technique using the PEST suite of tools (Doherty, 2016) to automate portions of the calibration.

The main goal of the flow model recalibration was to optimally match observed aquifer heads using reasonable hydraulic properties and boundary conditions. Target heads were selected based on data quality and location. As stated earlier, average water levels for the updated period of record up to the year 2022 were used to represent average long-term flow conditions for simulation of contaminant transport into the future. The selected set of 61 targets is also 4 more than those used in the previous modeling effort. Polygonal areas presumed to be dry based on stratigraphic elevation relative to water surface were also updated and incorporated as soft calibration targets to verify that the pattern of dry cells computed by the model matched those inferred from stratigraphic and observed water elevation

surfaces. These dry areas were updated based on the latest observed locations of the dry areas at the site.

For each flow model simulation, a head residual (or error) is computed for each head target by subtracting the observed head from the simulated head. The goodness-of-fit statistics for these residuals are then compared to commonly accepted criteria for groundwater flow model calibration. Specifically, a calibration is sought that has a mean error within 0.5 ft of zero, and has a root-mean-square error (RMSE) less than one-tenth of the observed head range across the area of interest. For this model, the RMSE should be less than 2.8 ft. Another measure of calibration quality is the mean-absolute error (MAE), which is calculated as the mean of the absolute value of each residual. The MAE is less affected than the RMSE by outliers. Thus, when the MAE is much lower than the RMSE, a few poorly matched head targets (outliers) are likely having a large effect on the calibration statistics.

Head calibration alone is usually not sufficient to ensure that a groundwater flow model is a reasonable representation of reality. Another goal of groundwater flow calibration should be to match observed groundwater discharge conditions. Updated flow measurements at several locations along Pen Branch were used to estimate a target for the volume of baseflow contributed from the model area (SRNS, 2023). Additionally, a small-scale watershed model was also simulated using the Soil & Water Assessment Tool (SWAT), version SWAT 2012, from within the Hydrologic and Water Quality System (HAWQS) web-based modeling platform (HAWQS 2024 and SWAT 2012) to provide a localized estimation on baseflow to Pen Branch. As a result, the estimated baseflow target for flow from the model to Pen Branch and its tributary was revised from 0.35 cubic feet per second (cfs) as used in the previous model to 0.25 cfs for use in this updated model. This flow does not include the discharge to the wetlands, which is assumed to mostly be lost to evapotranspiration on an average annual basis.

The main parameters that were adjusted in the flow calibration were the horizontal and vertical hydraulic conductivities of the aquifers and confining units, recharge rate, drain conductance, seepage face elevation offset and specified head values. In the end, two main parameters had any significant change in the final calibrated model, the specified head values and the hydraulic conductivities in the LAZ. Final drain conductance values were also updated in some cells in the MAZ to account for the

revised baseflow target but not significantly. Table 2 provides the post-calibration parameter values for the updated model.

The calibration statistics are provided in Table 3 and indicate that the updated model is as well-calibrated as the previous model if not better. Goodness-of-fit calibration statistics of 2.24 ft for RMSE, 0.00 ft for mean error, and 1.57 ft for MAE were achieved for the calibration. These values are very similar and slightly better compared to the previous modeling effort and within the calibration goal of 2.78 ft. Table 4 provides a comparison of the observed and modeled head targets for groundwater wells and the calculated residual head value (residual = observed – modeled). It should be noted that some wells show high residual heads. Such residuals are sometimes encountered due to inherent uncertainties in the conceptualization and parameterization of the numerical model. In general, modeled water heads are slightly lower than observed heads in all three aquifers. The modeled hydraulic heads are, on average, lower in the TZ due to large residuals in a few wells. These wells could have local heterogeneities, not represented in the model, impacting the water levels. The overall statistics indicate a well-calibrated model. However, qualitative checks to test the goodness-of-fit of the model were also employed.

Figure 8 through Figure 10 show the modeled water levels in the three aquifers – TZ, MAZ, and LAZ. The location and magnitude of computed head residuals are also identified on these figures. In general, the simulated flow fields closely resemble the interpreted potentiometric maps from the annual Effectiveness Monitoring Report (EMR) for the CMP Pits (SRNS, 2023). In addition, the head residuals are randomly distributed geospatially, indicating minimal spatial bias. Additionally, the dry areas simulated by the model shown in purple are a good match with the dry areas determined to be dry prior to calibration indicated by the thick brown polygonal outlines. The blue flooded areas on these figures indicate wetlands simulated by the DRN package which are a good match for where we observe wetlands in the field. Plots of simulated (modeled) vs. observed heads and residual vs. observed heads are included in Figure 11. The observed vs. simulated heads are grouped closely along the 1:1 line indicating little systemic bias in simulating the water levels. The residuals are also grouped evenly along the 0ft-axis indicating a lack of bias towards negative or positive residual values. The simulation indicated that Pen Branch and all wetlands and seepage faces receive about 0.39 cfs, with 0.21 cfs directly discharging into Pen Branch, which is consistent with the soft baseflow target of 0.25

cfs. Based on all measures of quantitative and qualitative checks employed to test the goodness-of-fit of the updated model, the model meets criteria for conducting predictive fate and transport simulations.

Particle tracking was not conducted for the updated model since the underlying transport model properties, including the equilibrium constant (K_d) and retardation coefficients (R), are assumed to have remained unchanged from the previous model (Tetra Tech, 2017). Therefore, it follows that the underlying transport model remains the same with relation to aquifer and constituent properties. However, the constituent concentrations were altered to reflect newly available data since the last model update in 2017.

4.0 UPDATED PREDICTIVE SIMULATIONS WITH THE SOLUTE TRANSPORT MODEL

As stated earlier, the underlying solute transport model was not modified apart from the constituent concentrations. The numerical code (MT3DMS) and solute transport parameterization such as dispersivity, sorption coefficient (K_d), and bulk density values were retained from the previous modeling effort (Tetra Tech, 2017).

The bulk density (ρ_b) and sorption coefficient (K_d) values determine the mass adsorption capacity of the solids to the COIs (PCE, TCE, lindane and 1,4 dioxane) under the assumption of equilibrium sorption. Higher adsorption results in slower movement of the COIs also known as retardation of the contaminants. Similar to the previous model, a bulk density of 1.48 kg/L (92.4 lb/ft³ or 4.19E07 mg/ft³) was used throughout the model domain. Sorption is a function of the constituent organic-carbon partition coefficient (K_{oc}) and fractional organic content (F_{oc}) of the sediment.

$$(1) \quad K_d = F_{oc} K_{oc}$$

The organic carbon content in the solids (F_{oc}) for the various hydrostratigraphic units and the resulting estimated K_d and retardation factor (R) values for TCE and PCE are shown in Table 5. K_d and R values for lindane and 1,4-dioxane are shown in Table 6 and Table 7, respectively, for the various hydrostratigraphic units. These values, taken from the previous model report (Tetra Tech, 2017) and based on field-specific studies, have been kept unmodified in this model update since no new field-specific update was available.

The R describes the slowing down of the contaminants due to the adsorption process of the COIs on the porous media. R can also be understood as the ratio of the average groundwater velocity to the velocity of the contaminants. A retardation factor of 1.0 would result in the contaminant moving along with the groundwater as a non-reactive tracer such as chloride. A factor of 2.0 results in the contaminant moving at one-half the velocity of groundwater.

The equation for retardation factor is:

$$(2) \quad R = (1 + K_d(\rho_b/\theta))$$

Where:

R= retardation factor

K_d = equilibrium sorption coefficient

ρ_b = bulk density

θ = effective porosity

The environment in the wetlands area close to Pen Branch is conducive to reductive dechlorination, and is similar to the Twin Lakes portion of C Area, where degradation is known to be occurring. There are also multiple lines of evidence that indicate significant degradation is occurring and have been outlined in previous reports. However, for this model, no credit is taken for degradation in the Pen Branch wetlands, beyond the 25-year half-life as done in the previous modeling effort (Tetra Tech, 2017). Lindane and 1,4, dioxane are conservatively assumed to not degrade in the solute transport model.

The major change in the updated predictive solute transport model were the initial constituent concentrations. Constituent plumes were created by mapping the highest sampled groundwater concentration available from the year 2022. For transport simulations these concentrations are assumed to be the initial plume concentrations at the end of the year 2022. Figure 12 and Figure 13 show the initial plume concentrations for PCE and TCE, respectively. Selection of the maximum observed concentration and subsequent spatial application of that concentration generally creates more mass in the system than is truly present at the site. Therefore, the predictive results may have some inherent inconsistencies in the early-time conditions (2023 and the next few years) until the excess

mass in the system becomes stabilized. Such early-term errors can also lead to minor cumulative errors for later-time conditions (20+ years). However, the assumption of using maximum observed concentrations is the most conservative estimate and will provide robust values of potential future impacts to the surface water bodies.

Predictive modeling was conducted by running the solute transport model forward from the initial conditions starting on January 1, 2023, for up to 100 years. The predictive simulations show the estimated future fate and transport of the COI plumes. For each COI, initial plume conditions are applied at the end of the year 2022 and 100 years are simulated up to the end of 2122. Note that the transport model initial conditions are based on 2022 plume configurations. This ensures that the initial mass, concentrations, and plume extent are consistent with the currently available data and conceptual model. Concentrations are initialized in model layers representing the different formations at the site. Simulated concentrations of PCE and TCE at the Pen Branch groundwater discharge location are presented below. Based on the initial conditions, the wetlands adjoining these locations appear to provide significant degradation of PCE and TCE. Previous studies (GeoTrans 2002) suggest that the modeled PCE and TCE discharge concentrations may be reduced by two orders of magnitude due to the wetlands. The degradation processes occurring in the wetlands were not simulated in the modeling efforts. However, the baseflow and surface water flow do provide a dilution effect on the constituent concentration migrating via groundwater. To simulate this in the model, a dilution factor estimation was used to predict the average constituent concentrations in surface water.

4.1 Dilution Factor and Impact to Surface Water

As mentioned earlier, a small watershed-scale surface water model was built and run independent from the groundwater model. The surface water model was simulated using SWAT 2012 from within the HAWQS web-based modeling platform. At the beginning of the surface water modeling it was assumed that all surface water in Pen Branch, upstream of the area of discharge from CMP pits plumes, will dilute the groundwater discharge from the COI plumes from CMP pits. Therefore, the following can be estimated:

1. the groundwater baseflow and runoff to Pen Branch, upstream of the length of Pen Branch impacted by the COI plumes; and
-

2. groundwater discharge to Pen Branch that is impacted by the COI plumes

The dilution factor will be the ratio of flow rates estimated in 1 and 2 above. Dividing the groundwater concentrations at Pen Branch by the dilution factor will provide the predicted surface water concentrations of the COIs.

To obtain conservative estimates, the model used a maximum area impacted by the COI plume at any point during the predictive simulation. This provides the highest possible groundwater discharge to Pen Branch from the COI plumes. Higher groundwater discharge estimates from the COI plumes decrease the calculated dilution factor, making the estimated surface water concentrations higher and therefore, more conservative.

The watershed model was used to estimate the groundwater discharge to Pen Branch from the maximum observed plume area for each constituent over the predictive simulation period till the end of the year 2122. Groundwater discharge and runoff to Pen Branch was also estimated for the watershed area upstream of the maximum plume area. The dilution factor was estimated by taking the ratio of the estimated flow rates. The dilution factor was therefore conservatively estimated having a value of approximately 5. However, due to the range of values provided by the SWAT 2012 output to account for uncertainties, the dilution factor may range from the conservative value of 5 to the least conservative value of 25.

4.2 PCE Transport

Figure 12 shows the initial PCE plume at the end of the year 2022. After 18 years of transport, at the end of the year 2040, the plume extends from the CMP Pits to Pen Branch, and is present above the MCL (5 µg/L) in all three aquifer zones as shown in Figure 14. Residual source material entrained in low-permeability sediments, as determined from the 2019 soil boring work, is continues to contribute mass to groundwater through year 2040.. The plume distribution after 38 years at the end of the year 2060 (Figure 15) is similar to the PCE plume in 2040 (Figure 14), but significantly more attenuated. However, groundwater concentrations in the LAZ near Pen Branch show an increase over these time periods as well as an increase in plume extent due to vertical migration. The plume extent is smaller in 2060 than in 2040 in the TZ and MAZ. After 100 years, at the end of the year 2122, the plume is

almost entirely attenuated to below the MCL as presented in Figure 16. However, in the LAZ a limited area above the MCL is still present in groundwater near Pen Branch. Therefore, the PCE transport model was extended to run for 150 years up to the year 2172. By the year 2172, the groundwater plumes in all three aquifers are shown to have completely attenuated and there is no predicted impact to groundwater near Pen Branch.

A maximum concentration of 49 $\mu\text{g/L}$ is estimated to be detected in the groundwater near Pen Branch in the first year (2023) of the simulation and this declines to below the 5 $\mu\text{g/L}$ MCL by the year 2126 (104 simulated years) which is 13 years longer than that estimated in the previous model. This may have occurred due to the cumulative effect of changes in the groundwater flow model for the LAZ formation as well as an increase in updated initial concentrations.

The estimated concentration impacts to groundwater near Pen Branch are presented in Table 8. However, note that the model does not account for degradation in the wetlands, which can be substantial, as described in the introduction to this section. An order of magnitude reduction in concentration due to degradation in the wetlands would result in discharge concentrations of PCE being below the MCL within the first year which is consistent with estimates from the previous model. Since degradation processes were not considered in the model, the estimated concentrations in surface water in Pen Branch using the dilution factor method was applied and explained in section 4.1. Table 9 presents the estimated PCE concentrations in Pen Branch assuming a conservative value of the dilution factor. Please note that the predictive simulations show that the estimated impact to Pen Branch is highest in the most recent year(s) after the simulation begins and the impact decreases over time. PCE discharge to surface water is anticipated to be below MCL within the five years considering only dilution and no degradation processes. This is consistent with existing data where PCE concentrations have not been detected in surface water in Pen Branch.

4.3 TCE Transport

Figure 13 shows the initial TCE plume at the end of the year 2022. TCE plume migration is similar to the PCE migration, as shown in Figure 17 through 19 for the years 2040, 2060, and 2122, respectively. As was the case for PCE, the TCE plume extends from the CMP Pits to Pen Branch and is present above the MCL (5 $\mu\text{g/L}$) in all three aquifer zones. The plume distribution after 38 years (at the end

of the year 2060, Figure 18) is similar to the plume at the end of the year 2040 (Figure 17), but significantly more attenuated. These predictive results are similar to the results from PCE transport simulations. Also, by 2060, most areas of the plume have attenuated to less than the MCL in the TZ and MAZ. After 100 years, at the end of the year 2122, the plume is entirely attenuated as presented in Figure 19.

Simulated discharge concentrations begin at 19 ug/L and stay above the MCL of 5 µg/L for 55 years which is seven years longer than the previous model results. As noted above, this may be due to cumulative effects of the updates to the groundwater flow and solute transport model. Additional degradation within the wetlands could further reduce the simulated TCE concentrations. An order of magnitude reduction results in the TCE concentration being below the MCL for the entire duration of the 100-year simulation period. Since degradation processes were not considered in the model, estimated concentrations in surface water in Pen Branch using the dilution factor method were applied as explained in section 4.1. Table 9 presents the estimated TCE concentrations in Pen Branch assuming a conservative value of the dilution factor. Please note that the predictive simulations show that the estimated impact to Pen Branch is highest in the most recent year(s) after the simulation begins and the impact decreases over time. TCE discharge to surface water is estimated to be below MCL for the entire simulation considering only dilution and no degradation processes. This is consistent with existing data where TCE concentrations have not been detected in surface water in Pen Branch.

4.4 Lindane Transport

Lindane is also a COI for groundwater at the CMP Pits, and is modeled in this study. However, the initial concentrations of lindane are fairly low (Figure 20) compared to those from the previous model. As stated earlier, these initial concentrations are based on the most recent field data. Lindane does not appear to impact the Pen Branch in any significant (3 decimal place precision) concentration either in groundwater near Pen Branch or in surface water as presented in Table 8 and Table 9. Consequently, the 0.2 µg/L MCL for lindane is predicted to never be exceeded at discharge locations. Lindane transport results are consistent with the previous model results.

4.5 1,4-Dioxane Transport

1,4-Dioxane is also a COI for groundwater at the CMP Pits, and is modeled in this study. Unlike lindane, the initial concentrations of 1,4-dioxane are higher in this updated model as compared to the previous model (Figure 20). The initial plume has a spatial extent reaching the Pen Branch wetlands. Therefore, the maximum 1,4-dioxane concentration appears at the Pen Branch wetlands within the first year but does not persist till the end of the first completed year of the model. The discharge concentrations decline from then on and remain below the RSL of 0.46 µg/L. 1,4-Dioxane does not appear to impact the Pen Branch in any significant concentration either in groundwater near Pen Branch or in surface water as presented in Table 8 and Table 9 throughout the model runs.

5.0 SUMMARY AND CONCLUSIONS

The updated numerical model of groundwater flow and transport at the CMP Pits includes new hydrologic, chemical, and stratigraphic data. This model uses reasonable assumptions and was calibrated to head measurements at monitoring wells resulting in acceptable calibration statistics. The transport model uses the current plume maps and updated field data from the year 2022 as initial conditions to perform predictive transport simulations for the four COIs.

Previously identified dry areas within aquifers were confirmed to have significant influence on the contaminant transport pathways. The most recent interpretation of the spatial extent of the dry areas was used in this updated model. As more water quality data is gathered, continual update to the transport model will improve the understanding of these contaminant pathways and the impact of the dry areas.

The surface water data gathered at the CMP pits over the last few years was also analyzed during the model update and used as a soft calibration target for the flow model update. The flux discharge estimated by the model and that observed in the field data are fairly close which indicates that groundwater- surface water interaction and volumetric flux estimates provided by the model are fairly accurate on an annual averaged basis.

For all COIs except PCE, predictive simulations indicate that discharge concentrations are not anticipated to impact the surface water in Pen Branch over the MCLs at any time during the 100-year

simulation and attenuation of the groundwater plumes is predicted. Predictive results for PCE do show exceedances in surface water near Pen Branch for year 5 (end of the year 2027). However, as explained earlier, the wetlands adjoining the groundwater discharge locations along Pen Branch appear to provide significant degradation of PCE and TCE. Previous studies and empirical data collected in Pen Branch indicated that the modeled PCE and TCE discharge concentrations are reduced by up to two orders of magnitude, resulting in both PCE and TCE concentrations currently being below MCLs in Pen Branch and remaining below MCLs throughout the simulation period of 100 years.

The updated model results also include consideration of dilution processes. Upon applying a dilution factor, discharge concentrations of PCE are anticipated to decrease below MCLs within five years by the end of the year 2027. Modeled 1,4-Dioxane and lindane discharge concentrations are predicted to remain below MCLs or RSLs and therefore appear to be much less important COIs than PCE and TCE at the CMP Pits.

It should be noted that there are several factors that limit the predictive accuracy of the transport model including model parameterization and simplifying assumptions such as specified head and flux conditions. The model currently assumes fairly homogeneous properties for each of the aquifer formations, which is a simplified representation of heterogeneous field conditions. Also, quantification of the process of sorption is uncertain and affects the longevity of the plume. Degradation of PCE and TCE are assumed to be relatively slow (25 years). No degradation was conservatively assumed for lindane and 1,4-dioxane and the dilution factor was calculated using conservative assumptions.

Despite the uncertainties in the current updated model, both qualitative and quantitative calibration criteria were met and it is a useful tool to predict the future impact on Pen Branch in support of evaluating the monitored natural attenuation (MNA) remedy at the CMP Pits OU.

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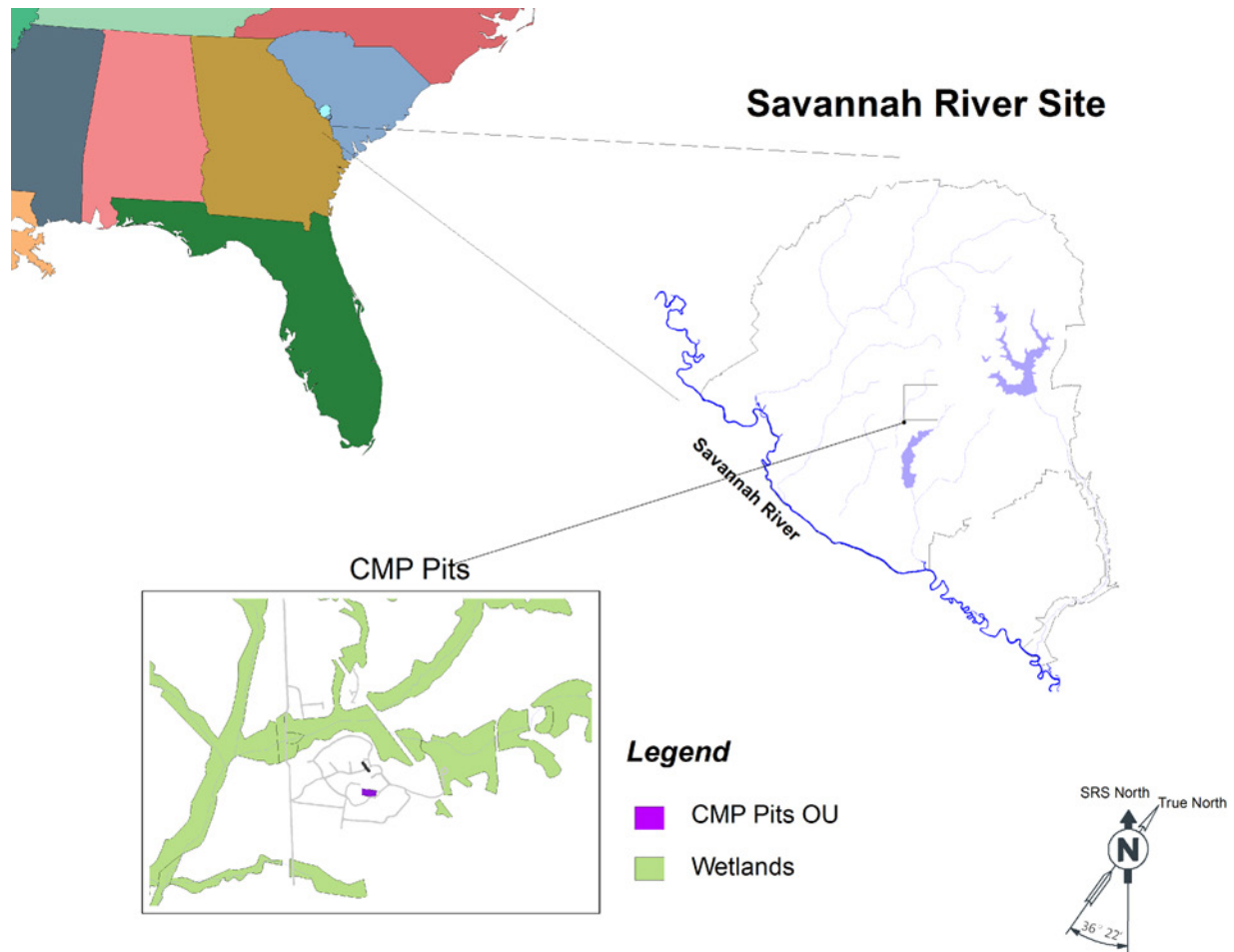


Figure 1. Location of the Chemicals, Metals, and Pesticides (CMP) Pits Operational Units (OU)

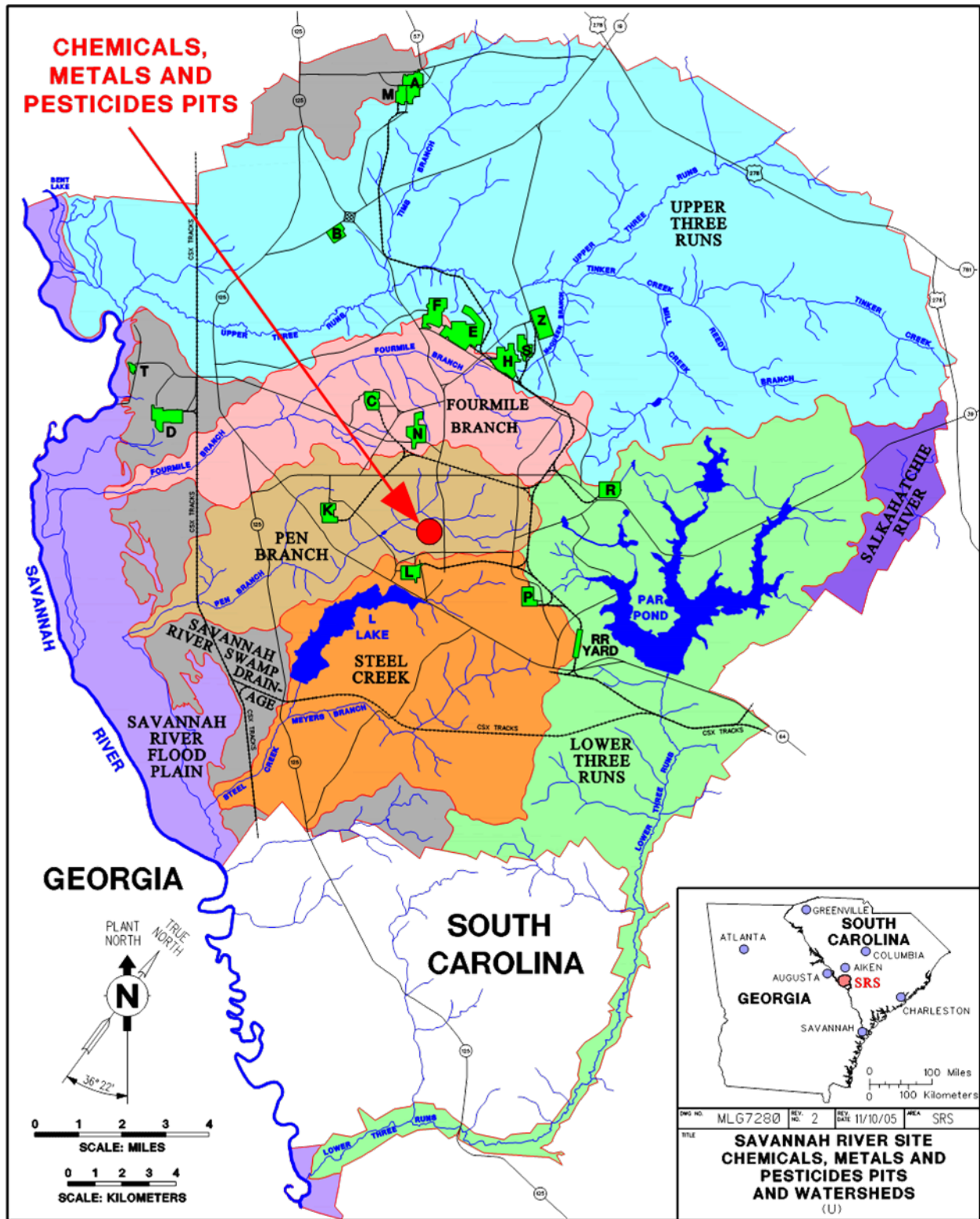


Figure 2. Location of the CMP Pits OU Relative to Surface Water Bodies

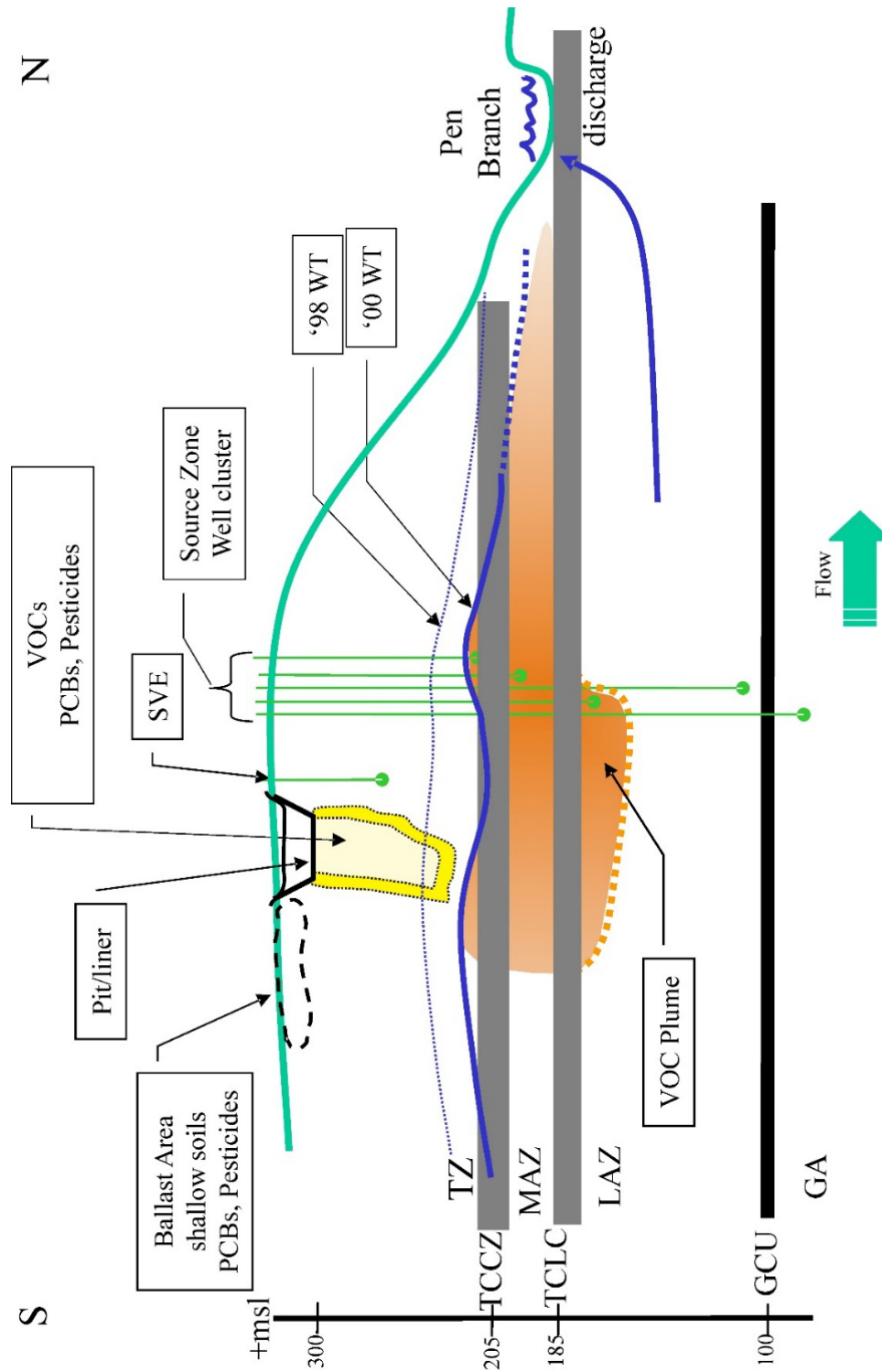


Figure 3. Hydrogeologic Conceptual Model for the CMP Pits Site (after GeoTrans 2002a)

COMPARISON OF CHRONOSTRATIGRAPHIC, LITHOSTRATIGRAPHIC AND HYDROSTRATIGRAPHIC UNITS

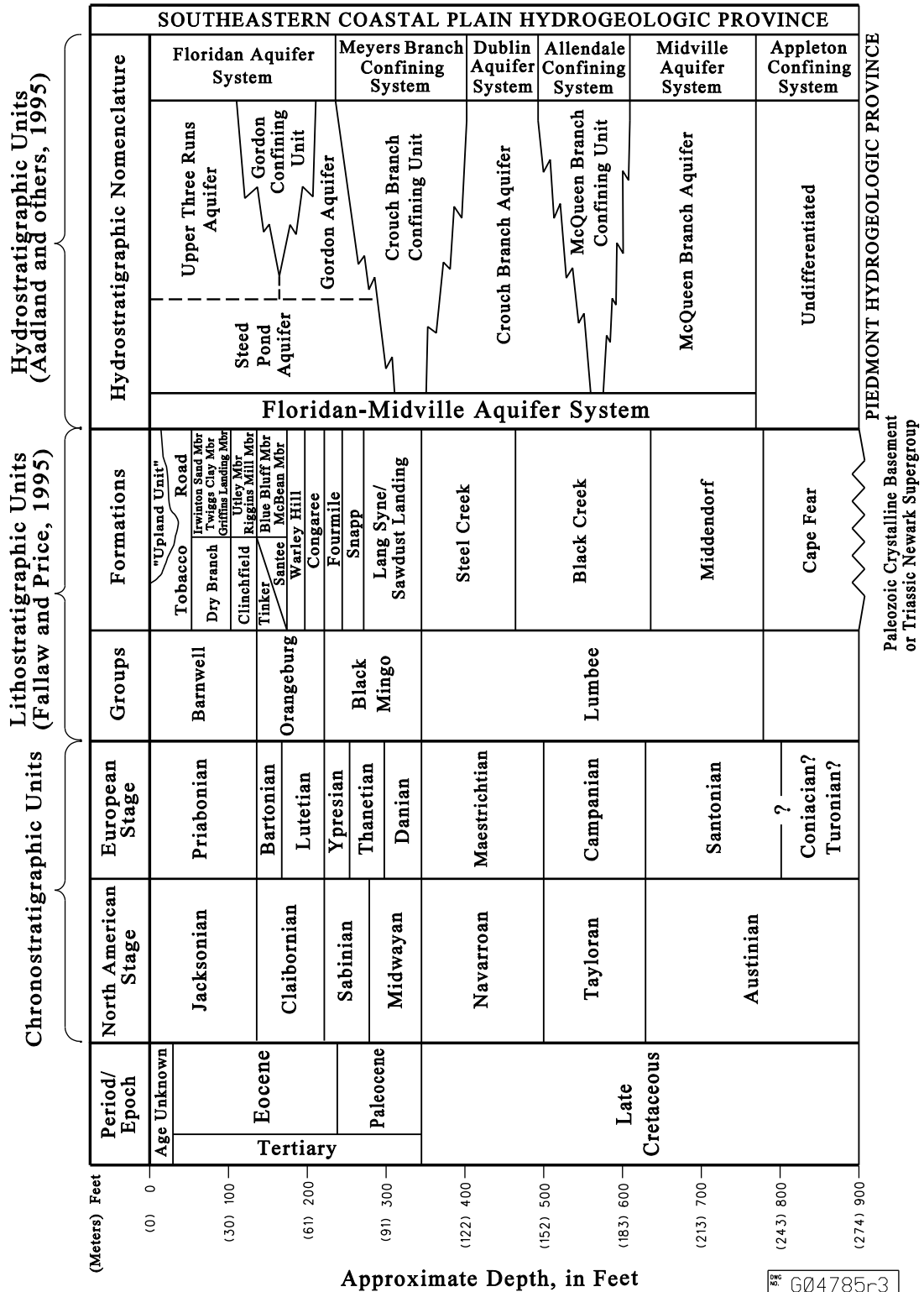


Figure 4. SRS Geologic Stratigraphy

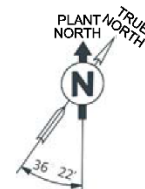
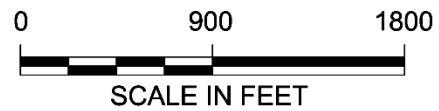
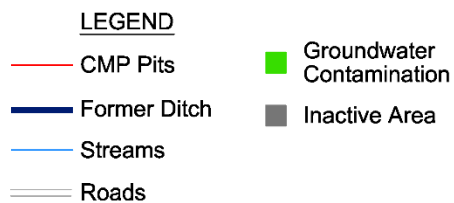
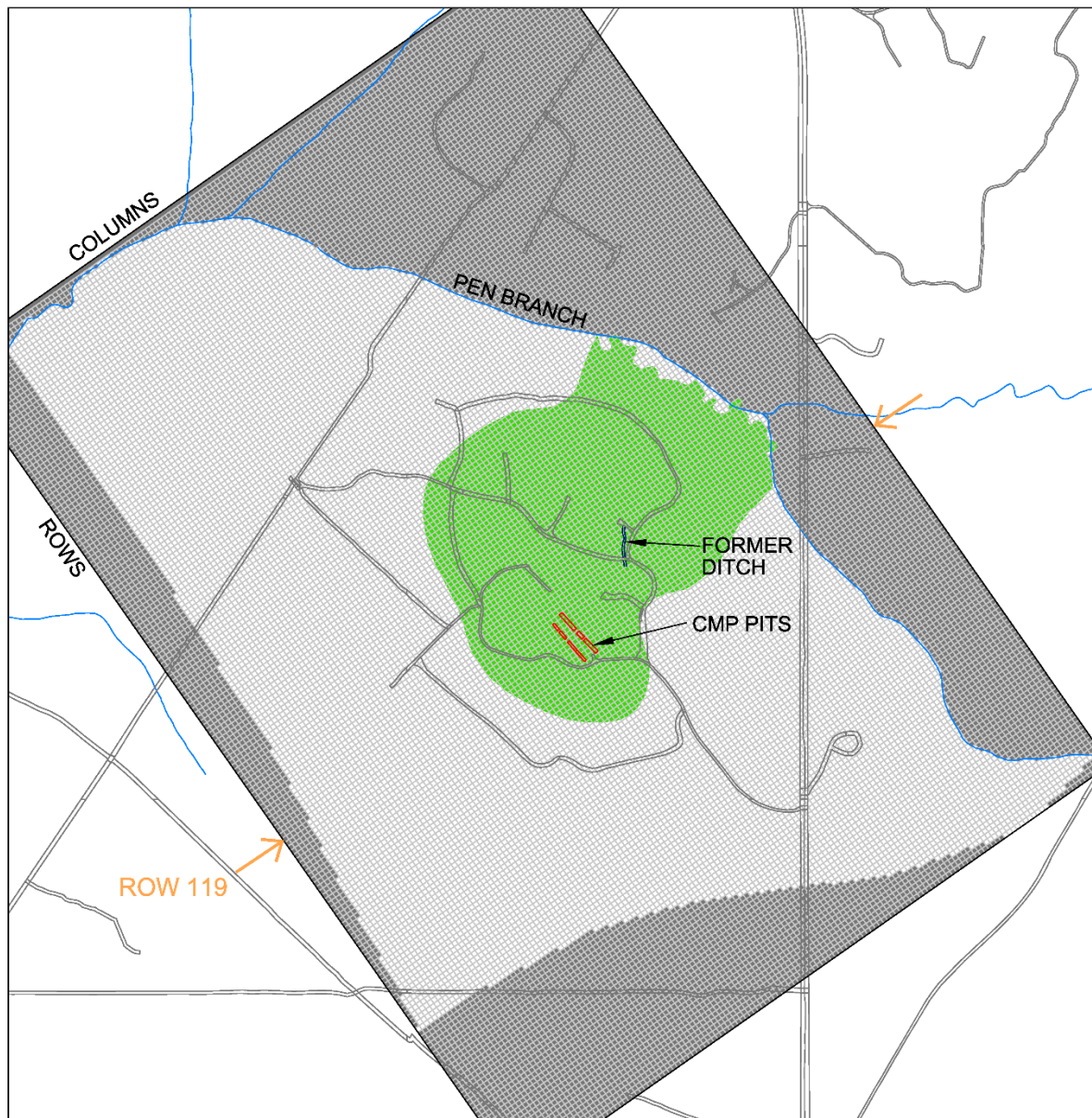


Figure 5. Model Domain and Grid

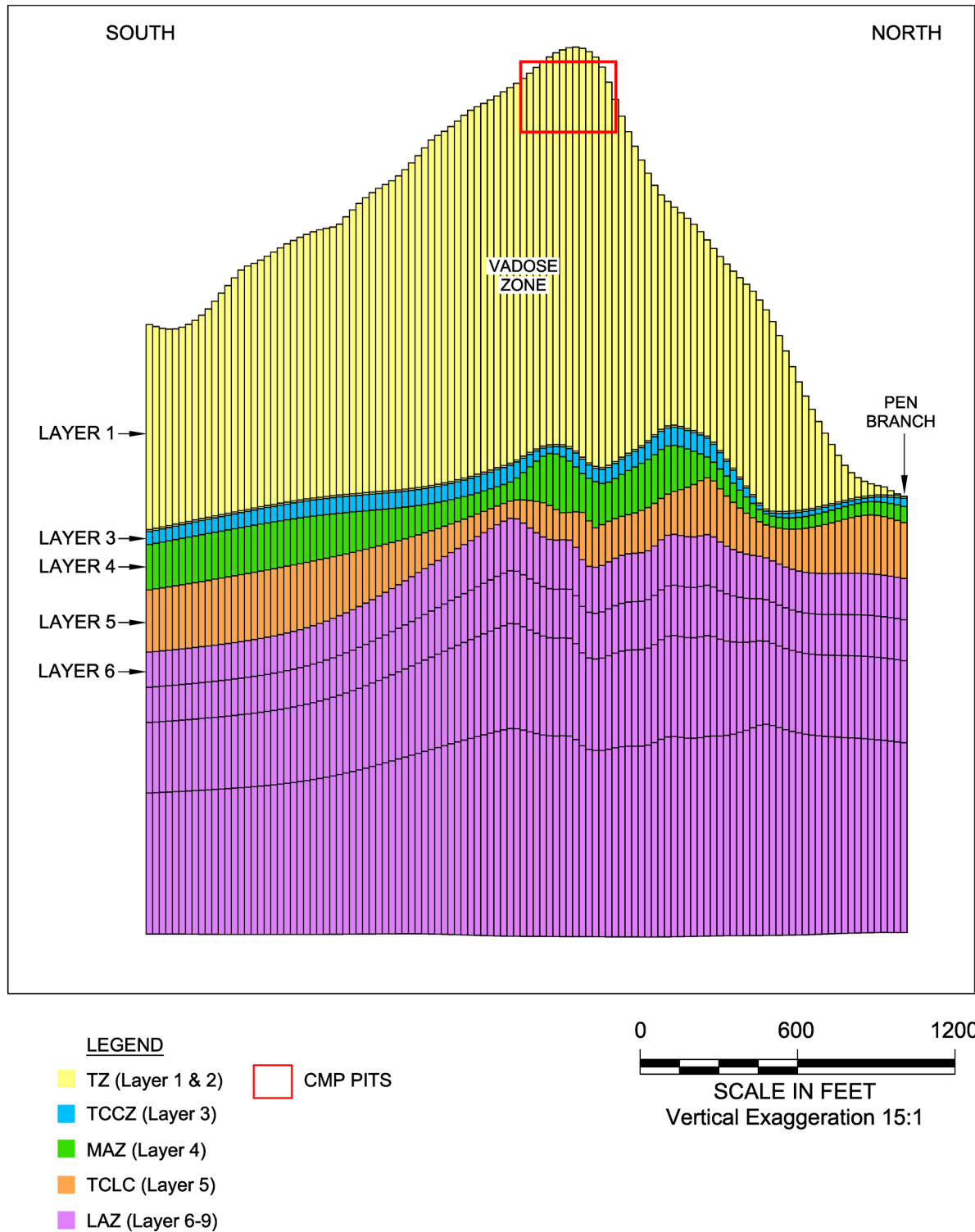
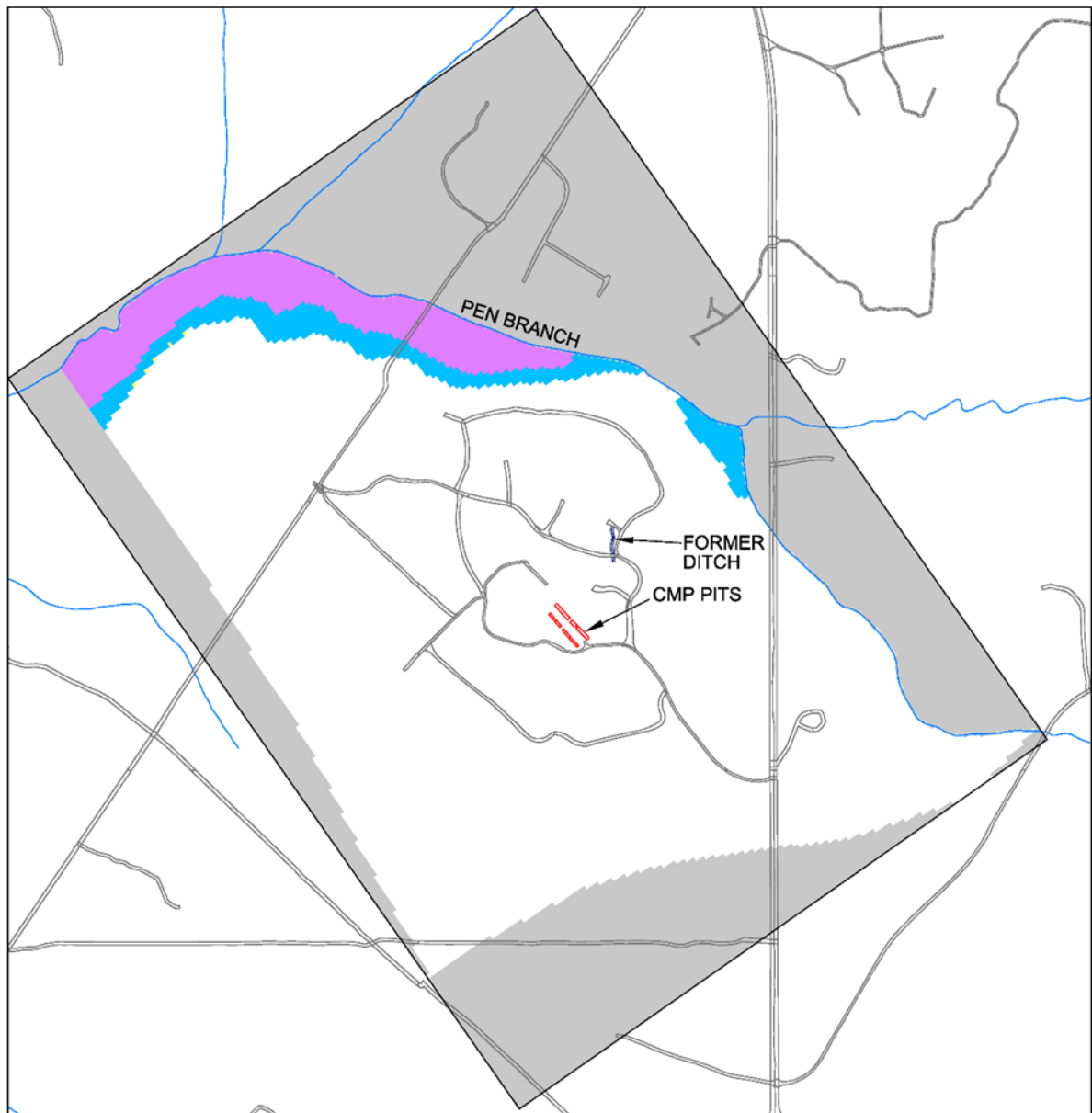


Figure 6. Cross-section Along Row 119 Showing Model Layering



LEGEND

- Inactive for Flow - All Layers
- Inactive for Flow - Layers 1-2
- Inactive for Flow - Layers 1-4

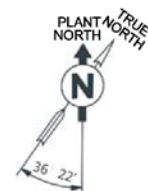
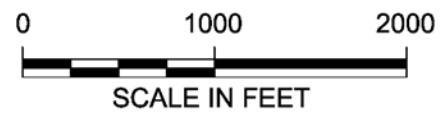


Figure 7. Inactive Area in the Model

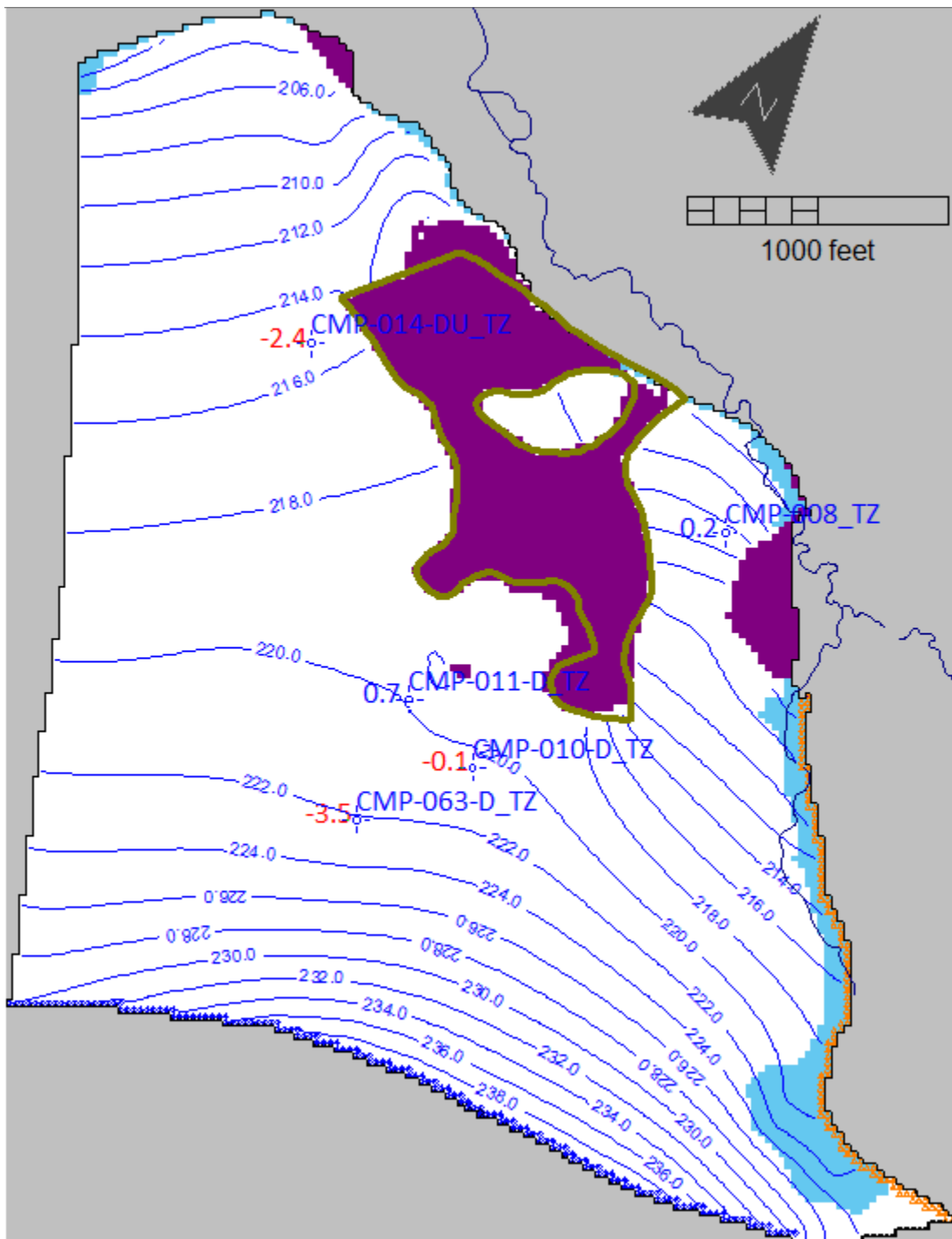


Figure 8. Potentiometric Surface and Head Residuals in the TZ

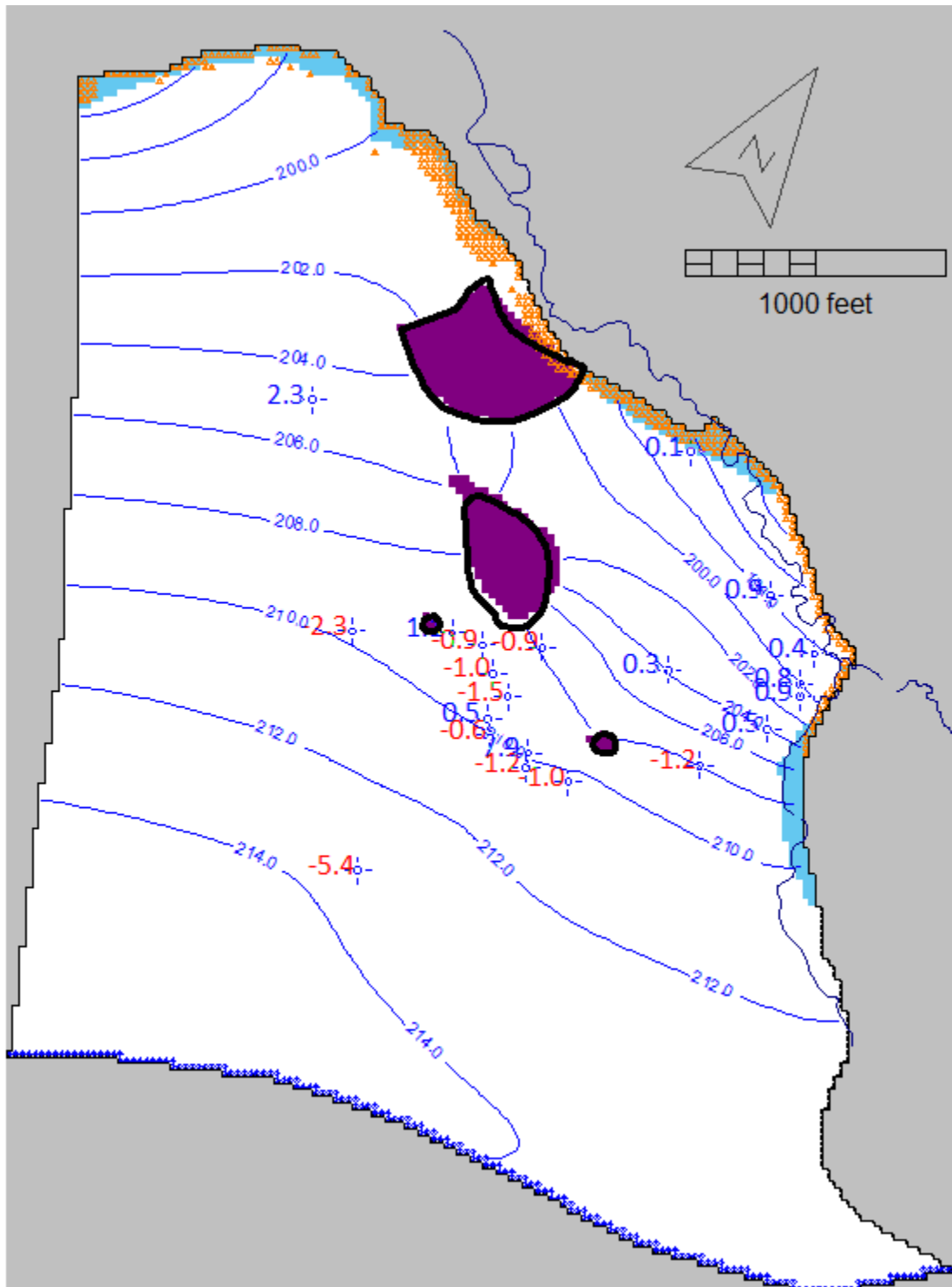


Figure 9. Potentiometric Surface and Head Residuals in the MAZ

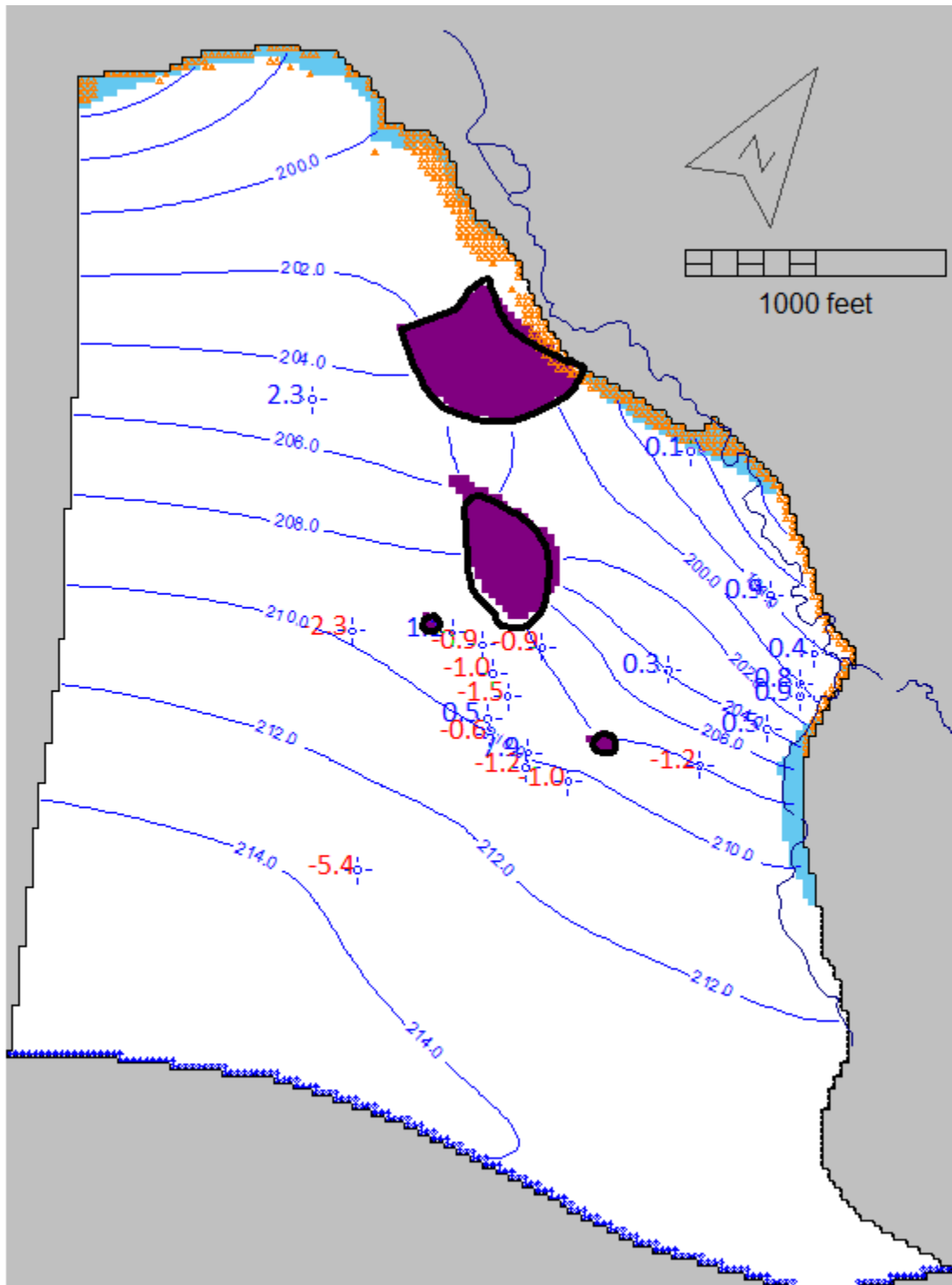


Figure 10. Potentiometric Surface and Head Residuals in the LAZ

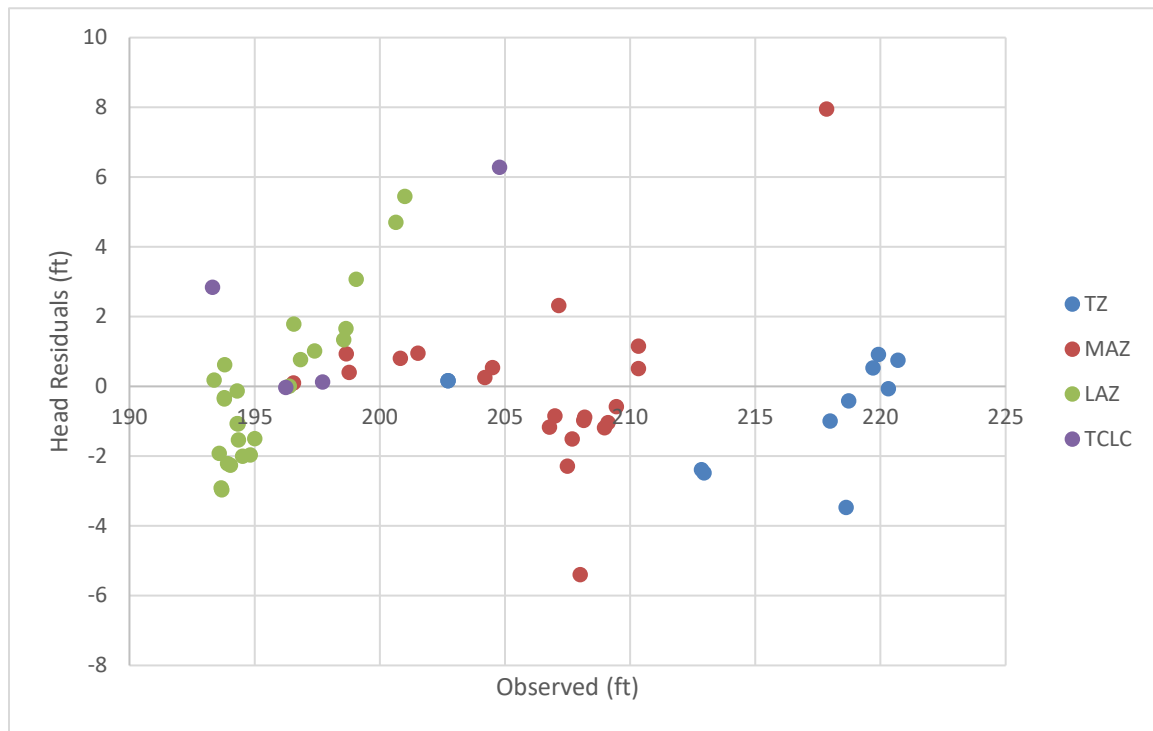
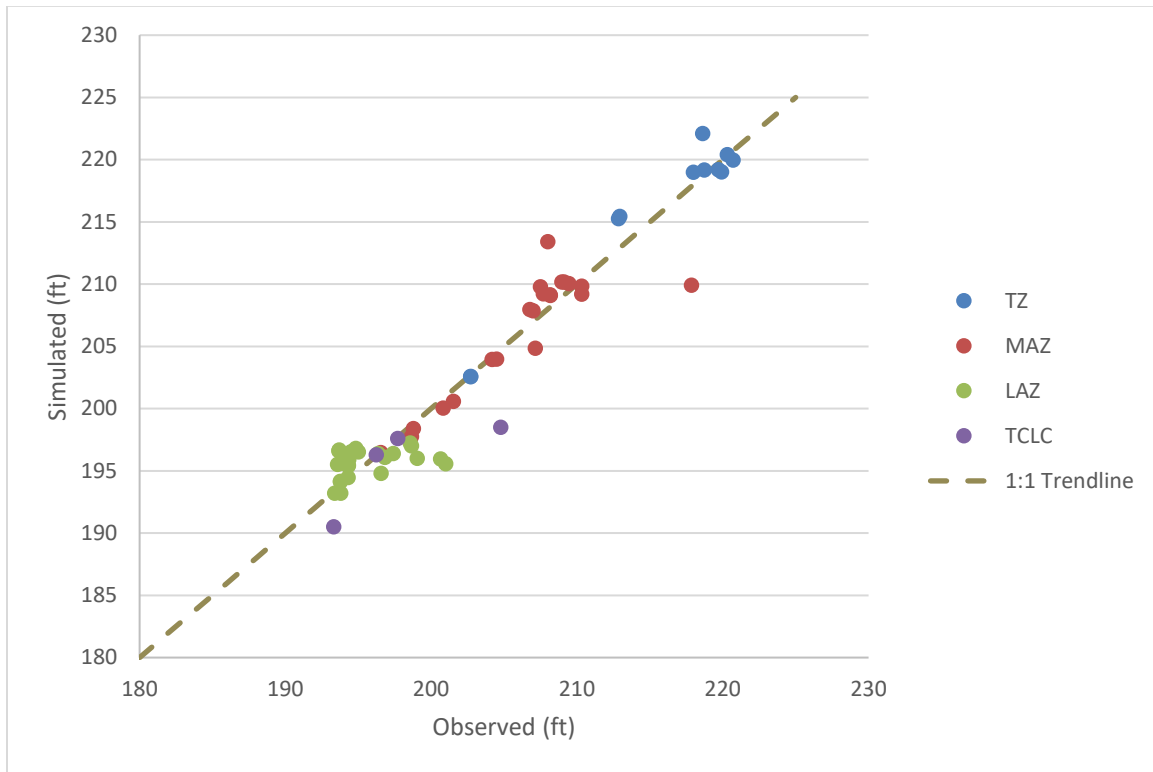
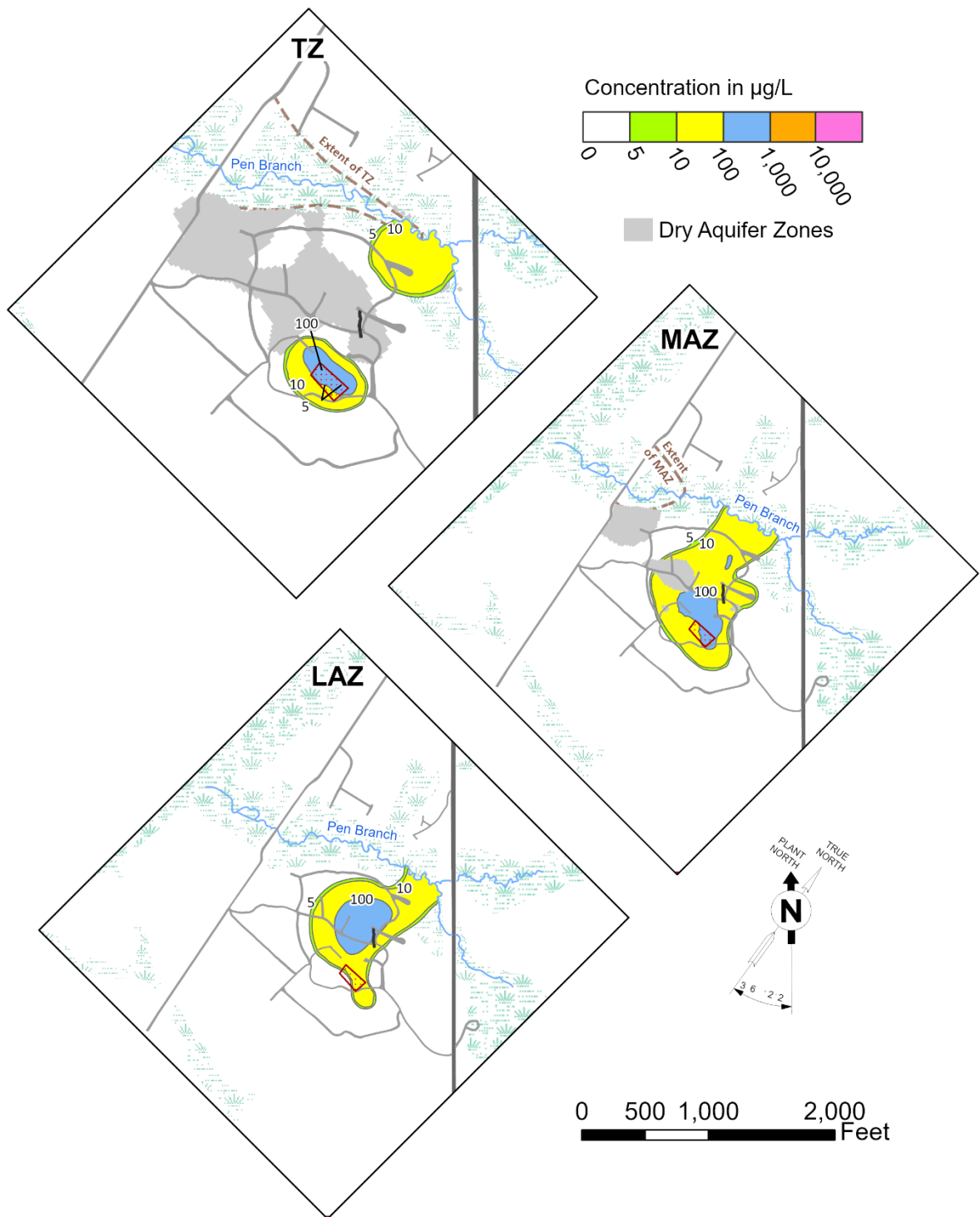


Figure 11. Comparison of Modeled vs Observed Heads and Head Residuals vs Observed Heads



CMP_Pits_Modeling_PCE_2023

Figure 12. Initial PCE Plume for All Aquifers (end of 2022)

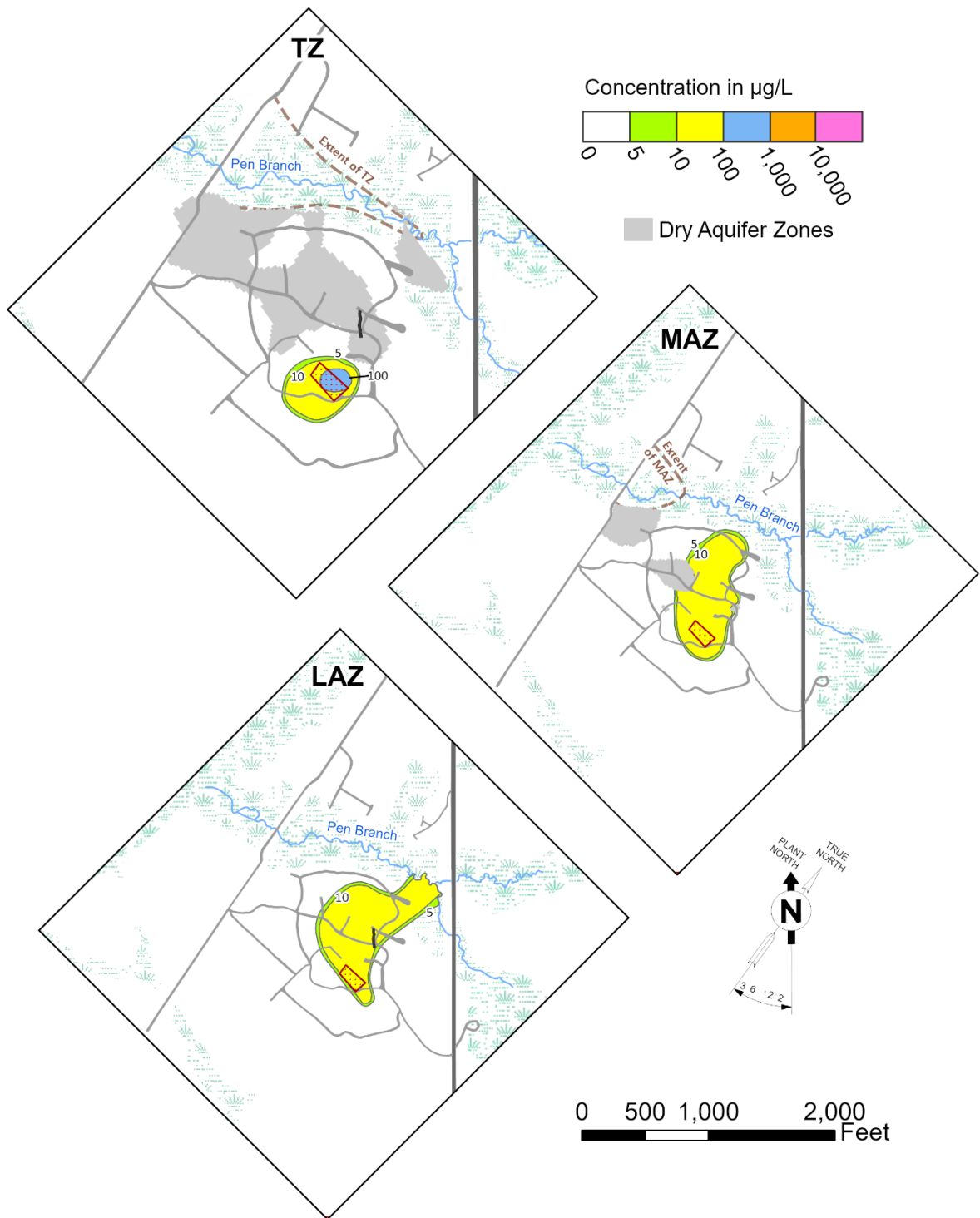
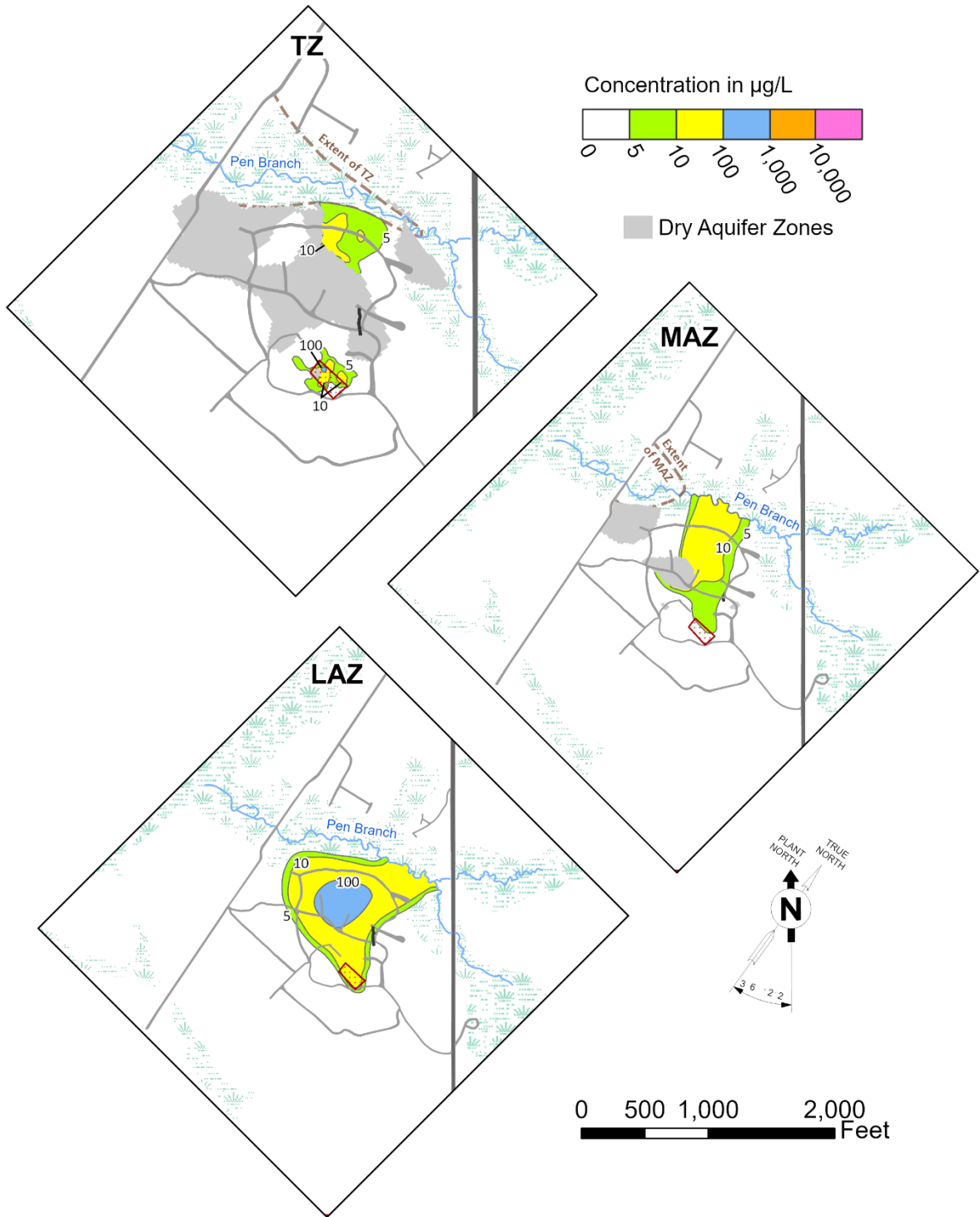
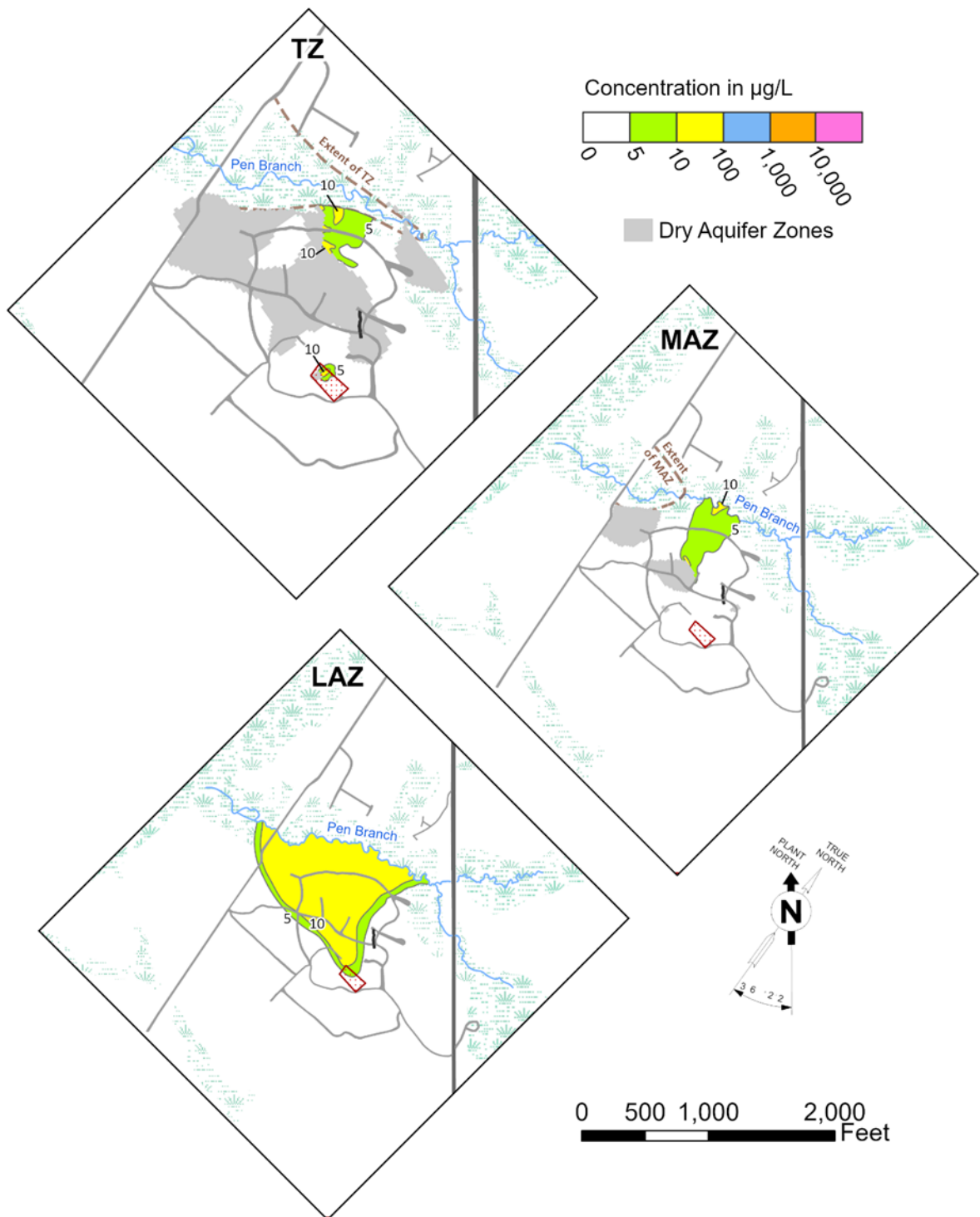


Figure 13. Initial TCE Plume for All Aquifers (end of 2022)



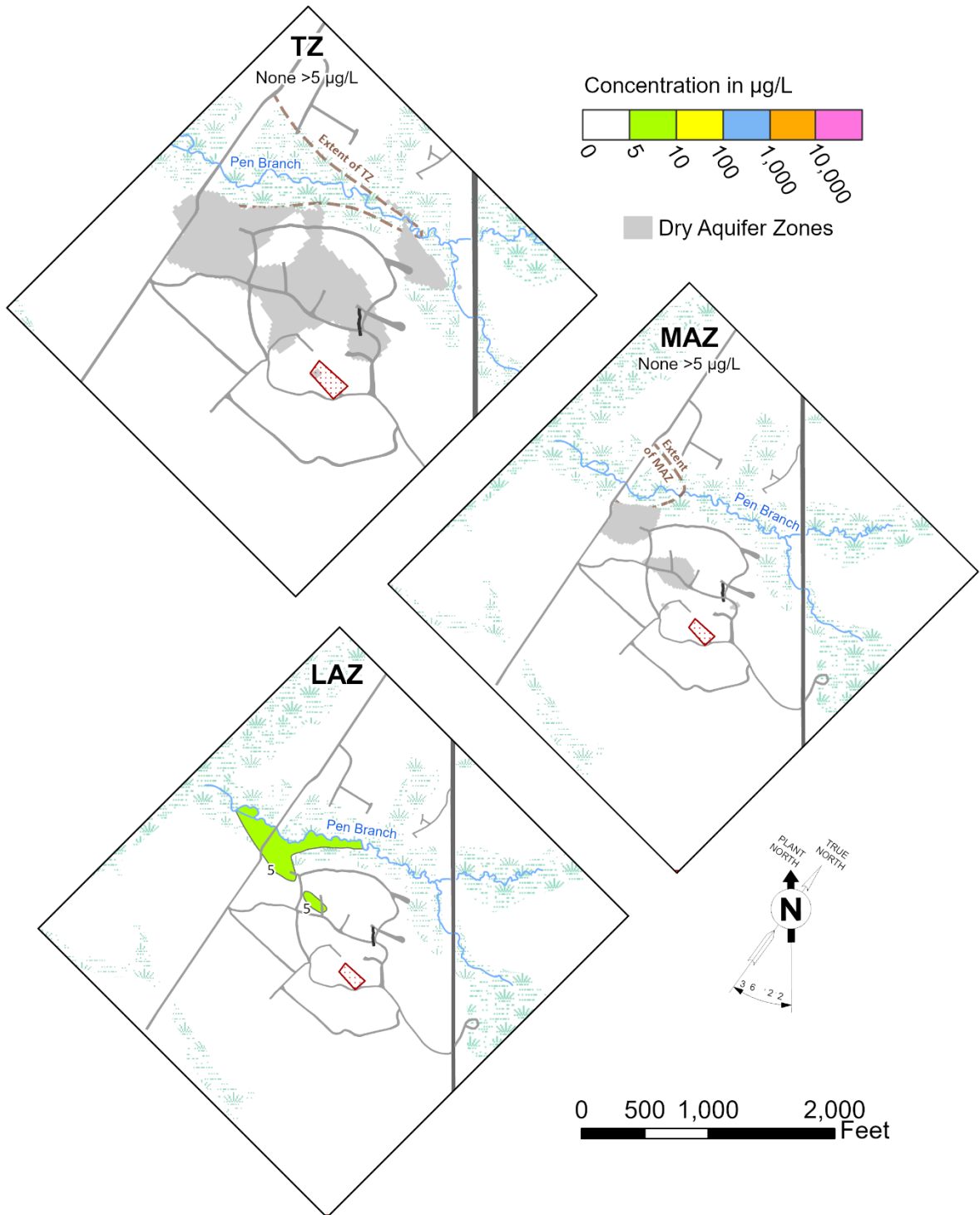
CMP_Pits_Modeling_PCE_2040

Figure 14. Modeled PCE Plume in the Year 2040



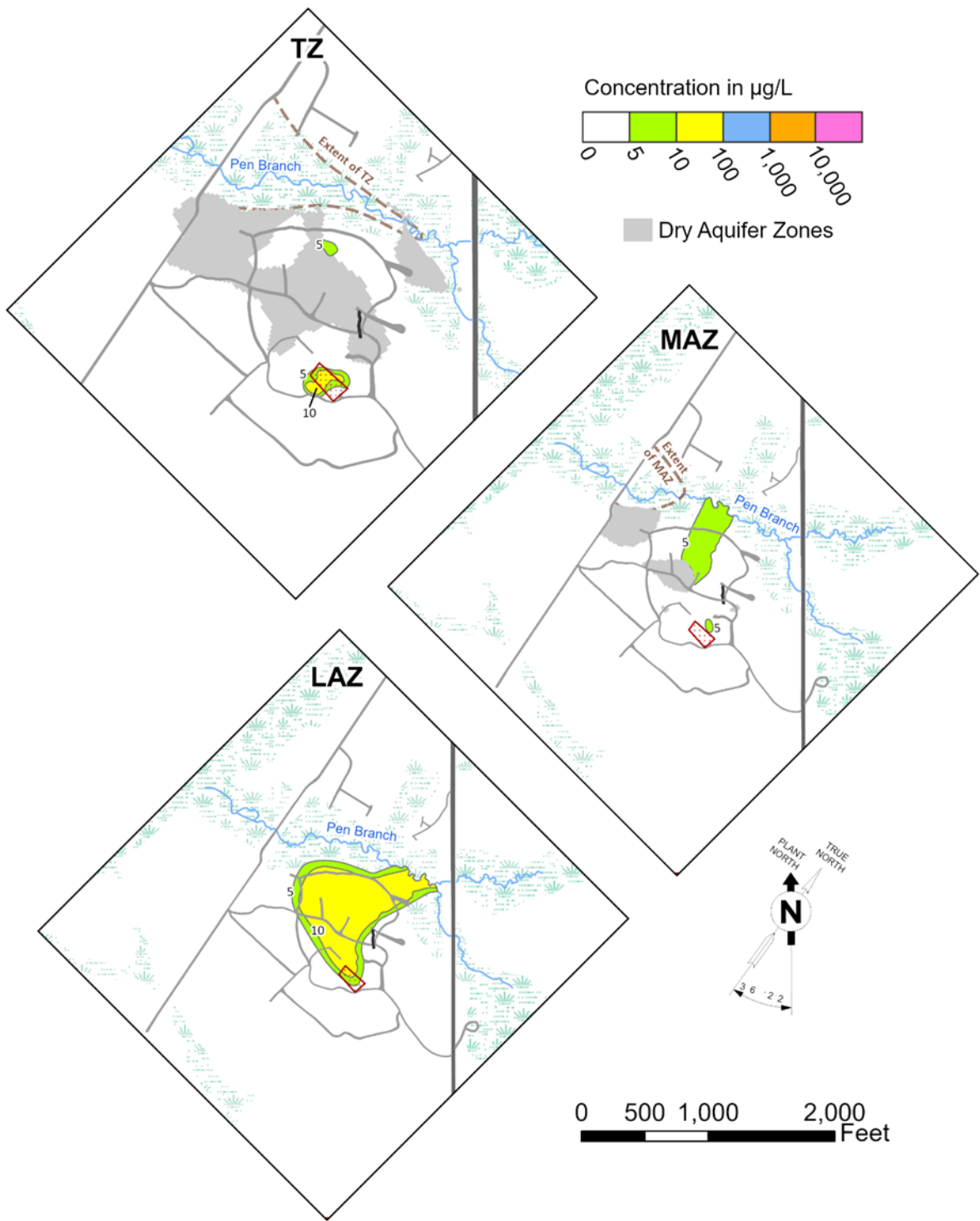
CMP_Pits_Modeling_PCE_2060

Figure 15. Modeled PCE Plume in the Year 2060



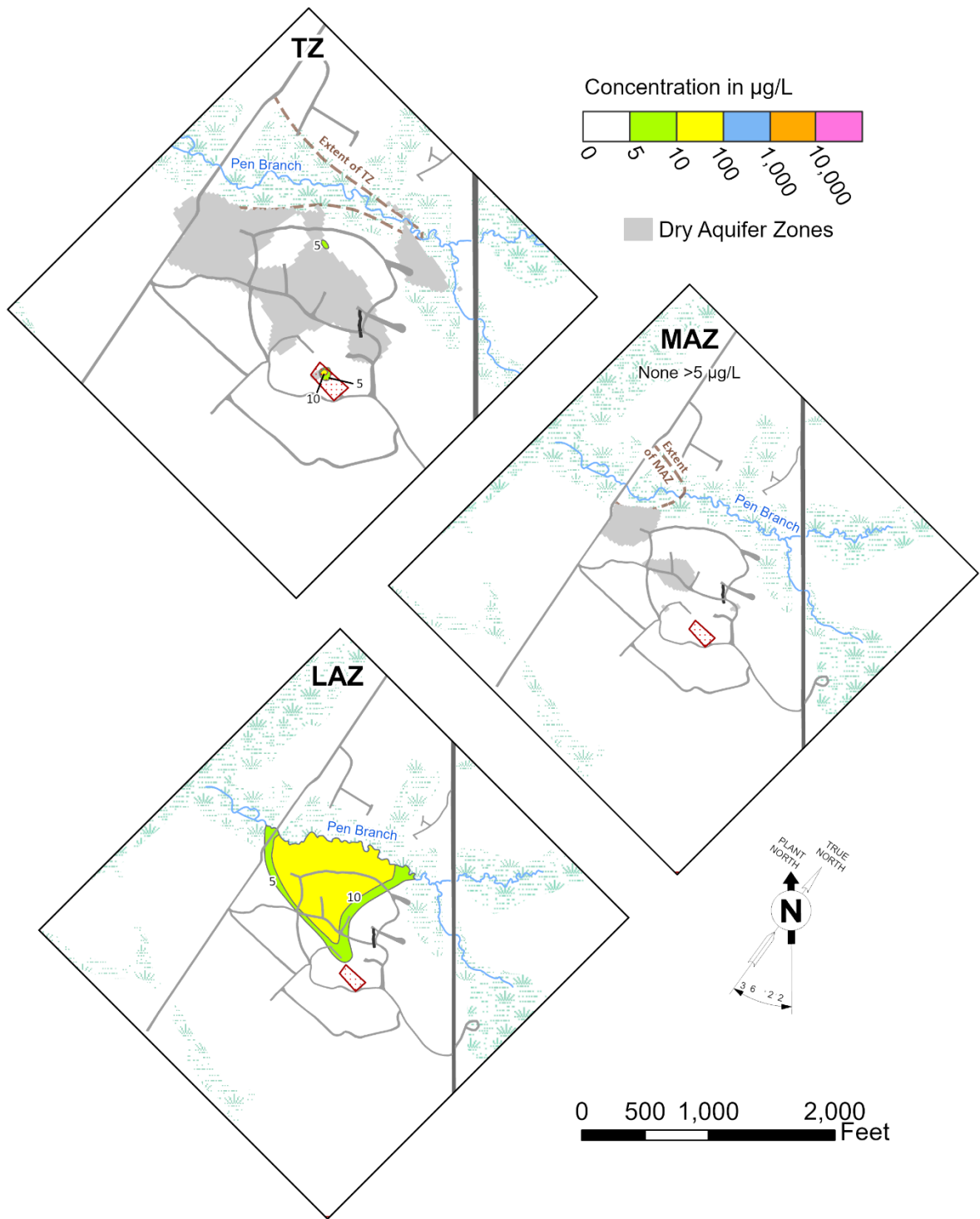
CMP_Pits_Modeling_PCE_2122

Figure 16. Modeled PCE Plume in the year 2122



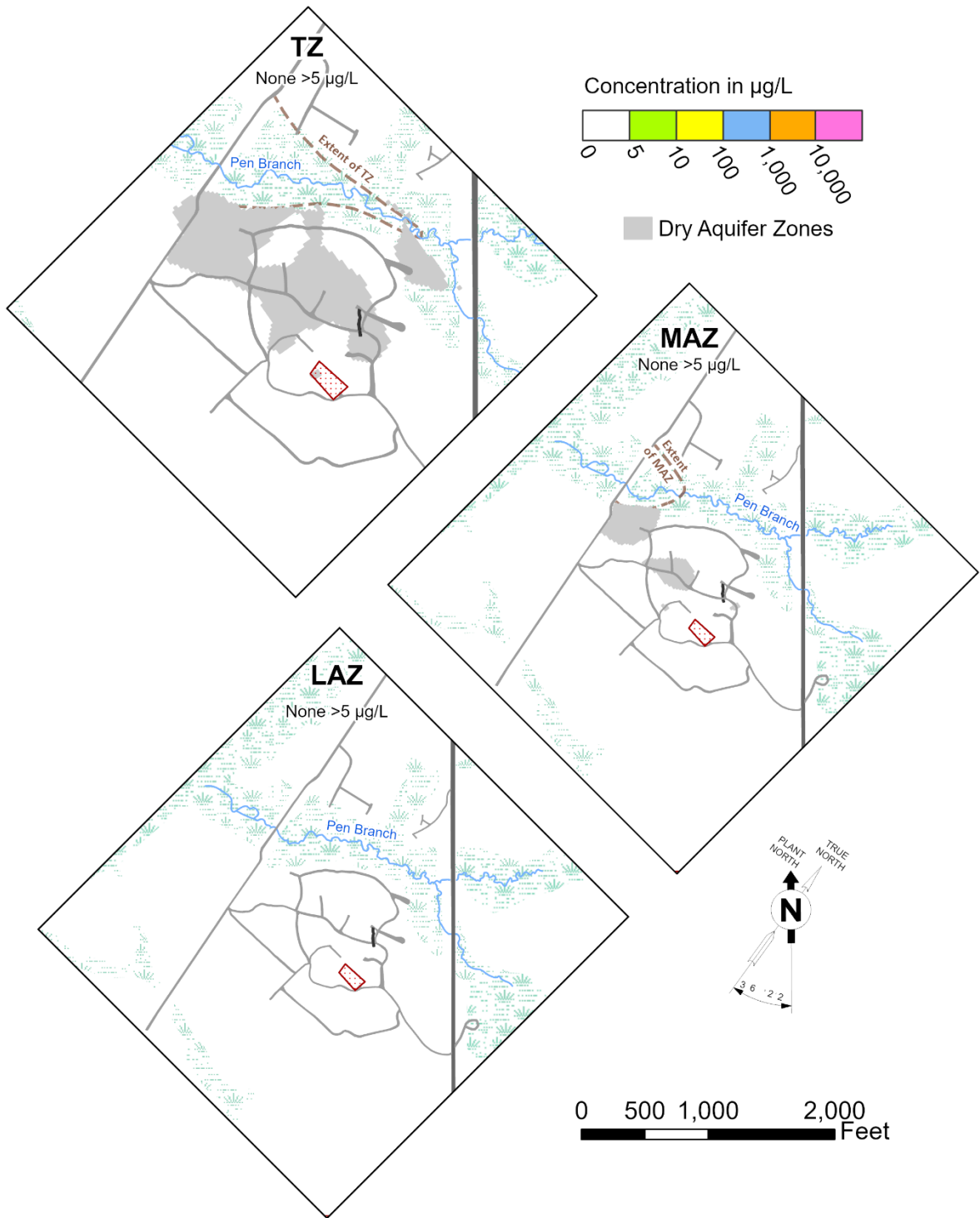
CMP_Pits_Modeling_TCE_2040

Figure 17. Modeled TCE Plume in the year 2040



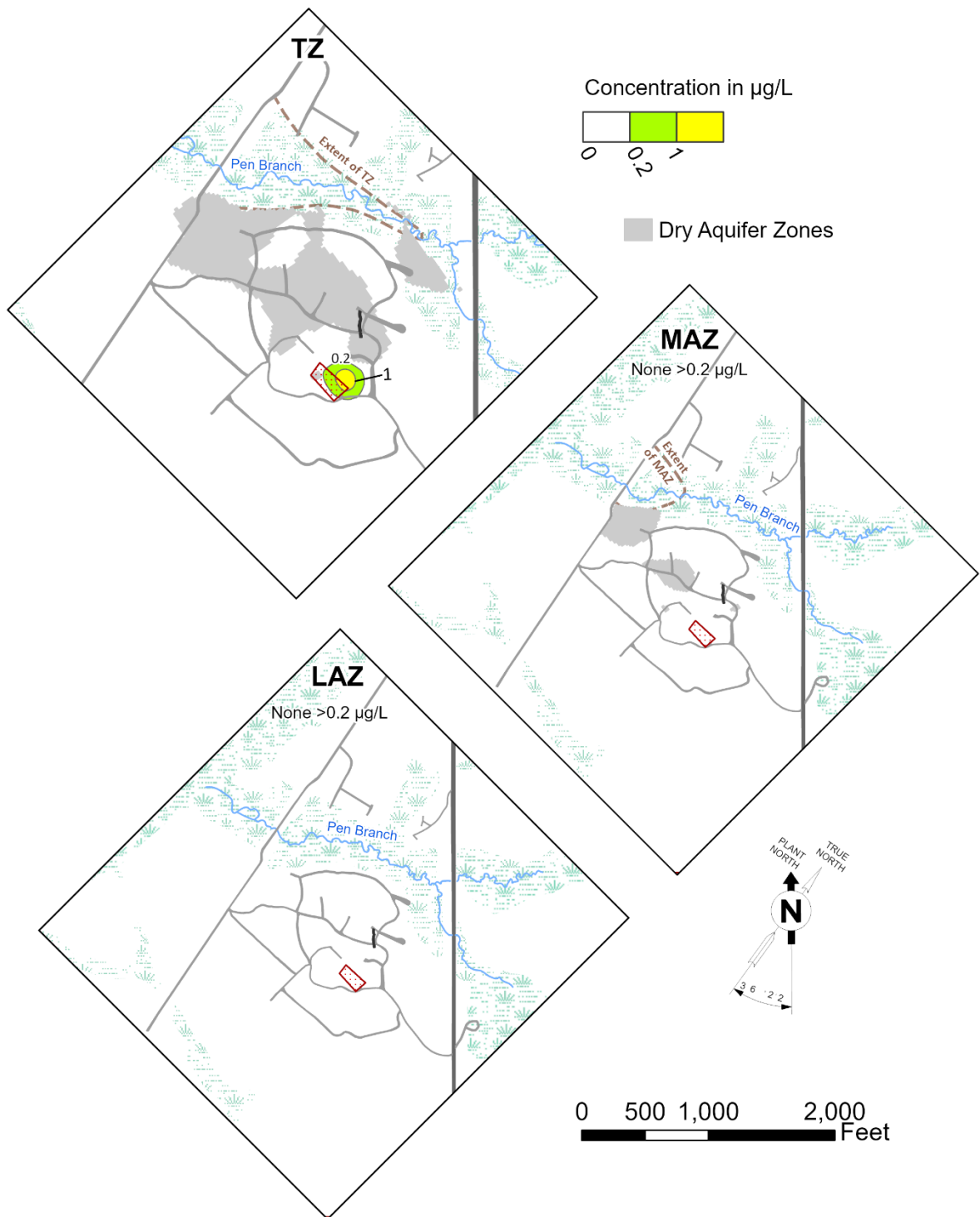
CMP_Pits_Modeling_TCE_2060

Figure 18. Modeled TCE Plume in the year 2060



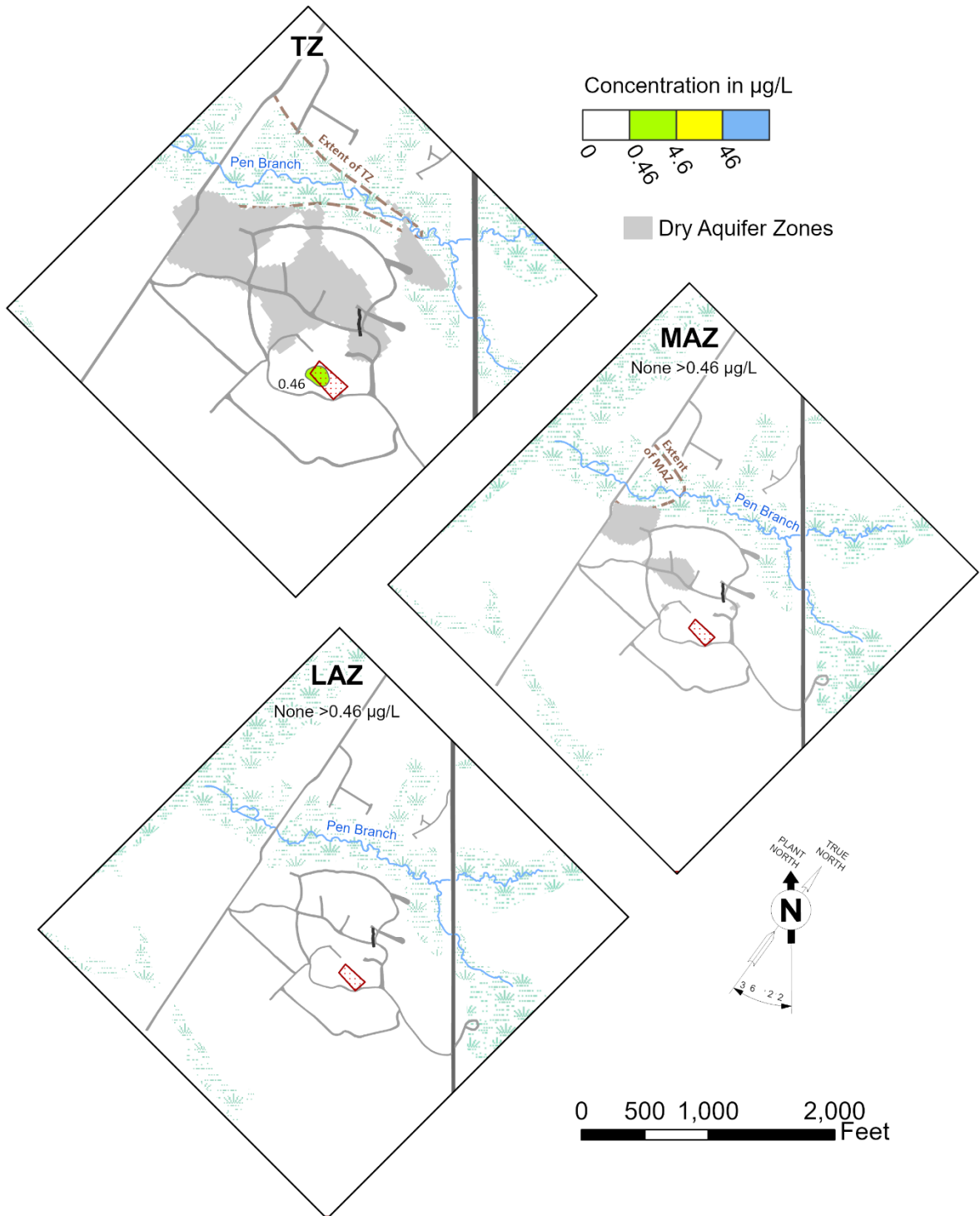
CMP_Pits_Modeling_TCE_2122

Figure 19. Modeled TCE Plume in the year 2122



CMP_Pits_Modeling_Lindane_2023

Figure 20. Initial Lindane Plume for All Aquifers (end of 2022)



CMP_Pits_Modeling_1,4-Dioxane_2023

Figure 21. Initial 1,4-Dioxane Plume for All Aquifers (end of 2022)

Table 1. Water Level (ft) Statistics for the Previous Model (Tetra Tech 2017) and the Period of Record Considered for the Current Updated Model

	Average	High	Low	Range
Previous Model (Fall 2016)	202.9	240.8	177.9	62.9
Current Model (Average of Period of Record [1984 – 2022])	201.7	239.8	179.4	60.4
Difference	[1.2]	[1]	[1.5]	[2.5]

Table 2. Model Parameters (Post-Calibration)

Parameter	Final Calibrated Value			
		Unit	$K_x = K_y$	K_z
Hydraulic Conductivity (ft/d)	TZ	8	0.08	
	TCCZ Base	0.21	0.0021	
	TCCZ High	0.58	0.0058	
	MAZ	50	0.5	
	TCLC Base	0.22	0.0022	
	TCLC Low	0.0003	0.000003	
	LAZ	30	0.30	
Upland Recharge Rate (in/yr)	16.0			
Slope Recharge Rate (in/yr)	13.34			
Capped Recharge Rate (in/yr)	1.2			
Wetland Recharge Rate (in/yr)	0			
Drain Conductance (ft ³ /d/ft)	Unit	Pen Branch	Seepage Face	Wetlands
	TZ	0.16	10	0.01
	MAZ	0.5-50	1.0	1.5
	LAZ	0.75	N/A	1.5
Specified Heads on Model Perimeter (ft)	Unit		Value	
	TZ		230-240	
	MAZ		213-215	
	LAZ		194-200	

Table 3. Comparative Model Calibration Statistics (Previous vs Updated)

Aquifer	Mean Error (ft)		Mean-Absolute Error (ft)		Root-Mean Square Error (ft)	
	Previous	Updated	Previous	Updated	Previous	Updated
TZ	-0.27	-0.67	0.96	1.12	1.13	1.56
MAZ	-0.29	0.00	1.96	1.51	2.41	2.35
LAZ	-0.72	-0.07	1.62	1.71	2.28	2.16
All Targets	-0.51	0.00	1.62	1.57	2.15	2.24

Table 4. Head Residuals post-Calibration Simulation

Table 4: Head Residuals Post-Calibration Simulation				
Name	Unit	Observed (ft)	Modeled (ft)	Residual (ft)
CMP-008	TZ	202.72	202.56	0.16
CMP-008	TZ	202.72	202.57	0.16
CMP-013-D	TZ	219.92	219.00	0.91
CMP-014-D	TZ	212.95	215.43	-2.48
CMP-030-D	TZ	217.98	218.98	-0.99
CMP-034-D	TZ	218.73	219.15	-0.42
CMP-035-D	TZ	219.70	219.17	0.53
CMP-010-D	TZ	220.32	220.39	-0.07
CMP-011-D	TZ	220.70	219.96	0.74
CMP-014-DU	TZ	212.85	215.24	-2.39
CMP-063-D	TZ	218.63	222.10	-3.47
CMB-015-I	MAZ	217.85	209.91	7.94
CMB-024-I	MAZ	208.97	210.16	-1.19
CMP-014-CR	MAZ	207.15	204.83	2.32
CMP-030-C	MAZ	207.49	209.78	-2.29
CMP-036-D	MAZ	204.50	203.96	0.54
CMP-037-D	MAZ	201.53	200.58	0.95
CMP-038-D	MAZ	200.83	200.02	0.80
CMP-039-D	MAZ	198.77	198.38	0.40
CMP-040-D	MAZ	198.66	197.73	0.92
CMP-041-D	MAZ	196.55	196.46	0.09
CMP-044-D	MAZ	210.33	209.19	1.15
CMP-045-D	MAZ	208.19	209.07	-0.88
CMP-046-D	MAZ	208.15	209.13	-0.98
CMP-047-D	MAZ	207.69	209.20	-1.52
CMP-048-D	MAZ	207.00	207.85	-0.85
CMP-050-D	MAZ	209.12	210.17	-1.05
CMP-051-D	MAZ	204.19	203.94	0.25

Table 4: Head Residuals Post-Calibration Simulation

Name	Unit	Observed (ft)	Modeled (ft)	Residual (ft)
CMP-052-C	MAZ	210.33	209.82	0.50
CMP-059-C	MAZ	209.44	210.03	-0.58
CMP-063-C	MAZ	208.00	213.40	-5.40
CMP-065-BU	MAZ	206.77	207.95	-1.18
CMP-008-B	TCLC	197.72	197.60	0.12
CMP-031-C	TCLC	204.78	198.50	6.28
CMP-043-D	TCLC	193.32	190.48	2.84
CMP-055-C	TCLC	196.25	196.28	-0.03
CMP-010-C	LAZ	198.65	196.99	1.66
CMP-032-C	LAZ	194.35	195.89	-1.54
CMP-033-D	LAZ	193.78	194.15	-0.36
CMP-052-BU	LAZ	196.38	196.38	0.00
CMP-054-C	LAZ	194.34	195.42	-1.08
CMP-058-B	LAZ	195.01	196.51	-1.50
CMP-060-B	LAZ	193.38	193.20	0.18
CMP-015-B	LAZ	201.01	195.56	5.44
CMP-035-B	LAZ	194.52	196.53	-2.01
CMP-050-B	LAZ	193.69	196.66	-2.97
CMP-011-B	LAZ	197.40	196.39	1.01
CMP-012-B	LAZ	193.59	195.51	-1.92
CMP-013-B	LAZ	193.92	196.14	-2.22
CMP-014-B	LAZ	193.80	193.19	0.62
CMP-030-B	LAZ	194.30	195.37	-1.07
CMP-055-B	LAZ	196.56	194.78	1.78
CMP-061-B	LAZ	193.78	194.12	-0.33
CMP-062-B	LAZ	198.56	197.22	1.33
CMP-064-BU	LAZ	199.06	195.99	3.06
CMP-010-B	LAZ	193.67	196.58	-2.91
CMP-031-B	LAZ	194.31	194.44	-0.13

Table 5. Fractional Organic Content (F_{oc}), Equilibrium Dissociation Constant (K_d), and Retardation Factor (R) values by Hydrostratigraphic Unit for TCE and PCE

Layer	F_{oc} (%)	K_d (L/kg)	R (-)
Transmissive Zone	1.0	2.65	14.1
Tan Clay Confining Zone	1.2	3.18	16.7
Middle Aquifer Zone	0.3	0.80	4.9
Tan Clay Lower Clay	0.3	0.80	4.9
Lower Aquifer Zone	0.3	0.80	4.9

Source: Tetra Tech, 2017

Table 6. Fractional Organic Content (F_{oc}), Equilibrium Dissociation Constant (K_d), and Retardation Factor (R) values by Hydrostratigraphic Unit for Lindane

Layer	F_{oc} (%)	K_d (L/kg)	R (-)
Transmissive Zone	1.0	11	55.3
Tan Clay Confining Zone	1.2	13.2	66.1
Middle Aquifer Zone	0.3	3.3	17.3
Tan Clay Lower Clay	0.3	3.3	17.3
Lower Aquifer Zone	0.3	3.3	17.3

Source: Tetra Tech, 2017

Table 7. Fractional Organic Content (F_{oc}), Equilibrium Dissociation Constant (K_d), and Retardation Factor (R) values by Hydrostratigraphic Unit for 1,4-Dioxane

Layer	F_{oc} (%)	K_d (L/kg)	R (-)
Transmissive Zone	1.0	0.17	1.8
Tan Clay Confining Zone	1.2	0.2	2.0
Middle Aquifer Zone	0.3	0.05	1.3
Tan Clay Lower Clay	0.3	0.05	1.3
Lower Aquifer Zone	0.3	0.05	1.3

Source: Tetra Tech, 2017

Table 8. Predicted Impacts to Groundwater Near Pen Branch

COI	MCL or RSL (µg/L)	Maximum Concentration (µg/L)	Year of Maximum	Year Concentration Drops below MCL
PCE	5	49	1	104
TCE	5	19	1	55
Lindane	0.2	N/A	N/A	1
1,4-Dioxane *	0.46	0.46	1	1

* RSL, all others list MCL

Table 9. Predicted Impacts to Surface Water in Pen Branch

COI	MCL or RSL (µg/L)	Dilution Factor (-)	Maximum Concentration in Groundwater (µg/L)	Maximum Concentration in Surface Water (µg/L)	Year of Maximum	Year Concentration Drops below MCL
PCE	5	5	49	9.8	1	5
TCE	5	5	19	3.8	1	-
Lindane	0.2	5	N/A	N/A	-	-
1,4-Dioxane *	0.46	5	0.46	N/A	-	-

* RSL, all others list MCL

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