Section 7
Transport Model

Groundwater transport model simulations were performed to investigate the potential for constituents from the fly ash at the site to migrate in groundwater and impact downgradient receptors, either in the short term, or over a period of up to 200 years in the future.

The simulated steady-state groundwater flow fields developed as described in Section 6.5 were used to project potential future constituent transport in groundwater resulting from the site. The transport model was not calibrated because the currently available groundwater quality data does not provide a basis for calibration. The lack of calibration based on field observation of an established plume increases the range of the most-probable results for the transport simulations in groundwater. For the simulations, a reasonable range of source loading rates and transport properties was simulated based on data available prior to golf course construction (URS, 2001b) and site-specific post-construction data (MACTEC, 2009), literature, and past experience.

CDM considered the ten constituents identified in Section 3 as being potentially above the baseline in selecting the constituents for transport purposes. In addition to these ten constituents, CDM also considered arsenic (**Table 7-1**). The criteria that CDM considered in selecting the constituents for transport include their presence in the fly ash, leachability tests performed on the fly ash, available regulatory standards/criteria, and mobility.

Nitrate was selected for transport modeling because it is currently above the baseline concentrations in shallow onsite groundwater; it has a Federal Maximum Contaminant Level (MCL), and is present in the fly ash. Because nitrate is highly mobile, it will be present in groundwater in a relatively short period of time following fly ash emplacement. However, this high mobility will also cause nitrate to be depleted from the fly ash in a relatively short time frame. As a result, a constituent with lower mobility was considered to represent constituents that will continue to be leached for longer periods of time into the future. Arsenic was selected for long-term leaching scenario because it has a lower mobility; it has a low MCL, and is present in the fly ash and leachate samples. Arsenic is a high toxicity metal of great concern as a drinking water constituent.

The recent upper surficial aquifer A well data yielded 21% of samples with arsenic concentrations above the MCL of 10 ug/L. It is noteworthy that background arsenic concentrations can be greater than the MCL in ambient groundwater. Furthermore, arsenic was found in MACTEC's fly ash analyses, and in TCLP results on stabilized ash samples as used in the fill (URS, 2001b).

Groundwater transport of nitrate was also simulated. Nitrate transport in groundwater is not subject to significant adsorption/retardation. In the transport simulations, it therefore functions as a conservative tracer of flow pathways from the

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beneath the footprint of the fly ash into shallow groundwater. If generated in sufficient quantity from the ash, nitrate may also function as a tracer in the field.

7.1 Model Code

DYNTRACK is the companion solute transport code to DYNFLOW. DYNTRACK has been developed over the past 20 years by CDM engineering staff. DYNTRACK has also been reviewed and tested by the IGWMC (van der Heijde 1985). It has been accepted by the US EPA for use, and has been used in several litigation cases.

DYNTRACK is a fully three-dimensional particle tracking and solute transport code. In simple particle-tracking mode, DYNTRACK simulates the mean advective flow path of dissolved solutes using 3-dimensional flow fields developed by DYNFLOW. In full transport mode, the code simulates the advection, dispersion, adsorption, and decay processes controlling solute transport in groundwater.

DYNTRACK uses a Lagrangian approach to approximate the solution of the partial differential equation of transport. This process uses a random walk method to track a statistically significant number of particles, wherein each particle is advected with the mean velocity within a grid element and then randomly dispersed according to specified dispersion parameters.

In DYNTRACK, a solute source can be represented as an instantaneous input of solute mass (represented by a fixed number of particles), as a continuous source on which particles are input at a constant rate, or as a specified concentration at a node. The concentration within a particular zone of interest is represented by the total number of particles that are present within the zone multiplied by their associated solute mass, divided by the volume of water within the zone. DYNTRACK also has the capability to simulate first order decay, nonlinear equilibrium sorption and non-equilibrium sorption (or kinetics).

7.2 Input Parameters

7.2.1 Source Representation

CDM's field investigation attempted to collect samples from leachate wells completed within the fly ash to allow direct laboratory measurements of constituents in leachate to represent the source water quality. However, insufficient leachate was found in the fly ash at the three boring locations where the leachate wells were planned for installation. CDM assumes that the water levels in the fly ash were low during the investigation because insufficient infiltration had accumulated in the fly ash since the fly ash was emplaced. As a result, the source representation required use of the available leaching data for the fly ash and simulations of leaching based on geochemical data.

Figure 7-1 shows the estimated area of fly ash, inferred by CDM using an incomplete map of areas of fly ash obtained from the URS hydrogeologic report (URS, 2001a) and

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an early map of planned topographic contours of the golf course (March 2002 site plan) , downloaded from the City of Chesapeake website. As-built information for the golf course was not available. CDM assumed that no fly ash was placed in low-lying areas or ponds. The estimated footprint of the areas receiving fly ash totals approximately 92.4 acres. The estimated total mass of stabilized ash used to construct the golf course was 1.5 million tons, projected by URS (2001b) and cited by MACTEC (2009).

Precipitation and irrigation water infiltrating into the landfill from the ground surface and not lost to evapotranspiration is assumed to percolate in a primarily vertical direction through the fly ash and underlying soil until it reaches the saturated groundwater zone. In the groundwater transport model, the total simulated arsenic and nitrate mass were applied to groundwater evenly over the entire estimated area of fly ash shown in Figure 7-1, at a vertical depth equivalent to the approximate base of the fly ash (top of natural surficial silt/clay layer). For mass loading purposes, CDM used an arsenic value of 43 mg/kg arsenic in fly ash. This value was calculated from the average concentration of 59 mg/kg from most recent investigations less the 95% confidence interval of the mean of 16 mg/kg. The source loading rate (total mass flux) applied to the transport model was calculated as the product of the volumetric rate of infiltration (groundwater recharge) through the fly ash and the estimated constituent concentration in the infiltrating water (leachate) when it reaches the groundwater table. Various combinations of infiltration rates and concentrations were simulated. Development of source loading rates is described in more detail below.

Over time, it is recognized that the source of constituents in the landfill will become depleted. It is assumed that the arsenic concentrations in the leachate will exhibit first-order decay. An initial arsenic source loading rate, ranging from approximately 30 to 878 grams/day, based on source loading calculations and available data, was applied in the arsenic transport simulations as shown in **Table 7-2**. Source loading rates applied in the nitrate simulations are also shown in Table 7-2. The estimated mass loading rates to groundwater and half-life values representing the rate of source decay in Table 7-2 were calculated as described below, based on available data.

Infiltration rates through the fly ash, representing leachate production, were estimated based on HELP model results discussed in Section 5.3. Values of 15.8 in/yr and 7.5 in/yr are representative of the upper and lower ends of the range of reasonable leachate production rates generated by the HELP model, respectively, and are in general agreement with the local groundwater infiltration rates in the calibrated groundwater models. Based on the groundwater flow model simulations, the lower end of this range may more reasonably estimate true annual infiltration and leachate production rates, as the HELP model was developed for the purpose of conservatively estimating leachate production rates for landfill design. Source loading estimates for the transport model simulations were generated using both infiltration values.

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It was generally assumed that the relationship between a concentration of a constituent in the fly ash and its concentration in leachate produced by the fly ash is represented by a linear relationship, expressed by the partitioning coefficient (K_d). Instantaneous equilibrium between the liquid and solid phases is assumed.

The leachate concentration multiplied by the infiltration rate was then used to generate an annual source loading rate estimate to groundwater beneath areas of emplaced fly ash. For arsenic, concentrations were assumed to be constant over each year. Using a similar approach for nitrate, concentrations were assumed to be constant over just a ten-day period, because it is quite soluble in water. Over time, as the quantity of available arsenic or nitrate in the landfill is depleted, concentrations of the constituent in the leachate will likewise decrease.

In the transport model, the parameter K_d is used to calculate the source loading rate, and, indirectly, the rate of source depletion, as described in this section, as well as the retardation factor (R) as described in Section 7.2.2.

The initial estimate of available constituent mass for transport into groundwater as leachate was calculated in two different ways for each chemical investigated for the transport model analysis, arsenic and nitrate, based on available data, to obtain a reasonable range of source loading rates for the transport model simulations. These values are summarized in Table 7-2.

The two methods employed for the arsenic simulations were leachate loading based on TCLP results from fly ash samples and leachate loading based on total constituent concentrations in fly ash. Because the TCLP data represent leaching based on a very short period of time, these results represent the lower bounds of the effects of the fly ash on leachate water quality that can be reasonable expected. Under the actual site conditions, the fly ash will be in contact with the leachate water for a much longer period of time and the constituent concentrations will likewise increase. As a result, the second method was employed to provide and upper bound on the reasonable constituent concentrations in leachate. The upper bound method based on the total arsenic concentrations in fly ash are believed to be most representative of actual conditions. Because of nitrate's high degree of solubility, the lower bound of the leachate water quality was represented by assuming that slight nitrate retardation would occur during leaching. The upper bound assumed that all nitrate would be leached from the fly ash in the first flush of leachate water. The differences in results between the two methods were relatively small and the resulting range is believed to be representative of the actual conditions.

Arsenic Method #1: Leachate loading from TCLP results
Toxicity Characteristic Leaching Procedure (TCLP) concentrations were used to estimate the total mass of leachable constituents in the fly ash (Method #1). This method was also employed by URS (2001b), who performed TCLP analyses on ash amended with various amounts (1%, 3%, and 5%) of both cement kiln dust and lime kiln dust. MACTEC (2009) indicated that the fly ash was generated by amending raw

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fly ash with approximately 2% of an unspecified combination of cement kiln dust and lime kiln dust. Thus, the mass of leachable arsenic in the fly ash was estimated using the average TCLP analysis results for the fly ash amended with 1% and 3% of both cement and lime kiln dusts as reported by URS (2001b) in Table 2.5 of their report: average = 0.23 mg Arsenic/L (equivalent to 230 ug/L). In Method #1, this TCLP concentration is used to estimate the total mass of mobile or leachable arsenic in the fly ash.

To perform the standard TCLP analysis, a sample of the treated fly ash was combined with 20 times its mass in acidic aqueous leaching fluid, agitated by end-over-end rotation of the testing vessel for 18 hours, filtered, and the resultant fluid analyzed for the chemicals of concern. To calculate an equivalent mass of leachable arsenic in the fly ash at the site, used to determine source loading rates for the transport model, the average of the measured arsenic TCLP values was multiplied by 20 to estimate the concentration of mobile arsenic in the fly ash: 4.6 mg Arsenic/kg stabilized fly ash. Thus, it was assumed that the total mass of the analyte in TCLP leachate represents the total mass available to be leached from the original sample under natural conditions, with time.

K_d values for arsenic have been reported in the literature (e.g., EPA, 1996 and EPA, 2004); they are typically variable, but most lie between 20 and 30 liters/kilogram (L/kg). The smaller average value, 20 L/kg, was selected for the transport model calculations to simulate a conservative situation with maximum arsenic concentrations in the leachate. Simulations of a K_d of 30 L/kg were performed as sensitivity runs. Source loading rates calculated using Arsenic Method #1 ranged from approximately 30 to 96 milligrams per day (mg/d), as summarized in Table 7-2.

Arsenic Method #2: Leachate loading from total concentration in fly ash
MACTEC (2009) tested four fly ash samples collected from three borings within the site. The average of the four arsenic analytical results was 42.7 mg Arsenic/kg of fly ash. For the purpose of generating a conservative upper limit, Method #2 assumed that all of the arsenic mass present in the fly ash would be available to be leached into groundwater, a situation that would be very unlikely in reality. Method #2 then proceeded in the same manner as Method #1 to derive an estimated initial source loading rate using as a basis the assumed K_d relationship and the infiltration rate. Source loading rates estimated using Arsenic Method #2 were approximately one order of magnitude higher (more conservative) than Arsenic Method #1, based on the higher estimate of initial arsenic mass in the fly ash.

Nitrate Method #1: Leachate loading based on K_d
Nitrate is negatively charged, and thus, unlike arsenic and most positively charged metals, can move relatively unaffected by adsorption through the mostly slightly negatively charged soil particles. Nitrate Method #1 assumed slight adsorption. An R of 1.1 was selected, and the corresponding K_d was back-calculated based on the retardation equation below.

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$$R = 1 + \{(\rho_b/n) \times K_d\}$$

Where

ρ_b is the soil bulk density, 1.65 mg/cm³; and
n is the soil porosity, 0.382, based on fly ash boring B1B data reported by
MACTEC (2009).

In this case, the equivalent value of K_d for nitrate was calculated to be 0.023 L/kg. The average "nitrate as nitrogen" concentration in the fly ash from three soil borings was read from the measurements in Table 15 (MACTEC, 2009), and converted to a nitrate concentration of 14.5 mg/kg. Due to its high degree of solubility, the entire nitrate mass in the fly ash was assumed to be leachable. Just as described above in Methods #1 and #2 for arsenic, K_d was used to apportion nitrate from the fly ash to the leachate; except that constant concentrations and source loading rates were assumed for 10-day time increments rather than 1-year increments, due to its high solubility. An estimated initial source loading rate of 122 - 258 kilograms per day (kg/day) to the groundwater beneath the footprint of the fly ash was estimated using this method, depending on the infiltration rate used. The source loading rate decays exponentially with this method, because the leachate concentration is directly dependent on the total mass available in the solid phase. This method does not assume an upper limit for the nitrate concentration in the leachate.

Nitrate Method #2: Leachate loading based on all nitrate mobilized in the first pore volume
Due to the high solubility assumed with Nitrate Method #1, CDM applied a second method for comparison. Nitrate Method #2 assumed that the entire nitrate in the fly ash was flushed out in a volume of water equivalent to the first pore volume of leachate at a constant concentration by direct infiltration of recharge. Thus, the concentration of nitrate in the first pore volume was the total estimated mass of nitrate in the solid fly ash, divided by the total pore volume. The porosity value measured in soil boring B1B (MACTEC, 2009) of 0.382 was used. The number of days required for this first pore volume to flush entirely through the fly ash was calculated by dividing one pore volume by the product of the area of the solid ash fill and the estimated infiltration rates provided by the HELP Model. After the first pore volume passes through the source, it is completely exhausted, so that its nitrate concentration was assumed to go to zero. Estimated constant source loading rates using Nitrate Method #2 ranged from approximately 25.8 kg/day for 2.1 years (767 days), to 12.2 kg/day for 4.4 years (1,615 days).

Although for arsenic and other metals, the annual amount of decay in the source material is expected to be quite low, over a long period of time such as several hundred years, the source depletion may become significant. Where depletion of the constituent source was simulated, the rate of depletion was estimated by calculating the product of the leachate concentration and the leachate infiltration volume over a given time period (one year for arsenic and 10 days for nitrate) to estimate the overall

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constituent mass reduction in the fly ash during that same time period. The soil/water partitioning coefficient, K_d, was used to estimate a constant equilibrium concentration in the leachate based on the concentration of constituent mass in the fill. Leachate was assumed to reach steady-state concentrations between soil and water based on a linear relationship expressed by K_d. This is a reasonable assumption because the rate of leachate movement through the fly ash is slow.

The estimated mass in the leachate resulting from this calculation for the initial time period was then subtracted from the mass in the solid fly ash, resulting in a new mass of constituent in the fill during the subsequent time period; these calculations were performed in an iterative fashion. The resulting mass reduction was plotted versus time, and the coefficient of decay, λ, was determined by a fit to an exponential function, as follows.

$$Cs\,(t) = Cs\,(t_0) * e^{-\lambda t}$$

Initial mass loading rates and coefficients of decay for various combinations of K_d, infiltration (leachate production) rates, and initial mass of constituent in the fly ash were calculated using this method as summarized in Table 7-2.

As expected, the coefficients of source decay are faster for the higher infiltration rates, because more leachate is in contact with the fill in any given time period. Therefore, these simulations represent a conservatively high estimate of the rate of leachate transport into groundwater, as well as of source decay. The lower infiltration rates generate less leachate, and the constituents are more slowly released into underlying groundwater. The source loading rates are most sensitive to the assumption of the available mass that can be leached out of the fly ash.

7.2.2 Transport Parameters

Model parameters used in the transport computations are summarized in **Table 7-3** and include:

- Effective porosity – Advective velocity is inversely proportional to the effective porosity of the aquifer material. Effective porosity is typically less than total porosity because most of the groundwater flow will typically occur in a subset of the soil pores. This is especially the case for heterogeneous soils, and also for vertical transport for confining layers where much of the groundwater flow may occur in discontinuities in the silt/clay layer. Computationally, changes of effective porosity specifications have the same effect on simulation results as changes to adsorption/retardation. Since the effect of adsorption/retardation on arsenic transport simulation results is much greater than the effect of effective porosity, a single effective porosity value (0.20), rather than a range, was assigned in the arsenic simulations.

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■ Adsorption/retardation – Adsorption to the soil of solutes, most notably charged species such as arsenic, tends to slow the migration of the solute relative to the advective velocity of the groundwater. Arsenic adsorption is often quantified by adsorption isotherm equations, non-linear relationships which typically relate the degree of interaction with the solid matrix based on its content of iron oxides and iron oxy-hydroxides. Since this level of detail regarding the fly ash and native soils was not available, the simpler K_d approach was used, providing a more empirical description of arsenic adsorption, which is in fact often linear over the relatively small concentration range applicable here. Retardation factors were estimated from K_d values, a bulk density of the soil of 1.65, and a measured porosity of 0.382 in the fly ash using the standard groundwater retardation equation. Transport of nitrate, a soluble anion, is not expected to be significantly retarded in groundwater.

■ Dispersivity – This parameter controls the variability of transport velocity about the mean rate. Dispersion computations, based on Fick's Law, cause the simulated plume to spread somewhat in both longitudinal (parallel to direction of flow) and transverse directions. The dispersivity values assigned are in the range commonly used for this type of transport modeling. The simulation results are not very sensitive to dispersivity parameters.

■ Source decay, λ - First order decay of the source concentrations was estimated for various combinations of K_d values, leachate infiltration rates (recharge), and initial available mass (source loading), as described above. These values were converted to a half-life and are summarized in Table 7-2.

■ Constituent decay in the aquifer was not simulated for either arsenic or nitrate. Arsenic is a metal and will not degrade or otherwise decay; nitrate is assumed to be stable in groundwater.

Table 7-3 shows the range of transport parameters used in this study. Unless otherwise specified, these values were applied to all transport simulations.

7.3   Transport Simulations

Transport simulations were run using the combinations of source terms, source decay, and transport parameters indicated in Tables 7-2 and 7-3 for a period of 200 years. Particles representing constituent mass were introduced at model nodes located within the areas of estimated fly ash emplacement at an elevation corresponding to the approximate top of the silt/clay layer noted beneath the site. Where this was above the simulated water table, the mass was allowed to migrate downward into groundwater under a unit hydraulic gradient until the water table was reached. The High Flow Calibrated Model provided the groundwater flow field used as the basis of the transport simulations. This model was selected because it represents a conservative estimate of the water flux underneath the site, and would generate reasonable worst-case conditions of constituent migration with time.

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The particle transport paths are derived from the groundwater flow model and are representative of the site-wide flow field. Small-scale variations in the actual particle flow paths in actuality can vary from those simulated by the flow model because small-scale influences on the migration paths are not conventionally characterized for the purposes of a site-wide model. Small-scale influences can be caused by features such as small areas of differing K and small areas where the potentiometric surfaces differ from those included in the model. However, the overall simulation results and the site-wide transport model are valid.

Transport simulation results are illustrated at 5, 20, and 200-year intervals for arsenic simulations in **Figures 7-2** to **7-13**. These figures show calculated concentrations in the top of the surficial aquifer, beneath the silt/clay layer. The arsenic simulations indicate that predicted concentrations are most sensitive to the initial estimate of leachable mass in the fly ash. In addition, it takes approximately 20 years for the arsenic to migrate vertically downward through the silt/clay layer to the upper surficial aquifer. This vertical flow rate would be accelerated by preferential flow pathways in areas where the silt/clay layer is compromised.

Once in the surficial aquifer, the flow field beneath the site is significantly influenced by the ditches. The transport simulations confirm that arsenic migration is likely to be generally toward the ditches, where it would be discharged to surface water. Little to no arsenic migrates down into deeper portions of the surficial aquifer or to off-site locations in the simulations.

A time history of simulated nitrate and arsenic concentrations in the upper surficial aquifer is shown for three locations in **Figure 7-14**. This figure shows that location 3, downgradient of the southern drainage ditch, is not impacted by contaminants in the model simulations.

Subsequent to arsenic mass leaching through the silt/clay layer and reaching the upper surficial aquifer, arsenic concentrations off-site are not expected to be impacted by the fill. After 200 years, the arsenic concentrations beneath the site footprint are estimated to be 0.01 to 0.10 mg/L, or conservatively estimating the total amount of leachable arsenic in the fill, as high as 1-2 mg/L in the upper 15 feet of the surficial aquifer, according to model simulations.

Nitrate simulations, which represent the maximum distance that constituents from the site would be expected to travel since the retardation of this chemical is negligible, show a similar pattern, except that the source of nitrates is expected to deplete much more rapidly than for arsenic or other metals that are highly retarded (adsorbed to soils).

Nitrate simulations show that there is potential for mass to travel deeper into the surficial aquifer with time beneath the footprint of the site, although the same basic pattern is observed of ultimate discharge to the surface drainage system in the transport model, such that mass does not appear likely to migrate off-site. The nitrate

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simulations can be considered representative behavior of a conservative tracer in groundwater. Their transport is much more rapid in the groundwater than arsenic. Mass that migrated deeper beneath the footprint of the fill did not migrate beyond the influence of the surface drainage ditches in the simulations.

7.4   Sensitivity Analysis

A series of sensitivity simulations was run varying K_d, retardation, source decay, and initial source strengths, as described in Section 7.2. The nitrate simulations represent an analysis of the sensitivity of the transport model to the very high retardation factors estimated for metals.

The transport model was found to be very sensitive to assumptions about both the initial quantity of leachable mass in the fly ash and the adsorption characteristics of the material, as shown by the differences between the transport model results for arsenic and nitrate. Available information that would allow for more precise calculation of these parameters, and/or documentation on this is sparse.

The groundwater flow field was found to greatly limit offsite migration. When the water table is below the level of the ditches such as following heavy rainfall, groundwater could migrate underneath the ditches on a temporary basis. However the simulations indicate that the ditches exert a sufficiently strong hydraulic force on the aquifer on both upgradient and downgradient sides of the ditches that any leachate that may migrate beneath the ditches during periods of high ditch water levels will be pulled back and discharge to the ditch when the water levels recover to normal.

Assumptions about the solubility and leachability of the nitrate into groundwater dominated the nitrate simulations. The fly ash is likely to release nitrate into the groundwater more slowly than simulated in this model. However, while the arsenic source is likely to continue for a period of 200 years or more, appreciable leachable nitrate is expected to be depleted within a few decades at the most conservative estimate.

Because the expected rate of mass transport is low for arsenic simulations relative to depletion of the constituent source due to its high adsorption to soils, the transport model is not particularly sensitive to the rate of infiltration through the fly ash or the source decay, but is sensitive, within the site area, to the total quantity of mobile arsenic that is assumed.

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