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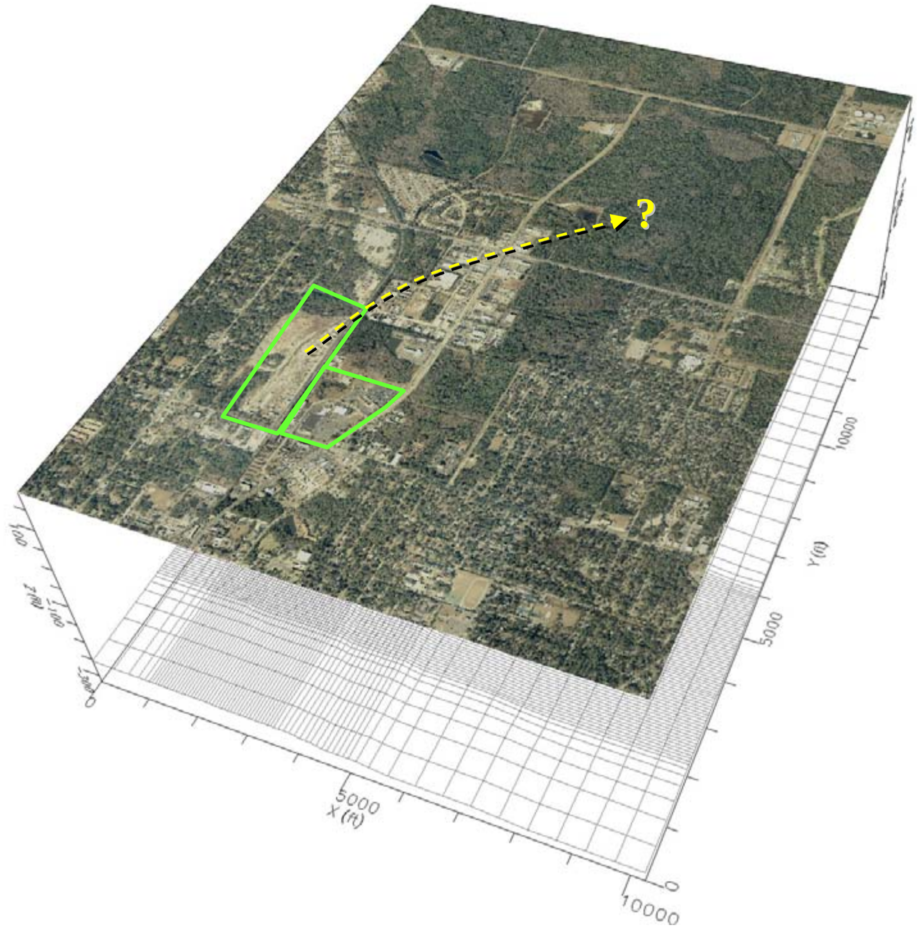
Technical Memorandum



A Critique of the GeoTrans Flow and Transport Model, Koppers, Inc. Site, Gainesville, Florida

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1.0 Introduction

Waterloo Hydrogeologic, Inc. (WHI) evaluated a model developed by GeoTrans Inc. (GeoTrans Model) for the Koppers portion of the Cabot Carbon/Koppers Superfund Site (the Site) located in Gainesville, Florida. The model is intended to simulate the groundwater flow system and fate and transport of dissolved contaminants at the Site. A special consideration was the potential for Site contaminants to migrate into the Upper Floridan Aquifer. The GeoTrans Draft Report dated October 5, 2004, gives a detailed description of the Site characterization and the original GeoTrans Model (GeoTrans, 2004).

To evaluate GeoTrans' model, the original model files were imported into WHI's graphical user interface Visual MODFLOW. This interface allows efficient visual inspection of model files (2-D aerial and cross-sectional as well as 3-D views), as well as running additional scenarios to assess the relevance of key model assumptions and simplifications.

The proceeding pages describe our results and comments regarding the existing GeoTrans model and modifications that would enhance the ability of the GeoTrans model to be used as a predictive tool at the Site. Discussion related to the following items are provided:

- Description of the GeoTrans Model Setup and Parameters
- Description of the WHI (Base Case) Model Setup and Parameters
- Simplifications and uncertainties identified for the GeoTrans Model
- Import of the GeoTrans Model into WHI's Visual MODFLOW and additional simulations to evaluate
    a) Migration pathways of groundwater flow
    b) Fate and transport of naphthalene
    c) Impact of effective porosity on travel times in the Upper Transmissive Zone of the Floridan Aquifer
- Results observed from the model modifications
- Summary and Recommendations

2.0 The GeoTrans Model

The GeoTrans model is described in the report: *Addendum 7: Groundwater Flow and Transport Model: Draft Report, Koppers Inc. Site, Gainesville, Florida (2004)*. The report presents much of the input and assumptions associated with the GeoTrans Model; however, during our work it was evident that there were reporting mistakes and omissions that do not allow for a perfect correlation between the model files and what was reported.

The following information taken from the modeling report (GeoTrans, 2004) summarizes the GeoTrans Model.

Model Domain and Discretization

The GeoTrans model area extends from approximately 2,000 feet south of the Site to approximately 2 miles north, where it incorporates the southwestern corner of the Murphree Wellfield (Figure 3-1, GeoTrans, 2004). The model consists of 92 rows by 72 columns by 11 explicit layers, for a total of 6624 grid cells per each layer. Grid spacing varies from 60 by 60 feet at the Site to 500 by 500 feet near the external model boundaries.

The 11 specific layers in the GeoTrans Model represent:
- The Surficial Aquifer (Layer 1),
- The Hawthorn Group (Layers 2 through 9) and
- The Upper Floridan Aquifer, comprised of the:
  - Ocala Limestone (Layer 10: Upper Transmissive Zone),
  - Ocala/Avon Park Contact or Ocala Lower Transmissive Zone (Layer 11); and
  - A low permeability, dense carbonate deposit (100 feet thick) separating the two water-producing zones and acting as a semi-confining unit (SCU) represented as an *implicit layer*.

The Surficial Aquifer is a 20- to 30- feet thick unconsolidated, fine- to medium-grained sand, with thin layers of interbedded silt and clay deposits. The Hawthorn Group is a thick sequence (120 to 125 feet) of low-permeability clay and silt deposits with interbedded higher-permeability sand, silty sand and carbonate deposits.

Within the Upper Floridan Aquifer, the Ocala Upper Transmissive Zone (UTZ) is approximately 100 feet thick. A 100-foot semi-confining unit (SCU) separates the Ocala UTZ from the Lower Transmissive Zone (LTZ). The LTZ is at the base of the Ocala Limestone and the top of the Avon Park Formation and is approximately 100 feet thick. The majority of water (up to 85%) from the Murphree Wellfield is produced from this lower zone. The SCU is implicitly represented in the model by a lower vertical conductance between Layers 10 and 11 rather than as a distinct explicit layer. This representation is discussed further later in this document.

Model Boundary Conditions

The GeoTrans Model assigns a combination of no-flow and specified-head boundary conditions to Layers 1, 10 and 11. Layer 1 has specified-head conditions in the southwestern corner of the grid, with no-flow conditions on the remainder of the boundaries. The boundary conditions for Layers 10 and 11 of the model consist of no-flow boundaries on the northern and eastern sides of the model, and time-variant specified-head boundaries at the southern and northwestern corners. Model Layers 2 to 9 have no-flow conditions specified on all four boundaries.

Model Parameter Values

Model parameters (K_x, K_y, Effective Porosity, Storage Coefficient) for each of the hydrostratigraphic units are given in Table 1 (next section). More detailed descriptions are found in the GeoTrans Draft Report.

MODFLOWT (GeoTrans, 1997), an extension of the USGS MODFLOW code, was used to simulate the groundwater flow system, and fate and transport of naphthalene in the GeoTrans model; MODPATH (Pollock, 1994) was used to simulate migration pathways and average groundwater travel times to the Murphree Wellfield Area.

The dissolved-phase organic plumes at the Site are conceptualized to be a result of residual NAPLs dissolution from groundwater flowing through contaminated areas. Source areas in the Site model are represented by specified constant-concentration boundaries that provide a continuous source of dissolved-phase contaminant to the local groundwater. Based on the estimated range of source zone naphthalene concentrations obtained at the site, a constant source concentration of 10,000 μg/L was applied to Model Layers 1, 5 and 8 beneath the footprints of the four source areas (i.e. the Surficial Aquifer and the Upper and Lower Hawthorn Groups). A smaller source of naphthalene was also entered in Layer 10 (the Ocala UTZ) beneath the footprint of the former North Lagoon.

The GeoTrans Model was calibrated using historic groundwater level information at wells throughout the model domain. Well pumping rates were defined during the time-varying simulations using actual pumping rates. GeoTrans used a total of 5,105 time-varying water-level measurements obtained from wells within the model area, which were then compared to the model simulations. The normalized root mean square error (normalized to the total head drop change in the model domain) is 1.5%. The match between the observed and calculated groundwater levels varied from well to well during the simulation. The following general trends are noted regarding the model calibration:

- The Lower Hawthorn Group Clay wells heads plotted in Figure 3-9 of the GeoTrans Report consistently showed lower observed heads when compared with simulated results, and
- The Surficial Aquifer, Upper and Lower Hawthorn Groups and Ocala UTZ wells show good correlation to simulated head results.

The model was not calibrated using groundwater flow information, such as discharge to wetlands. This means that the calibration achieved in the GeoTrans model does not consider the interaction between groundwater and surface water features within the model domain. During groundwater modeling studies there are often different hydraulic conductivity and transmissivity value distributions that can adequately match observed groundwater levels. Completing a calibration to estimated and measured flow rates (to surface water such as wetlands and streams) helps to reduce the nonuniqueness of the calibration to groundwater levels alone. In addition, groundwater flow rates predicted with the groundwater model (inflows and outflows) would typically be part of this analysis as well as matching gradients and observed concentrations at selected locations in the model.

3.0 The WHI Model

To facilitate the assessment and evaluation of the GeoTrans model, WHI imported the model input files provided by GeoTrans into Visual MODFLOW. Within the Visual MODFLOW model, the code MODFLOW (McDonald and Harbaugh, 1988) was used to simulate groundwater flow, and MODPATH (Pollock, 1994) was used to determine migration pathways and travel times for particles from the Site to the Murphree Wellfield. Contaminant transport (naphthalene) simulations were completed with the code MT3D99. Arsenic transport was not simulated in this first phase.

Table 1 (below) shows the parameters that were modified in the imported WHI Base Case Model. The first modification to the imported model was to represent all hydrostratigraphic layers within the model explicitly. The implicit semi-confining unit (SCU) within the Upper Floridan Aquifer between layers 10 and 11 in the GeoTrans Model was represented explicitly within the WHI Model to enable subsequent evaluation of this modeling assumption. Specifically, Layers 11 and 12 represent the SCU and the Ocala LTZ, respectively within the WHI model (Figure 1).

During the model import and verification process, GeoTrans provided valuable assistance. Hydraulic conductivity values remained the same, except where the SCU was introduced. Effective porosities in several of the model layers were also modified in the WHI Model to reflect inconsistencies between the GeoTrans Report and corrected information provided by GeoTrans by emails or telephone. Because the effective porosities were modified, the K_d of naphthalene was adjusted in each layer to match the retardation factors used in the GeoTrans Report to see if the two models matched in an initial check (this was necessary because GeoTrans used retardation factors calculated with effective porosities stated in the report but not used in the actual simulations. Visual MODFLOW automatically calculates the retardation factor based on the effective porosity used. MODFLOWT apparently uses externally calculated retardation factors and these were not changed when different effective porosities than those stated in the report were used in the simulations). A first order biodegradation rate constant of 0.0006 day^{-1} was used in all layers of the model.

As in the GeoTrans Model, naphthalene sources were emplaced in the WHI Model as constant concentrations beneath the footprints of each of the four source areas. The sources in the Surficial Aquifer, the Upper Hawthorn and Lower Hawthorn Groups (Layers 1, 5 and 8 of the Base Case model) were fixed at 10,000 μg/L. In addition, as in the GeoTrans Model, another source was placed at a constant concentration of 1,240 μg/L in the Ocala UTZ (Layer 10) beneath the footprint of the former North Lagoon.

A well located at the southeastern region of the model was included in the GeoTrans files which were imported by WHI. This well is not pumping so does not affect the flow results.

Although minor differences may exist between the two models, the overall flow conditions as determined by the GeoTrans Model were matched by the WHI Base Case Model.

Table 1 Parameters in the GeoTrans Model and WHI Base Case Model layers

Hydrogeologic Unit	GeoTrans Model Layers	WHI Base Case Model Layers	GeoTrans Model K_x, K_y (ft/d)	WHI Base Case K_x, K_y (ft/d)	GeoTrans Draft Report Effective Porosity	WHI Base Case Effective Porosity and actual GeoTrans Porosity	GeoTrans Model Storage Coefficients	WHI Base Case Storage Coefficients
Surficial Aquifer	1	1	21	21	0.2	0.2	0.027 – 0.094	0.027 – 0.094
Upper Hawthorn Clay Unit	2,3	2,3	0.01	0.01	0.35	0.15	1.5e-6 – 1.0e-5	1.5e-6 – 1.0e-5
Upper Clayey Sand	4,5	4,5	0.3	0.3	0.25	0.15	7.5e-5 to 2.0e-4	7.5e-5 to 2.0e-4
Middle Hawthorn Clay Unit	6	6	0.01	0.01	0.35	0.15	5.0e-6 to 2.0e-5	5.0e-6 to 2.0e-5
Lower Clayey Sand	7	7	0.3	0.3	0.25	0.15	1.5e-5 to 7.0 e-4	1.5e-5 to 7.0 e-4
Lower Sand	8	8	3	3	0.2	0.2	5.0e-4 to 1.5e-3	5.0e-4 to 1.5e-3
Lower Hawthorn Clay Unit	9	9	0.01	0.01	0.35	0.15	3.5e-5	3.5e-5
Ocala UTZ	10	10	23/10*	23/10*	0.15	0.15	8.5e-4 to 1.05e-3	8.5e-4 to 1.05e-3
SCU**		11		1.0e-6		0.15**		1.0e-11
Ocala LTZ	11	12	175/75*	175/75*	0.15	0.15	1.0e-3	1.0e-3

* Hydraulic conductivity applied near Murphree Wellfield Area

** Explicit SCU is only in the WHI Model

4.0 Potential Issues with the GeoTrans Model

Flow Boundary Conditions

Transient specified head boundaries (time-varying constant heads) were used in the model (shown in Figure 2). The model Report recognizes that prescribing constant head boundaries may force the model solution, but states that the low permeability of the Hawthorn Group would make the impact of such boundary conditions minimal. However, the same cannot be said for the highly permeable Ocala Limestone. Due to the relatively small model domain and proximity to user-specified head values, this approach could lead to high parameter correlation, and in consequence, highly non-unique calibration. This means that several combinations of model input parameters can result in equally good 'calibrated' models. Yet, model predictions may be different. In addition, no-flow boundaries were used close to the wellfield, based on an assumption of axi-symmetric behavior of the potentiometric surface surrounding the Murphree Wellfield, which may or may not be correct and may also force the solution. The only way to minimize boundary effects would be to enlarge the model domain.

Model Layer Discretization

Transport models usually require a larger number of numerical layers to adequately represent the vertical contaminant distribution and transport pathways within a hydrostratigraphic unit. GeoTrans used a single layer approach for the Ocala limestone that assumes the entire Ocala UTZ is contaminated, and no vertical variation of concentration occurs. This approach could in principle be conservative, but because of dilution within the entire 100 ft thick aquifer, there could be zones within the aquifer with higher concentrations than those predicted.

GeoTrans used an implicit layer to represent the low permeability dense carbonate SCU separating the UTZ from the LTZ. This simplification was commonly used many years ago in MODFLOW simulations (called the Quasi Three-Dimensional Approach) when computer memory was a limiting concern, but is less frequently used today because memory is not a problem and fully three-dimensional representations of aquifer systems are more flexible and accurate. Implicit layers have a number of limitations. They assume fully vertical movement of groundwater and contaminants, as well as no transient storage effects. Contaminant transport and groundwater flow simulation within implicit layers is also not possible.

Aquifer Parameters

Transmissivities and Hydraulic Conductivities

Excluding the uncertainty in the conceptualization of the groundwater flow at this site and the choice of the effective porosity, transmissivity (and associated hydraulic conductivity), is one of the most important issues with the GeoTrans Model. It is generally accepted and frequently reported that the thickness of the UTZ of the Ocala Limestone is approximately 100 ft. Within the GeoTrans Model Report, hydraulic conductivity for this unit was reported to be 23 ft/day at the Site and surrounding area. Near the Murphree Wellfield, the hydraulic conductivity was reduced to 10 ft/day in the UTZ. GeoTrans says this reduction was necessary so the *transmissivity values would correspond with values used in the GRU regional model* and to more accurately represent increased drawdowns in this area (p. 13, GeoTrans, 2004). The transmissivity distribution used in Layer 2 (Upper Floridan Aquifer) of the GRU Modflow Regional Model is given in the figure below, scanned from a GeoSys modeling study of travel times in the vicinity of the Murphree Wellfield (GeoSys, 1997). Each grid cell is 0.25 miles by 0.25 miles. The GRU Model does not distinguish between the UTZ and the LTZ, making them both part of Layer 2, the Upper Floridan Aquifer. GeoSys points out that the lowest transmissivities in the model are in the immediate area of the expansion wells and are 15,111 ft^2/day (approximately 32 ft/day based on an estimated thickness of 465 feet for Layer 2). In the Murphree Wellfield (L-shaped dark area in the figure) they are approximately 26,500 ft^2/day (57 ft/day). The transmissivity distribution in the figure shows that with the exception of a small area immediately south and slightly to the west of the Murphree Wellfield, where the transmissivity is 15,111 ft^2/day (32 ft/day), most of the transmissivities in the regional model that correspond to the domain of the GeoTrans model range from 26,500 (57 ft/day) to 57,500 ft^2/day (124 ft/day). The GRU Model hydraulic conductivities within a half-mile south and west of the Murphree Wellfield (corresponding to the northeast corner of the GeoTrans model) vary from 32 ft/day to 124 ft/day. Based on matching the GRU Regional Model transmissivities as GeoTrans' report states, there seems to be no justification for using 10 ft/day in the vicinity of the Murphree Wellfield as the lowest value reported in the GRU model near the wellfield is 32 ft/day. In an earlier report by GeoSys (1991) cited in Appendix C, they reported transmissivities in the range of 3,300 to 15,000 ft^2/day for the UTZ, which corresponds to hydraulic conductivities from 33 to 150 ft/day (based on a thickness of 100 feet).

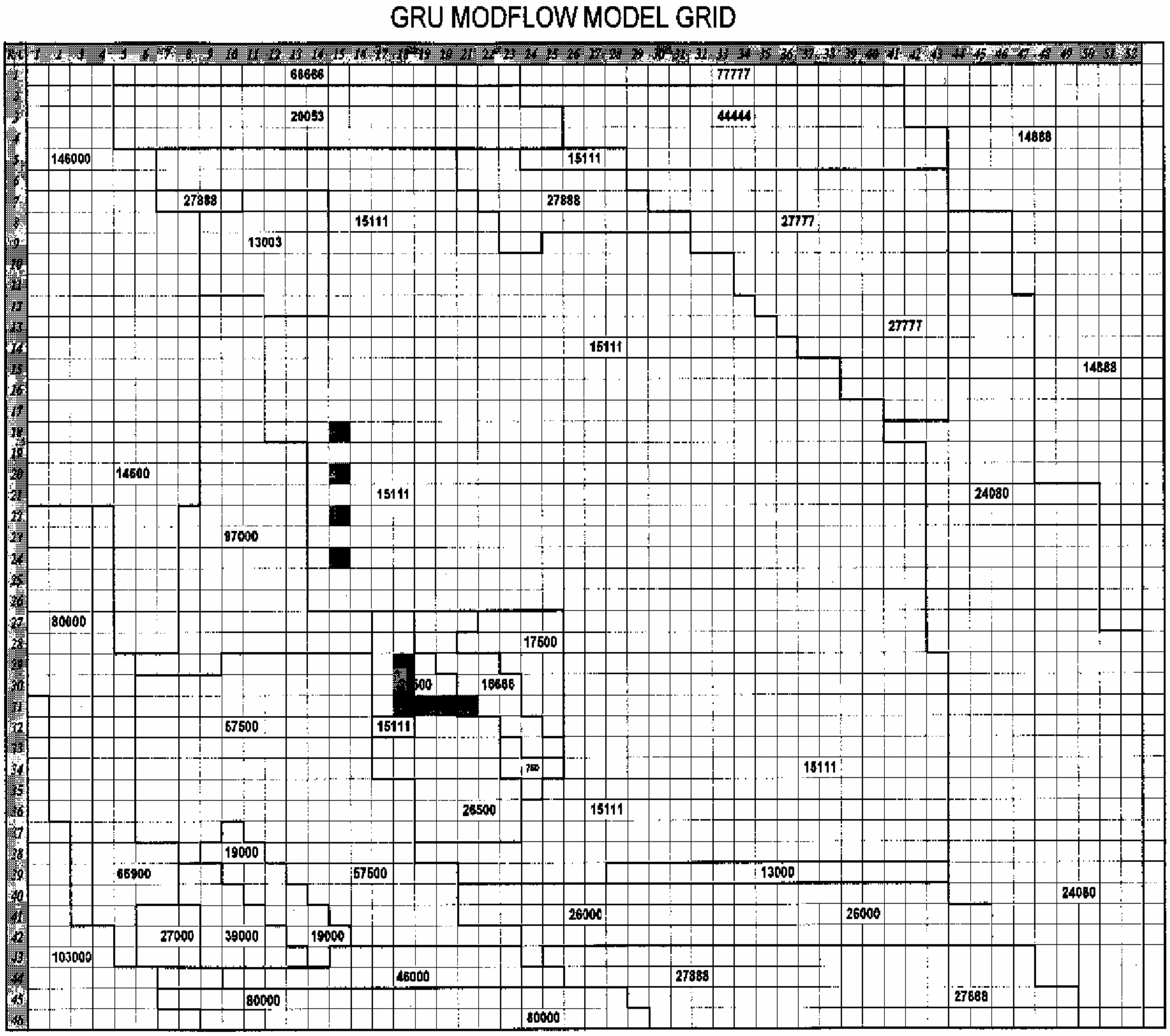

Figure 10. Transmissivity zones for Layer 2 in the MODFLOW model.

Transmissivity, which is the product of hydraulic conductivity and the layer thickness (T=K*b), is used in the model input files to define groundwater flow within the UTZ of the Ocala limestone layer of the GeoTrans Model. Upon review of the model input files for transmissivity for this layer, we noted that this layer is simulated as having, on average, a calibrated transmissivity of 4600 ft^2/day (everywhere except in the vicinity of the wellfield where it is lower). Appendix B contains a partial presentation of transmissivity values sent to Waterloo by GeoTrans.

With the hydraulic conductivity value listed in the report of 23 ft/day, this implies that the UTZ has an actual thickness of approximately 200 ft (i.e. T=K*b => b=T/K or 4600 ft^2/day divided by 23 ft/day = 200 ft). This results in an aquifer thickness for the Ocala UTZ that is too large by a factor of two. Groundwater fluxes in the GeoTrans Model are calculated using Darcy's law, and seepage velocities are calculated with the following expression:

Seepage Velocity = Hydraulic Conductivity * Hydraulic Gradient / Effective Porosity

With the Ocala Limestone UTZ being represented with a layer that is 200 ft thick (instead of 100 ft), the hydraulic conductivity that is used to determine velocities is too small by a factor of two. This means that groundwater flow velocities within the Ocala UTZ are being underpredicted within the GeoTrans Model by a factor of two as well. If the correct thickness of 100 ft were used for the Ocala UTZ, a hydraulic conductivity of 46 ft/day would have to be used to achieve the calibrated transmissivity value of 4600 ft^2/day (Figure 3). Furthermore, because the velocities in the GeoTrans Model are being underpredicted , it is likely that the hydraulic gradients within the model are not consistent with the values reported for the Ocala UTZ. This is discussed in Section 6.2.

It is important to note that this difference does not change the model predicted heads or flow rates (flowrates are a function of velocity and area available for flow), since the same transmissivity ($\cong$ 4600 ft^2/day) is achieved in both cases (23 ft/day * 200 ft = 4600 ft^2/day or 46 ft/day * 100 ft = 4600 ft^2/day). The direct implication of this is that the advective seepage velocity (Darcy flux divided by the effective porosity for flow) should have been twice as high as that predicted by the GeoTrans Model due to the doubling of the hydraulic conductivity. More specifically, the travel times for particles released in the Ocala UTZ to reach the Murphree Wellfield should be a minimum of 51 years (Figure 4b: using GeoTrans' assumption of an effective porosity for flow of 0.15), and not the 110 to 135 years that was predicted by the GeoTrans model (pg. 22, GeoTrans, 2004).

The likely possibility of horizontal anisotropy occurring in the Upper Floridan Aquifer was not evaluated by GeoTrans. Karstic aquifers commonly have anisotropic and heterogeneous conditions, especially where dissolution conduits, pipes, cavities and fractures are present as can be seen in the outcrops of the UTZ of the Ocala Limestone in the nearby Haile Quarry and Chastain Pit (see photos in Appendix D). Anisotropic and heterogeneous conditions and their impact on travel times, pathways and the Murphree Wellfield capture zone should be considered in future modeling work.

Specific Storage Coefficient

The value of the specific storage coefficient (S_s) was used to cross check the thickness used by GeoTrans in their modeling of the Ocala Limestone UTZ. The S_s value used for the Ocala UTZ in the GeoTrans Model was given as 5.0e-6 ft^{-1} (Roemer, 2005). This S_s value and the storage coefficient (S) values used in the GeoTrans Model were used to check the thicknesses GeoTrans used with the following calculation:

Thickness = Storage Coefficient / Specific Storage Coefficient

In the original Draft Report by GeoTrans, the storage coefficient for the Ocala Limestone UTZ is given as a range between 8.5e-4 and 1.05e-3 (Table 3-1, page 12). For the specific storage coefficient of 5.0e-6 ft^{-1} in the Ocala UTZ, the thickness of the Ocala UTZ in the GeoTrans Model is calculated to be between 170 and 210 ft. This thickness is consistent with the thickness of approximately 200 feet determined using the hydraulic conductivity and transmissivity information provided in the GeoTrans Model Report and the transmissivity input files (see Appendix B). The true thickness, however, is approximately 100 feet.

Effective Porosity

Tabulated effective porosities (N_e) in the model report were not the same as those used in the model files used by GeoTrans. The table below shows both reported values and those actually used in the model array files (the inconsistency was discovered and reported by GeoTrans during a QC check).

Table 2 Reported and model files effective porosity values

Hydrostratigraphic Unit	Model Layers	Reported N_e	Array Files
Surficial Aquifer	1	0.2	0.2
Upper Hawthorn Clay	2,3	0.35	0.15
Upper Clayey Sand	4,5	0.25	0.15
Middle Hawthorn Clay	6	0.35	0.15
Lower Clayey Sand	7	0.25	0.15
Lower Sand	8	0.2	0.2
Lower Hawthorn Clay	9	0.35	0.15
Ocala Limestone UTZ	10	0.15	0.15
Ocala LTZ	12	0.15	0.15

While GeoTrans used lower effective porosities in their simulations than those stated in the report, we believe for a number of technical reasons detailed in Appendix C that the values for the clay units and Ocala Limestone should be much smaller. Groundwater travel times are directly proportional to effective porosities: the smaller the effective porosity, the shorter the travel time (higher velocity) between the site and the Murphree Wellfield.

Contaminant Transport Boundaries and Transport Parameters

Retardation factors (R_f) used in the WHI Base Case Model do match the values reported in the GeoTrans Model Report, which were used in GeoTrans' simulations. The retardation factors used in the WHI Base Case model, however, were smaller than what they should have been if the correct effective porosities had been used to calculate them (Visual MODFLOW automatically calculates the retardation factor based on the K_d, effective porosity and the dry bulk density). To achieve the same retardation factors GeoTrans used, yet at the same time use different effective porosities, K_d was adjusted in the WHI Base Case Model to compare with GeoTrans' results (in other transport simulations, Figure 10, for example, the correct retardation factors based on the lower effective porosities GeoTrans used in their simulations were used). GeoTrans apparently calculated retardation factors externally using the higher effective porosities stated in their report. Later when they used lower effective porosities in their simulations, they did not recalculate the correct corresponding retardation factors, using instead the ones calculated previously based on higher effective porosities. Retardation was assumed not to occur in the UTZ and LTZ of the Floridan Aquifer ($K_d = 0.0$). The smaller the retardation factor, the faster the predicted movement of contaminants. The correct higher retardation factors will result in slower velocities and longer transport times.

Table 3 Reported retardation factors versus values used in model files

Hydrostratigraphic Unit	Model Layers	Report Rho	Report K_d	Report N_e	Report R_f	Correct N_e	R_f calculated with correct N_e	Base Case Model Files
		g/cm^3	(mL/g)					
Surficial Aquifer	1	1.6	0.7728	0.200	7.180	0.2	7.182	7.180
Upper Hawthorn Clay	2,3	1.6	0.7728	0.350	4.530	0.15	9.243	4.530
Upper Clayey Sand	4,5	1.6	0.7728	0.250	5.950	0.15	9.243	5.950
Middle Hawthorn Clay	6	1.6	0.7728	0.350	4.530	0.15	9.243	4.530
Lower Clayey Sand	7	1.6	0.7728	0.250	5.950	0.15	9.243	5.950
Lower Sand	8	1.6	0.7728	0.200	7.180	0.2	7.182	7.180
Lower Hawthorn Clay	9	1.6	0.7728	0.350	4.530	0.15	9.243	4.530
Ocala UTZ	10	1.6	0	0.150	1.000	0.15	1	1.000
Ocala LTZ	12	1.6	0	0.150	1.000	0.15	1	1.000

Naphthalene first-order biodegradation rates were obtained from conservative values from the existing literature. Although this is a highly site-specific value, the values used by GeoTrans are within the range typically used in modeling studies for anaerobic decay of this compound.

Source Characterization

Source concentrations were obtained from measured concentrations in monitoring wells and source delineation was previously assessed by GeoTrans (2004). The same source delineation and concentration values (10,000 µg/L) were assigned to Layers 1, 5 and 8, following the footprints of the four known source areas and distributed over the entire layer thickness. It's important to note that outside the defined areal extent of these four source areas and throughout all the layers GeoTrans assumed dissolved phase concentrations are initially zero. A smaller source in model Layer 10 (Ocala UTZ) was also used, with a constant concentration value of 1,240 µg/L, encompassing the footprint of the former Northern Lagoon and the entire thickness of the Ocala UTZ. This value was based on one of the measured concentrations at monitoring well FW-6 (GeoTrans, 2004).

A more conservative approach for the UTZ source would have been to assume that if DNAPL is found beneath the footprint of the Northern Lagoon, it is likely to occur beneath all other source areas. The impact of such an assumption could be easily implemented in the model.

Model's Ability to Reproduce Observed Concentrations of Naphthalene

The GeoTrans Report states that the modeling effort did not attempt to calibrate the transport model; however, it does believe that the model reproduces the observed concentrations in several wells and implies that this may be the case for other wells. We do not entirely agree with that comment. Table 4 below shows a comparison between simulated (calculated) and observed values for the Upper Hawthorn aquifer, as obtained from isoconcentration plots within the GeoTrans Model Report. Calculated concentrations were extracted directly from the model figures and are approximate. The column "Residuals (Calc-Obs)" clearly shows that in most locations the GeoTrans Model significantly underpredicts concentrations. In some locations near source areas, the GeoTrans Model significantly overpredicts concentrations.

An average value of 10,000 µg/L was used to represent source concentrations. However, some monitoring wells positioned within the source areas show concentrations considerably above this (over 20,000 µg/L for the Upper Hawthorn, and some presented concentrations significantly below this value). These differences in assigned source values and what was found may explain the poor correlation between calculated and observed values of concentration. Appendix A presents graphical representations of the data in Table 4.

Table 4 Model representation of Observed Naphthalene Concentrations – Upper and Lower Hawthorn

Monitoring Well	Group		Concentrations (µg/L)				Report figure	Notes
			OBS	CALC	Residual (Calc-Obs)	ABS Residual (Calc-Obs)		
HG-16S	Upper Hawthorn		7410.0	40.0	-7370.0	7370.0	5-3	
HG-10S	Upper Hawthorn		13200.0	10000.0	-3200.0	3200.0	5-3	Source Area
HG-5S	Upper Hawthorn	ND	0.0	0.1	0.1	0.1	5-3	
HG-9S	Upper Hawthorn		11400.0	10000.0	-1400.0	1400.0	5-3	Source Area
HG-11S	Upper Hawthorn		20200.0	10000.0	-10200.0	10200.0	5-3	Source Area
HG-15S	Upper Hawthorn		8690.0	10000.0	1310.0	1310.0	5-3	Source Area
HG-6S	Upper Hawthorn		49.4	10.0	-39.4	39.4	5-3	
HG-12S	Upper Hawthorn		4680.0	10000.0	5320.0	5320.0	5-3	Source Area
HG-4S	Upper Hawthorn		7620.0	10.0	-7610.0	7610.0	5-3	
HG-7	Lower Hawthorn	<	5.4	0.0	-5.4	5.4	5-4	
HG-16D	Lower Hawthorn		10500.0	1000.0	-9500.0	9500.0	5-4	
HG-5D	Lower Hawthorn	<	33.1	1.0	-32.1	32.1	5-4	
HG-8	Lower Hawthorn	<	5.4	10.0	4.6	4.6	5-4	
HG-2D	Lower Hawthorn		4410.0	0.0	-4410.0	4410.0	5-4	
ITF-1	Lower Hawthorn		411.0	10.0	-401.0	401.0	5-4	
HG-6D	Lower Hawthorn		4770.0	0.1	-4769.9	4769.9	5-4	
HG-4D	Lower Hawthorn		3490.0	0.1	-3489.9	3489.9	5-4	
HG-4I	Lower Hawthorn		6210.0	0.1	-6209.9	6209.9	5-4	
HG-10D	Lower Hawthorn		12000.0	10000.0	-2000.0	2000.0	5-4	Source Area
FW-3	Ocala UTZ	ND	0.0	0.0	0.0	0.0	5-5B	
FW-6	Ocala UTZ		1240.0	1240.0	0.0	0.0	5-5B	Source Area

FW-5	Ocala UTZ	ND	0.0	1.0	1.0	1.0	5-5B	
FW-1	Ocala UTZ	ND	0.0	0.5	0.5	0.5	5-5B	
FW-4	Ocala UTZ	ND	0.0	0.5	0.5	0.5	5-5B	
FW-2	Ocala UTZ	ND	0.0	0.0	0.0	0.0	5-5B	
MW-TP-1	Ocala UTZ	ND	0.0	0.0	0.0	0.0	5-5B	
MW-TP-2	Ocala UTZ	ND	0.0	0.0	0.0	0.0	5-5B	

5.0 Modifications Made to the WHI Model for Evaluation Purposes

Several modifications of the WHI Base Case Model were implemented to assess the effects of varying parameters (parameter uncertainty) and layer discretization on contaminant transport and the travel times of groundwater. The modifications are described in Table 5.

Table 5 Modifications to WHI Base Case Model

Description of Modification	
Scenario 1	WHI Base Case Model – no modification
Scenario 2	Doubled the original number of Hawthorn Group Clay numerical layers
Scenario 3	Quadrupled the original number of Hawthorn Group Clay numerical layers
Scenario 4	Increased K_x, K_y in Ocala UTZ from 23 ft/d to 92 ft/d (4 times)
Scenario 5	Decreased N_e in Ocala UTZ to 0.05
Scenario 6	Decreased N_e in Ocala UTZ to 0.01
Scenario 7	Increased Lower Hawthorn Clay Unit numerical layer by two
Scenario 8	Increased Lower Hawthorn Clay Unit and Ocala UTZ numerical layers by two
Scenario 9	Increased Lower Hawthorn Clay Unit layer by two; increased Ocala UTZ numerical layer by four
Scenario 10	Increased Lower Hawthorn Clay Unit layer by two; increased Ocala UTZ numerical layer by eight
Scenario 11	Increased Lower Hawthorn Clay Unit numerical layer by two and removed source zone in Ocala UTZ layer
Scenario 12	Increased Lower Hawthorn Clay Unit and Ocala UTZ numerical layers by two; removed source zone in Ocala UTZ layers
Scenario 13	Increased Lower Hawthorn Clay Unit numerical layer by two; increased Ocala UTZ numerical layer by four; removed source zone in Ocala UTZ layers
Scenario 14	Increased Lower Hawthorn Clay Unit numerical layer by two; increased Ocala UTZ numerical layer by eight; removed source zone in Ocala UTZ layer
Scenario 15	Decreased thickness of Ocala UTZ layer to ~100 ft; increased K_x, K_y to 46 ft/d to adjust for transmissivity
Scenario 16	For model with 100-ft thick Ocala UTZ layer, transport simulation was run using TVD rather than Upstream Finite Difference
Scenario 17	For model with 100-ft thick Ocala UTZ layer: increased number of Ocala UTZ numerical model layers to 10

Scenario 18	For model with 100-ft thick Ocala UTZ layer: decreased longitudinal/horizontal/vertical dispersivities from 100/10/1 to 3/0.3/0.03 ft
Scenario 19	For model with 100-ft thick Ocala UTZ layer: increased number of Ocala UTZ numerical model layers to 4; in the top Ocala layer, added a karst "channel" by increasing hydraulic conductivity to 4600 ft/d in selected cells
Scenario 20	For 100-ft thick Ocala Limestone UTZ layer: increased number of Ocala UTZ numerical model layers to 4; increased number of Semi-Confining Unit model layers to 3; increased number of Ocala LTZ numerical model layers to 3
Scenario 21	For 100-ft thick Ocala UTZ layer: decreased N_e in Ocala UTZ to a) 0.05 and b) 0.01
Scenario 22	For 100-ft thick Ocala UTZ layer: used K_d values from GeoTrans in Hawthorn Group allowing Retardation Factor to vary
Scenario 23	For 100-ft thick Ocala UTZ layer: removed decay constant of 0.0006 day^{-1}
Scenario 24	For 100-ft thick Ocala UTZ layer: used K_d values from GeoTrans in Hawthorn Group allowing Retardation Factor to vary, and decreased N_e to: a) 0.05 and b) 0.01
Scenario 25	For 100-ft thick Ocala UTZ layer: increased K_x, K_y to 115 ft/d, N_e is 0.15
Scenario 26	For 100-ft thick Ocala UTZ layer: increased K_x, K_y to 140 ft/d, N_e is 0.15, K_z = 1 ft/d
Scenario 27	For 100-ft thick Ocala UTZ layer: increased K_x, K_y to 140 ft/d, N_e is 0.15, K_z = 0.0035 ft/d
Scenario 28	For 100-ft thick Ocala UTZ layer: K_x, K_y = 140 ft/d, K_z = 0.0035 ft/d, N_e = 0.01
Scenario 29	For 100-ft thick Ocala UTZ layer: used K_d values from GeoTrans in Hawthorn Group allowing Retardation Factor to vary; removed Ocala UTZ source;
Scenario 30	For 100-ft thick Ocala UTZ layer: used K_d values from GeoTrans in Hawthorn Group allowing Retardation Factor to vary; removed Ocala UTZ source; decreased N_e to: a) 0.05 and b) 0.01

6.0 Results

6.1 Sensitivity of Particle Tracking Results

Particle tracking simulations representing the pathways a conservative dissolved phase constituent would follow in the WHI Model were performed using MODPATH. The starting locations were close to the four source areas in the Surficial Aquifer and the Hawthorn Group. Particles also were released from the Ocala UTZ, the Semi-Confining Unit (SCU) and the Ocala LTZ. The effects of varying hydraulic conductivity and effective porosity in the Ocala UTZ, and varying the number of layers in the Lower Hawthorn Clay Unit and Ocala UTZ, SCU and LTZ were examined in this series of modifications.

The WHI Base Case Model, using the same thickness of 200 feet for the UTZ that GeoTrans used, reproduces the GeoTrans Model particle travel times well, especially in the Ocala UTZ (Figure 6a). Table 6 gives the resulting particle travel times for each simulation. In the Ocala UTZ, the GeoTrans Model particle travel times range between 110 and 135 years while the WHI model travel times range between 102 and 124 years (Figure 4a). Similarly, particles beginning in the Surficial Aquifer require 209 to 337 years to travel to the Murphree Wellfield in the GeoTrans Model; particles require between 188 and 280 years to reach the wellfield in the WHI Base Case Model (not shown).

Decreasing the Ocala UTZ thickness to approximately 100 ft (with a consequent doubling of the hydraulic conductivity from 23 ft/day to 46 ft/day to maintain the calibrated transmissivity of 4600 ft^2/day) affects the time required for particles to reach the wellfield due to the substantially increased seepage velocity. In this situation (Scenario 15, using GeoTrans' effective porosity of 0.15), groundwater arrives in significantly less time (143 to 249 years for particles originating in the Surficial Aquifer (not shown), and 51 to 63 years, shown in Figure 4b, for particles originating in the Ocala UTZ). The direction that particles traveled is shown in three dimensions in Figure 6b.

Increasing the hydraulic conductivity in the Ocala UTZ (Scenarios 4 to 6, 21, 25 to 28) results in significantly reduced travel times, especially in the Ocala UTZ (Table 6).

Reducing the effective porosity in the Ocala UTZ can result in substantially reduced travel times. Particle pathlines from the Site to the Murphree Wellfield are shown in plan view and cross-section in Figures 4a (using GeoTrans' value of 200 feet thick for the Ocala UTZ) and 4b (using the correct value of 100 feet thick for the Ocala UTZ). Also shown are the minimum and maximum travel times for particles to reach the wellfield. Specifically, for an effective porosity of 0.15, particles originating in the Ocala UTZ reach the wellfield in 51 to 63 years. **For an effective porosity of 0.01, particles reach the wellfield in 4.3 to 5.0 years (by advective flow only, no retardation or decay).**

Table 6 Travel Times of Particles in the Surficial Aquifer and Ocala Limestone UTZ

Scenario Description	Travel Times (yrs)			
	Surficial Aquifer (Layer 1)		Ocala UTZ (Layer 10)	
	(minimum)	(maximum)	(minimum)	(maximum)
GeoTrans Model, (Report dated Oct 5, 2004)	207	337	110	135
WHI Base Case Model	188.1	280.1	102.2	124.1
Scenario 4. K_x, K_y in Ocala UTZ increased to 92 ft/d (4 times original); near Murphree Wellfield, K_x, K_y = 10 ft/d	169	256	82	109
Scenario 5. Effective Porosity in Ocala UTZ decreased to 5% (original 15%)	127	225	35	42
Scenario 6. Effective Porosity in Ocala UTZ decreased to 1% (original 15%)	102	203	8	9
Scenario 7. Lower Hawthorn Clay Unit refined by 2	188.1	280.1	102.2	124.1
Scenario 8. Lower Hawthorn Clay Unit refined by 2; Ocala UTZ refined by 2	188.0	279.9	102.2	124.2
Scenario 9. Lower Hawthorn Clay Unit refined by 2; Ocala UTZ refined by 4	188.0	279.8	102.2	124.2
Scenario 10. Lower Hawthorn Clay Unit refined by 2; Ocala UTZ refined by 8	188.0	279.9	102.2	124.1

Scenario 15. Decrease Ocala UTZ thickness to ~100 ft; K_x, K_y = 46 ft/d (GeoTrans Ocala UTZ equivalent to 200 ft representation); K_z = 0.0035 ft/d	143	249	51	63
Scenario 21: For model with 100-ft thick Ocala UTZ layer: decreased Effective Porosity in Ocala UTZ to: a) 0.05 and b) 0.01	a) 112 b) 99	221 200	18 4.3	21 5.0
Scenario 25: Ocala UTZ layer = 100-ft thick: increased K_x, K_y to 115 ft/d, K_z = 1 ft/d; effective porosity is 0.15	135	232	40	48
Scenario 26: Ocala UTZ layer = 100-ft thick: increased K_x, K_y to 140 ft/d; K_z = 1 ft/d; effective porosity is 0.15	134	230	39	47
Scenario 27: Ocala UTZ layer = 100-ft thick: increased K_x, K_y to 140 ft/d; K_z = 0.0035 ft/d; N_e is 0.15	134	240	39	48
Scenario 28: Ocala UTZ layer = 100-ft thick: increased K_x, K_y to 140 ft/d, K_z = 0.0035 ft/d; effective porosity is 0.01	101	212	4.1	7.2

6.2 Sensitivity of Transport Simulation Results

Contaminant transport was simulated using MT3D99. Naphthalene sources were placed in the model as constant concentrations beneath the footprints of the four source areas. The sources in the Surficial Aquifer, the Upper Clayey Sand above the Middle Hawthorn Clay unit and the Lower Sand above the Lower Hawthorn Clay unit (Layers 1, 5 and 8 of the Base Case Model) are fixed at 10,000 µg/L; the source concentration in the Ocala UTZ (Layer 10 of the Base Case Model) is 1,240 µg/L and follows the footprint of the former Northern Lagoon. At all other locations, the concentrations are initially zero.

Table 5 gives the layer refinements used to observe the effects of discretization on contaminant transport. These simulations involve varying the number of model layers in the Lower Hawthorn Clay, and the Ocala Limestone UTZ, SCU and LTZ. Source zones in the Ocala UTZ in Scenarios 11 to 14, 29 and 30 have been removed. In Scenario 15, the modification consists of reducing the thickness of the Ocala Limestone from ~200 feet to ~100 feet (K_x and K_y are increased to maintain the same calibrated transmissivity used in the GeoTrans Model). Thereafter, the Ocala UTZ in all scenarios has a thickness of ~100 ft. The effects of decreasing the dispersivity (Scenario 18), adding a small karst channel northeast of the Site (Scenario 19), removing the decay constant (Scenario 23), and applying the K_d value for the Hawthorn Group from the original Draft Report thus allowing R_f to vary (Scenarios 22, 24, 29 and 30) were also examined.

Refinement of the layers while maintaining the original source zones does not result in significant differences in transport results within the model. This is due to the presence of a constant concentration source over the entire thickness of the model layer, particularly in the Ocala UTZ. The majority of the contaminant movement is vertical. As the number of model layers increases, vertical movement of the contaminant is somewhat slower at early times, but over the 3841 days of the simulation, the concentration distribution is similar (Figure 5). Laterally, the differences do not appear to be significant. Horizontal movement of the contaminant is significantly increased in the case where the Ocala UTZ thickness is reduced (Scenarios 15 to 28). As previously presented, the required increase in hydraulic conductivity (to maintain the same calibrated transmissivity with a smaller layer thickness) produces higher advective velocities by a factor of two. This results in a predicted plume footprint that is considerably larger than in other cases. Similar results were also obtained using the TVD (Total-Variation-Diminishing) transport solver (all other simulations used Upstream Finite Difference) (Figure 7).

The effect of decreasing the longitudinal, horizontal and transverse dispersivities is shown in Figure 8. Although reducing the dispersivities in the model decreased the footprint of the plume in this particular simulation, the result would not necessarily be the same for varying effective porosities. Figure 9 shows the effect of increasing hydraulic conductivity in a specified region in the Ocala UTZ to create a karst channel northeast of the Site. The result in this case is an elongated plume. Similarly, removing the decay constant of 0.0006 day^{-1} results in a much larger plume footprint (not shown).

A comparison of the contaminant plumes produced for effective porosities of 0.15 and 0.01 (K_d value for the Hawthorn Group of 0.7728 mL/g) is shown in Figure 10. Decreasing the effective porosity to 0.01 results in a much larger plume for each scenario, even after removing the 1,240-μg/L source zone from the Ocala UTZ, than the plumes produced using an effective porosity of 15%. Low concentrations (0.1 μg/L) reach the Murphree Wellfield after 3804 days (10.4 years) in the simulation containing the four source zones in the Hawthorn Group and the Ocala UTZ. Removing the source zone from the Ocala UTZ results in a groundwater plume of similar extent in the Ocala UTZ albeit of much lower concentrations.

6.3 Hydraulic Gradient Results

The hydraulic gradient in the Ocala UTZ, determined using data collected November 15-17, 2004, is 0.00045 (RETEC, 2005). The average hydraulic gradient calculated for the Site area in the GeoTrans Model and WHI Base Case Model is 0.0012 (outlined in green in Figure 11). The minimum gradient evaluated in the WHI scenarios presented previously resulted when K_x and K_y was increased to 115 ft/d (Scenarios 25) yielding a hydraulic gradient value of 0.0006. The value of 0.00045 determined using observed data was impossible to reproduce with the GeoTrans Model without modifying model boundary conditions and was not achieved in any of the WHI scenarios.

7.0 Summary and Recommendations

Several of the GeoTrans Model input parameter values (contained in the electronic model files they initially provided and used to run their model) differ from the numerical values of the same parameters reported in their Draft Report dated October 5, 2004. These include:

- Different values of effective porosities;
- Incorrect thickness of the Upper Transmissive Zone of the Ocala Limestone
- Incorrect hydraulic conductivity of the Upper Transmissive Zone of the Ocala Limestone

Additionally, the retardation factors stated in the report were the same as those used in their simulations although lower effective porosities were used in the simulations compared to the report, which would require higher retardation factors.

An important issue that should be resolved relates to the hydraulic conductivity of the Upper Transmissive Zone of the Ocala, represented in the model as layer 10. The calibrated transmissivity array used by GeoTrans shows an average value of 4600 ft^2/day. GeoTrans reports that the hydraulic conductivity they used was 23 ft/day, giving an average thickness of 200 feet (T/K) for the Upper Transmissive Zone. It is generally understood, and reported by GeoTrans that the thickness of this unit is approximately 100 feet. Based on discussions with GeoTrans it is our understanding that they used 200 feet for the thickness of the Upper Transmissive Zone of the Ocala Limestone, although their Figure 4-6 shows a thickness of approximately 100 feet, and 100 feet is mentioned throughout the report. Presuming the calibrated transmissivity is correct and the thickness is indeed 100 feet, the calibrated hydraulic conductivity must be approximately 46 ft/day.

The reported value of 23 ft/day should therefore be at least corrected to 46 ft/day. The direct consequence of this error is that contaminants move twice as fast via advective processes than predicted by the current GeoTrans Model. This means that the predicted travel time to reach the Murphree Wellfield in the Ocala UTZ should be on the order of 51 years instead of 118 years when an effective porosity of 0.15 is assumed (see Figure 4b). Other studies have reported values of hydraulic conductivity ranging from 33 ft/day to 150 ft/day (GeoSys, 1991, 1997). Higher hydraulic conductivities would result in faster travel times if the pathlines follow the same paths as indicated in Figure 4b. The correct hydraulic conductivities and degree and orientation of anisotropy for the UTZ between the site and the Murphree Wellfield are unknown and will require additional field work to determine.

The resulting hydraulic gradient in the Ocala UTZ of approximately 0.0012 calculated from the head results in the GeoTrans Model is not consistent with reported observed values from RETEC (2005) for November 2004, nor with the value of 0.0003 cited in the Draft Report (pg.6, GeoTrans, 2004). Unless there are seasonal or other hydrologic effects that explain this difference, the model would be expected to better match the gradient in the Ocala UTZ. This needs additional investigation.

WHI's model simulations indicate that the naphthalene contaminant plume in the Ocala Limestone would move off-site, but would reach a quasi steady-state before reaching the Murphree Wellfield based on the retardation and degradation rates prescribed in the GeoTrans Model and the effective porosity value of 0.15 that was used. This would not be true if there were significant dissolution cavities and conduits in this area and an effective porosity that would be much lower (to reflect higher velocities). As shown in Figure 10, the degree of contaminant transport is highly sensitive to the effective porosity. Furthermore, the distribution and extent of dissolution cavities and conduits is currently unknown and should be investigated because of the large influence they can have on seepage velocities and travel times to the wellfield.

Particle tracking results indicate that travel times for particles originating in the Ocala UTZ below the Site migrating to the Murphree Wellfield are highly sensitive to effective porosity values. Decreasing the effective porosity to 1% (from 15%) decreased the travel times from the original range of 51 to 63 years (using a thickness of 100 ft with a hydraulic conductivity of 46 ft/day for the Ocala UTZ) **to a range of 4 to 5 years (shown in Figure 4b).** Appendix C (prepared by Stan Feenstra) provides a literature review and detailed discussion of the effective porosities for flow in the Hawthorn Formation clays and the Ocala Limestone. His literature review notes that effective porosity values for the Hawthorn clays and the UTZ are likely to be 5% or substantially less, not the 15% chosen by GeoTrans.

Feenstra points out that no tracer tests have been performed in the Gainesville area to determine the effective porosity of the Ocala Formation. He notes that the United States Geological Survey has performed two tracer tests in the Ocala Formation at the Old Tampa Well Field (Robinson, 1995). At this location, the geologic description, hydraulic conductivity and matrix porosity of the limestone are comparable to the Ocala Formation in the Gainesville area. The effective porosity determined from tests conducted over a distance of 200 feet was determined to be 0.3 to 1.5%. This is the only quantitative measurement of the effective porosity for the Ocala Formation found in the published literature (Feenstra, Appendix C).

The effective porosity beneath the Koppers site can only be determined with a carefully planned tracer test, which we recommend because of the critical importance of this parameter. A model is only as reliable as the parametric data it uses. In the initial stages of a site investigation a model can provide guidance where data should be collected and, through sensitivity analyses, indicate which parametric data have the most impact on model predictions. A model's predictive capability in these early stages is limited by the amount and accuracy of the data. In subsequent stages, after sufficient characterization of the site and evolution of the site conceptual and numerical model, the model may develop into a reliable predictive tool.

Most of the characterization of the Koppers site has been focused on the Surficial Aquifer and the Hawthorn Formation, with some limited data collected in the upper portion (upper 25 feet) of the UTZ of the Ocala Formation. The model demonstrates that if the effective porosity is 1%, travel times to the Murphree Wellfield are quite rapid. At the moment, it is impossible to define the correct effective porosity to use for the Koppers site. It is our opinion that a conservative approach to dealing with the limited data in the literature and the karstic nature of the Floridan Aquifer is to use small values for the effective porosity (on the order of 1% or perhaps even less, similar to those found at the Old Tampa Wellfield, the only tracer study done in the Ocala Formation in Florida). In contaminant modeling studies where critical data such as effective porosities are limited or missing entirely, the model cannot make reliable predictions. In these cases and particularly when a water supply is potentially threatened, the prudent approach is to make direct measurements of concentrations as soon as possible. This can quickly confirm or refute the presence of arsenic, naphthalene and creosote-related compounds moving at potentially high velocities through the karstic Ocala Limestone's fractures, dissolution cavities and conduits toward the Murphree Wellfield.

It is our opinion that the best approach to measure potential contamination in karstic aquifers is to use multilevel transects placed in several strategic locations close to known source areas and with enough vertical sampling ports to ensure if a potential three-dimensional contaminant distribution exists, it will be found.

All of which is respectfully submitted,

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