FINAL REPORT Revision 1

DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS

EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Prepared for El Dorado Chemical Company El Dorado, Arkansas

December 1997

WCC File 97B061



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RISK ASSESSMENT

The protection of human health and the environment is the primary goal of regulatory requirements for cleanup and corrective action. The current risk assessment approach is a process developed over the last fifteen years that has evolved into using a conservative methodology to assist in addressing environmental issues. Risk assessment guidance incorporates the concept of reasonable maximum exposure (RME) which is always conservative (i.e., overestimates risk) in its assumptions. In keeping with this philosophy, conservative methodology and assumptions were utilized in the exposure assessment, the toxicity assessment, the groundwater modeling, and in all areas of the evaluation.

Risk assessment can contribute significantly to strategy development, risk management, decision making and evaluation of corrective action needs.

Woodward-Clyde (WC) was retained to use human health risk assessment procedures to develop target monitoring levels (TMLs) for the groundwater constituent of concern (COC) at the El Dorado Chemical Company (EDC) site in El Dorado, Arkansas. A TML is a concentration of a COC below which adverse effects to the exposed receptor are not expected to occur based on site-specific inputs. Therefore, a TML represents a concentration of a COC below which remediation is not necessary from a health risk standpoint. The objective of the risk assessment and methods that were used to develop the TML were provided in the Work Plan prepared by WC and submitted on September 19, 1996 to the Arkansas Department of Pollution Control and Ecology (ADPC&E) for approval. The Work Plan was subsequently approved by the ADPC&E on October 31, 1996.

The receptor populations evaluated under current and possible future conditions are off-site residents (child and adult) using groundwater as a drinking water source.

The COC, nitrate, is not classified as a carcinogen; therefore, the TML is developed based on noncarcinogenic risks.

The TML development quantitatively addresses the potential effects of the COC in groundwater at the EDC site. As specified by the approved Work Plan, nitrate is the COC and groundwater is the exposure medium for which the TML was calculated. Groundwater modeling was conducted to determine the maximum nitrate concentration that could potentially migrate to a receptor. This maximum concentration was compared to the published regulatory criteria including the United States Environmental Protection Agency (EPA) Safe Drinking Water Act Maximum Contaminant Level (MCL) for nitrate in groundwater. The groundwater modeling indicated that the MCL for nitrate of 10 mg/L should not be reached at any of the potential receptors. Calculations were performed for identifying TMLs for adult and child receptors at the receptor locations. However, the calculated health-based values were greater than the 10 mg/L MCL established by the EPA, and to be conservative, the MCL was used rather than the calculated values.

TML development is conducted by performing a risk assessment in reverse. Based on EPA policy, accepted carcinogenic risks and noncarcinogenic hazards are identified, and chemicaland medium-specific concentrations of each COC that do not exceed the identified risks and hazards are calculated for the potential receptors. The concentration at the on-site monitoring points which could result in exceeding that concentration is then calculated by modeling.

ECOLOGICAL EVALUATION

A WC biologist completed a site evaluation of Lake Kildeer and the small unnamed creek which receives discharge from outfall 001.

The creek downstream of Lake Kildeer is only about 1.5 feet deep and 5 feet wide for approximately 600 feet downstream of Lake Kildeer. The flow in the creek in this reach is primarily flow from outfall 001, and should not be impacted by the minimal contribution of groundwater.

CONTAMINANT FATE AND TRANSPORT MODELING

The contaminant fate and transport modeling was used to evaluate the potential for nitrate, at concentrations above the MCL, to reach the identified receptors via groundwater movement.

A horizontal transport model was used to evaluate the potential transport of nitrate in the groundwater to potential groundwater receptors. The International Ground Water Modeling Center's (IGWMC) Solute Program Package, Analytical Model for Transport of a Solute Plume from Point Sources in a Uniform Two-Dimensional Groundwater Flow Field (Plume 2D) was used to simulate the transport of the nitrate horizontally with groundwater to the To be conservative and protective of human health, the present nitrate receptor. concentrations in the groundwater were used to define the amount of nitrate source inputs to the groundwater in the horizontal transport model. The ADPC&E approved the use of this model in a transmittal dated October 31, 1996. Based on the results of the horizontal transport modeling, the nitrate would not exceed the MCL at the residential domestic water well, commercial water well, or municipal water well receptor locations. The maximum concentration modeled to reach the nearest downgradient domestic water well completed in the Cockfield formation was approximately one-tenth the MCL and required a time of 7,250 The maximum concentration modeled to reach the nearest years to reach the well. commercial water well was approximately three tenths of the drinking water MCL and required a time of 3,000 years. This was a very conservative model which considered only dispersion as an attenuation mechanism for nitrate. Sensitivity modeling was performed to evaluate the effects of attenuation by sorption (such as ion exchange) and by degradation The resulting maximum concentrations were substantially lower when these reactions. additional attenuation mechanisms were considered. Sensitivity modeling was also completed for hydraulic conductivity and dispersivity. The results support the conclusion that the MCL should not be exceeded at the receptors.

The results of the horizontal transport model were also used to calculate an attenuation factor for transport of nitrate from the site to the receptor. This nitrate attenuation factor was then multiplied by the nitrate MCL to calculate the TML for on-site monitor wells. The TML for on-site monitor wells is the nitrate concentration in those monitor wells below which the MCL would not be exceeded at the receptor. The calculated TML for on-site monitor wells is 9,180 mg/L based on the domestic water well and 3,607 mg/L based on the commercial water well. Note that water from commercial water wells is not used for drinking water and application of the drinking water MCL to a commercial well in calculation of the TML is a very conservative approach.

Calculations of the groundwater travel time for vertical movement of water from the Cockfield formation to deeper aquifers indicate that this should not be a pathway of concern for the nitrate present in the shallow Cockfield formation at the site.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the contaminant fate and transport modeling, it is concluded that the estimated human health risks are acceptable for all receptors evaluated. On-site groundwater concentrations below the TML of 3,607 mg/L should be acceptable with respect to health risk based on the very conservative application of the drinking water MCL to a commercial (non-drinking water) water well. On-site groundwater concentrations below the TML of 9,180 mg/L would be acceptable based on the nearest domestic water well.

Based on the findings, it is recommended that a 5-year semiannual groundwater monitoring program for nitrate be initiated for selected monitor wells. Annual monitoring reports would be submitted to the ADPC&E. After this 5-year period, a data review report will be prepared and submitted to the ADPC&E. The suggested approach also includes semiannual measurement of groundwater levels for all monitoring wells. The proposed monitoring well sampling locations are the following:

- Monitor Well MW-EDC-17 which is downgradient of Lake Kildeer
- Monitor Well MW-EDC-18 which is downgradient of Lake Kildeer
- Monitor Well MW-EDC-8 which had the highest nitrate concentration
- Monitor Well MW-EDC-2 which is at the upgradient portion of the EDC site

Annual reports to the ADPC&E would include analytical results and water level data. If onsite nitrate concentrations increase to or above the site-specific on-site TML for nitrate, corrective actions would be investigated. EDC is in the process of implementing Best Management Practices (BMPs) and upgrading its Waste Water Treatment Plant (WWTP) at the El Dorado facility which should reduce the potential for future releases of nitrate to the shallow groundwater, resulting in decreasing nitrate concentrations. With the anticipated decrease in groundwater nitrate concentrations due to BMPs and the future WWTP project, it is likely that no further action will be necessary. Lake Kildeer and the area downstream for at least one-half mile do not present substantial aquatic ecological receptors. Groundwater discharge, if any, to the creek in this area should be minimal compared to the total flow in the creek. Consequently, establishment of groundwater TMLs for nitrate should not be necessary to protect aquatic organisms, mammals, or fowl.

1.0 INTRODUCTION

A Phase II Groundwater Assessment (WC, June 1996) was performed by Woodward-Clyde (WC) at the El Dorado Chemical Company (EDC) site and was submitted to the Arkansas Department of Pollution Control and Ecology (ADPC&E) on June 19, 1996. Based on the Phase II Groundwater Assessment Report, nitrate was identified as the constituent of concern (COC). The rationale for selection of this COC is discussed in Section 2.0 of this report. WC was retained by EDC to develop a human health risk-based target monitoring level (TML) for the constituent of concern (COC) at the EDC site at El Dorado, Arkansas. TMLs are concentrations below which adverse health effects are not expected to occur based on site-specific exposure conditions. A report presenting development of TMLs was submitted to ADPC&E during February 1997. Based on discussions with ADPC&E it was decided to add an additional receptor location to the development of TMLs. This Revision 1 to the report includes the additional receptor, the nearest downgradient commercial water well.

WC's scope of work included developing a human health risk-based TML based on available analytical data, historical and current site information. The constituent of concern was selected and the corresponding TML was developed using site-specific conditions to evaluate potential exposure of receptors to nitrate at the EDC site.

The approach used in this study to quantify potential exposure was that in the approved Work Plan and followed current Environmental Protection Agency (EPA) guidance for human health risk assessments. Specifically, this study followed the guidance provided in the following EPA documents: *Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual* (EPA, 1989a); *Exposure Factors Handbook* (EPA, 1989b); *Superfund Exposure Assessment Manual* (EPA, 1988); and the *Dermal Exposure Assessment: Principals and Applications* (EPA, 1992b). These documents are intended to provide guidance only and professional judgment must also be exercised in applying the information to site-specific risk assessments.

In addition, the scope of this risk assessment included modeling potential migration of siterelated nitrate concentrations to identified site-related potential receptor population exposure points. The EPA Safe Drinking Water Primary Maximum Contaminant Level (MCL) for nitrate was compared to the modeled nitrate concentrations to evaluate potential need for remediation.

The development of risk-based TMLs and the modeling of potential groundwater constituent exposure point concentrations were designed and conducted to meet the objectives of identifying potential adverse health effects posed by the site and to evaluate the need for remedial action for groundwater.

An ecological evaluation was conducted at the site to determine if potential environmental receptors are present in surface water bodies that could receive discharge of groundwater from the site (i.e., Lake Kildeer and associated tributaries).

2.0 DATA EVALUATION AND IDENTIFICATION OF CONSTITUENTS OF POTENTIAL CONCERN

The first step in developing a human health risk assessment is to identify site-related potential constituents of concern (COCs). COCs are constituents that may be present at the site and which may pose a health risk to humans who come in contact with them.

For the EDC site, identification of COCs was based on data collected from sampling and chemical analysis of 22 monitor wells at the site, as documented in the Phase II Groundwater Assessment Report submitted to the ADPC&E on June 19, 1996. In the Phase II Groundwater Assessment Report, the list of constituents above detection limits were compared to published health criteria, including the primary MCLs and EPA proposed corrective action levels.

Nitrate was the only constituent determined to be present in the on-site groundwater monitor wells at concentrations above the respective primary MCL during the Phase II Groundwater Assessment. Nitrate was detected in 17 of the monitor wells at concentrations ranging from 0.2 to 1,010 mg/L. Concentrations for 10 of the 22 monitor wells were above the MCL for drinking water of 10 mg/L.

Nitrate is generally relatively mobile in groundwater due to the solubility of most salts of nitrate, and the generally low sorption of nitrate to soil. Nitrate may undergo sorption to soil through ion exchange. Nitrate can be biodegraded in denitrification reactions under anaerobic conditions. It can also be taken up by vegetation.

Nitrate in groundwater was first regulated in the United States in 1962. Nitrate is a major nutrient for vegetation and is an essential nutrient for all living organisms. However, in excessive amounts, nitrate may produce methemoglobinemia in human infants (Montgomery, 1985). The EPA regulates nitrate as a primary drinking water standard. Based on the frequency of detection, mobility and concentrations relative to the MCL, nitrate is a COC which will be included in this risk-based development of TMLs.

Following submittal and review of the reports from the Work Plan (WC, September 1996), use of risk assessment procedures to develop a site-specific TML for nitrate in groundwater was approved by the ADPC&E.

The Quality Assurance/Quality Control (QA/QC) of the analytical data obtained from the laboratory were reviewed per EPA guidance documents under the *National Functional Guidelines for Inorganic Data Review*, Revised June 1991. Following QA/QC data review, nitrate satisfied analytical data quality objectives.

3.0 TOXICITY ASSESSMENT

A toxicity assessment is conducted to characterize the evidence regarding the potential for a substance to cause adverse health effects to exposed populations and, where possible, to estimate the relationship between the extent of exposure and extent of toxic injury or disease (dose-response evaluation). Qualitative and quantitative toxicity information for the substances being evaluated are acquired through examination of relevant scientific literature that relates exposure to response in humans.

Nitrate is not considered a carcinogen. The toxicity of nitrate was evaluated using EPAderived and published toxicity factors that relate chemical "dose" to potential health effects. The toxicity factors are called "reference doses" for noncarcinogenic effects. The toxicity values are used in conjunction with the estimated chemical intakes developed in the exposure assessment to calculate the medium-specific noncarcinogenic TMLs. The toxicity assessment is presented in this section. A toxicity profile for nitrate is presented in Appendix A.

Noncarcinogenic effects are generally thought to have a threshold dose below which there are no observable effects. In developing a toxicity value for noncarcinogenic effects (i.e., reference dose), the approach is to identify this threshold dose. Reference doses (RfDs) are daily exposure levels that are not expected to result in adverse health effects to humans. RfDs are calculated by dividing the no-observed-adverse-effect level (NOAEL) from observations in exposed human populations or in experimental animals by uncertainty factors. Uncertainty factors are intended to account for specific types of uncertainty inherent in extrapolation from the available data, including variations in the sensitivity of individuals in a population, extrapolation from animal data to humans, limitations in exposure duration, and other limitations in the reliability of the experimental data. The resulting RfD is expressed in units of mg of chemical/kg of body weight/day. RfD values for inhalation exposure are often reported by the EPA as a concentration in air (in mg/m³). The methodology for deriving RfDs is more fully described in the Risk Assessment Guidance for Superfund (RAGS) document (EPA, 1989a). The EPA has developed various types of RfDs depending on: the exposure route (either oral or inhalation); the critical effect (i.e., developmental or other); and the length of exposure being evaluated (i.e., chronic, subchronic or single event). The EPA defines a chronic RfD as a daily exposure level below which no deleterious effects would occur during a lifetime. These chronic RfDs are used to evaluate the potential noncarcinogenic effects associated with exposure periods between 7 years and a lifetime. Subchronic RfDs have been developed by the EPA to characterize potential noncarcinogenic effects associated with shorter term exposures, i.e., periods between two weeks and seven years.

Since the EPA develops only oral and inhalation RfDs, there are no available, verified dermal RfDs. Due to the lack of available toxicity values for dermal exposure, the oral RfDs were used as surrogate values for dermal exposure in this assessment.

Table 3.1 summarizes critical toxicity values for nitrate.

4.0 EXPOSURE ASSESSMENT

Pathway-specific intake factors for the receptor populations were used to develop the Reasonable Maximum Exposure (RME) levels. The RME is defined from a set of exposure variables and assumptions such as body weight, ingestion rates, etc., that result in a maximum, yet plausible (i.e., 90th percentile exposure), scenario that can be considered to potentially occur at a site. To produce these RME-based intake factors, the maximally-exposed receptor populations and relevant exposure pathways must be identified, and the exposure algorithm (intake factor) must be calculated based on a set of exposure assumptions.

4.1 **RECEPTOR POPULATIONS**

The on-site exposure assessment was conducted based on current site conditions gathered from a review of public records and past site studies. The exposure assessment addresses the human receptors potentially exposed to groundwater from the site. Because the current land use is industrial, there is no realistic exposure potential for on-site receptor populations to groundwater. The land use restrictions for the EDC site include the following conditions:

• No use of groundwater from the shallow aquifer for drinking water.

The off-site receptors evaluated under current and possible future conditions are as follows:

• Off-site Residents (Adult and Child).

As proposed and approved in the Work Plan, the residential receptors have been evaluated in this risk assessment. The off-site residents (adult and child), could have the potential for exposure to site-related groundwater if nitrate from the site migrates in the groundwater to a water well used for drinking water. On-site and regionally, the direction of groundwater flow in the Cockfield formation is generally to the southeast. According to El Dorado's City Engineer, residents within the city limits of El Dorado are supplied water by the El Dorado

Public Works Department. The closest downgradient city of El Dorado public supply well is located (see Figure 4.1) approximately 1.4 miles south of the EDC site in Section 16 of Township 17 South, Range 15 West. The city of El Dorado well is 700 feet deep and is completed in the El Dorado aquifer. The El Dorado aquifer is separated from the shallow Cockfield formation by two thick clay layers and the Greensand aquifer (see Appendix D).

A well search was made of the Arkansas Geological Commission Well Drilling Report files. The search indicated that the nearest downgradient domestic well is located (see Figure 4.1) in Section 26 of Township 17 South, Range 15 West, approximately 4.7 miles from the EDC site. This domestic well is reported to be 40 feet deep and completed in the Cockfield formation. This well is potentially in the city of El Dorado water service area. For purposes of development of TMLs, this downgradient domestic well is considered the receptor point for off-site residents (adult and child). The well was installed in 1973. It is probable that the well is no longer used for drinking water, because of the availability of city water.

The nearest up-gradient domestic well is located (Figure 4.1) approximately 1.6 miles to the northwest of the site. It is reportedly 31 feet deep and completed in the Cockfield formation.

The search also indicated that the nearest downgradient commercial water well is located in Section 16 of Township 17 South, Range 15 West approximately 1.3 miles southeast from the EDC site, as shown in Figure 4.1. The well is reported to be 37 feet deep and completed in the Cockfield formation. Water from commercial water wells is not used for drinking water. However, this closest commercial water well has been evaluated in the development of TMLs as though it was used for drinking water. This is a very conservative approach.

4.2 EXPOSURE PATHWAYS

An exposure pathway describes a specific environmental transport pathway by which receptors can be potentially exposed to chemical constituents present at or originating from a site. An exposure pathway consists of four necessary elements:

- A source and mechanism of chemical release to the environment.
 - An environmental transport medium for the released chemical.
- A point of potential human contact with the medium and the receptors located at these points.
 - A human uptake route (intake of media containing site-related chemicals) at the point of exposure.

All four elements must be present for an exposure pathway to be complete and for exposure to occur. If any one of the four elements is absent, the pathway is incomplete and no exposure can occur. All potential exposure pathways are evaluated for each identified receptor to determine their significance. Complete exposure pathways are identified in this exposure assessment. Incomplete exposure pathways do not result in actual human exposure and therefore are not included.

4.2.1 Integration of Exposure Pathway: The Site Conceptual Exposure Model

The site conceptual exposure model is intended to summarize information on the anticipated primary sources of nitrate, chemical release mechanisms, transport media, potential receptors, exposure routes, and subsequent complete exposure pathways for nitrate at the EDC site. All potential exposure pathways are combined into the integrated site conceptual exposure model shown in Figure 4.2, which depicts complete, potentially complete, and incomplete pathways. The exposure model represents the cumulative information needed to evaluate whether exposure pathways warrant further consideration in the calculation of RMEs. Complete pathways are designated with a solid dot, while an open circle indicates a pathway considered to be potentially complete but currently not known to be complete under site-specific conditions. An "I" designates an incomplete pathway. As indicated on the site conceptual exposure model, migration of nitrate in the groundwater of the Cockfield formation to a water well used for drinking water is the pathway of concern.

4.3 QUANTIFICATION OF EXPOSURE

Exposure parameters define the magnitude, frequency and duration of exposure to COCs for the identified receptor populations. These parameters are chosen by making assumptions for each receptor population, resulting in estimates for each of the exposure pathways considered in the assessment.

The magnitude of exposure (or intake) to a chemical is a function of a number of assumptions, including variables that describe the exposed population (e.g., contact rate, exposure frequency and duration, and body weight). Each of the parameters can be described by a range of variables. Two types of exposure can be quantified: an average exposure and a reasonable maximum exposure (RME). The RME was used in this assessment. The RME was estimated using guidance provided in EPA's Risk Management Guidance for Superfund (EPA, 1989a) and is defined by selecting intake variable values so that the combination of all intake variables results in a maximum exposure that is reasonably expected to occur at the site. The RME represents approximately the 90th percentile exposure, that is, the exposure expected to occur in 1 of every 10 exposed individuals. The intent of the RME is to estimate a conservative, well above average, exposure case that is still within the range of possible exposures. In order to quantify RME exposures for the identified receptors at the site, medium-specific intake factors were developed.

The exposure assessment was conducted based on current site conditions and available future land use information. The exposure assessment addresses the potential receptor populations for exposure to site groundwater.

In keeping with the RME approach and incorporating conservative assumptions in the risk assessment, the following conservative assumptions were incorporated in this assessment for the EDC site:

Residential Receptors

• Residential exposures are quantified under the assumption of current conditions with general groundwater flow towards the southeast. The

nearest residential receptor is approximately 4.7 miles downgradient from the EDC site. This domestic water well was installed in 1973. It is conservatively assumed that the groundwater is still used for domestic purposes.

Residential exposures are assumed to take place through the use of groundwater as a household water source. All residences within the city limits are reportedly supplied by water from the city of El Dorado. There is, therefore, no current use of shallow groundwater as a domestic water source or drinking water supply inside the city limits. As stated above, the nearest downgradient domestic well found in the search of well logs is approximately 4.7 miles from the EDC site and may be outside the El Dorado city limits. It is not known if this well is currently used for drinking water.

- The probability of a current city of El Dorado resident installing a private water well in order to use groundwater as a household water supply is very low (as is discussed in detail in Section 7.0). Therefore, the probability of residential use within the city limits of the shallow groundwater for drinking water is very low. Consequently, the potential for the residential exposure pathway to be complete within the city is very low.
- The nearest downgradient commercial water well completed in the Cockfield formation is located approximately 1.3 miles southeast from the EDC site. Although water from commercial water wells is not used for drinking water, as a more conservative scenario, this well was also evaluated as though it was used for drinking water.

Groundwater Modeling

• The modeling effort assumed no vertical mixing below the monitored interval of the Cockfield formation.

- The groundwater modeling was based on interpretation of site-specific groundwater concentrations which may overestimate the amount of nitrate present.
 - The modeling assumed that the distance a COC traveled in groundwater is equal to the shortest distance between the originating point (the site) and the exposure locations. The flow of groundwater may actually be longer allowing additional time for attenuation of the nitrate.

The exposure assessment as well as the contaminant fate and transport model incorporated conservative, yet realistic, inputs and assumptions to result in an RME that is protective of the most sensitive members of an identified exposure population. The exposure assumptions are presented in detail in Tables 4.1 through 4.4. The complete discussion of the contaminant fate and transport modeling is included in Section 5.0, Appendix C (domestic water well), and Appendix D (commercial water well) of this report. The uncertainties and limitations of the conservative (RME) approach and the potential impact to the results are discussed in detail in Section 7.0.

4.3.1 Intake Factors/Exposure Pathways

The following intake factors are relevant to this risk assessment:

- Dermal contact with water (IF_{derm}): off-site residents (child and adult).
- Ingestion of water (IF_{oral}): off-site residents (child and adult).

Intake factors for each exposure pathway are determined by assimilating inputs for all exposure assumptions used to quantify exposures. The following equations are used to define each intake factor.

(i) For dermal contact with water, the intake factor (L/kg/day) is calculated as follows:

Intake Factor (IF_{derm}) =
$$\frac{SAxETxEFxEDxPCxCF}{BWxAT}$$

where:

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SA	=	Surface area exposed (cm ²)	
ET	=	Exposure time (hours/day)	
EF	=	Exposure frequency (days/year)	
ED	=	Exposure duration (years)	
PC	=	Permeability constant (cm/hr)	
CF	=	Conversion factor (L/cm ³)	
BW	=	Body weight (kilograms)	
AT	=	Averaging time (days)	

(ii)

For ingestion of groundwater, the intake factor (L/kg/day) is calculated as follows:

Intake Factor (
$$IF_{oral}$$
) = $\frac{IRxEFxED}{BWxAT}$

where:

IR	=	Ingestion rate (L/day)
EF	=	Exposure frequency (hours/day)
ED	=	Exposure duration (years)
BW	==	Body weight (kilogram)
AT	=	Averaging time (days)

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4.4 ENVIRONMENTAL EVALUATION

A WC biologist conducted a site visit to observe Lake Kildeer, the discharge (outfall 001) from Lake Kildeer, and the creek which receives this discharge. The purpose of the visit was to collect information on potential ecological receptors. The observations and associated evaluation are presented in the following paragraphs.

Lake Kildeer is a man-made impoundment which covers approximately 45 acres. The shoreline is primarily gentle sloping grassland except for the dam which is covered with rip-rap material. Habitat (i.e. vegetation) for fish appeared to be limited in the impoundment, which may be related to seasonal conditions. Deer, raccoon, and shorebirds tracks were observed along the shoreline.

Outfall 001 flows from the northeast corner of Lake Kildeer to the bed of a small unnamed creek. The small creek meanders through a wooded area with sand as the primary substrate. The width and depth of the creek are approximately 5 feet and 1.5 feet, respectively, and the flow is essentially from outfall 001. The habitat mainly consists of undercut banks, rock outcroppings, and root masses. Habitat is plentiful and diverse for small fish and benthos. Beaver activity was noted approximately 100 feet downstream of the discharge. The creek remains unchanged until another unnamed creek merges with it approximately 600 feet downstream from Lake Kildeer. This second small creek apparently contributes a heavy load of sand and diminishes the quality of habitat of the first creek after this convergence. Oligochaetes, chironomids, and coleoptera were present in this second unnamed creek. Deer, raccoon and muskrat tracks were common along the banks.

Approximately 2,200 feet downstream from Lake Kildeer, a teastain-colored backwater area was observed. Two parallel transmission line corridors extend across the creek approximately 2,400 feet downstream from Lake Kildeer. Deer stands are abundant near the transmission line corridors. Standing water was noted in the clearing of the second transmission corridor. Crayfish, amphibian egg masses, and aquatic vegetation (submerged and emergent) were abundant in this area. Deer, raccoon, and muskrat tracks remained abundant. A barn owl and a redtail hawk were observed in the clearing.

Immediately downstream of the second set of transmission lines, beaver were actively constructing dams creating parallel areas of standing water along the length of the stream. Mallards, black ducks and great blue heron were observed while walking through the area. Tracks of deer, raccoons and muskrats were observed. Crayfish were abundant in the areas of standing water and the carapace of crayfish litter were observed on the banks.

Near Highway 7 Spur (approximately 1.5 miles downstream from Lake Kildeer), access roads were common with a criss-cross maze of well-traveled trails. Bridges had been constructed for all-terrain vehicle crossings and deer blinds (>25) were scattered along the creek. The creek begins to broaden in this area and the depth increases significantly. Habitat quality begins to improve with the addition of woody habitat along the banks. The creek meanders unchanged through a wooded section adjacent to the railroad tracks until the crossing of Highway 7 Spur.

The creek continues flowing north of El Dorado primarily through private property. The next location visited was at the crossing of an unnamed county road located approximately 5 miles downstream from Lake Kildeer near the Missouri-Pacific railroad. The creek at this point has diverse habitats and is heavily tannin stained. Benthos present consisted of oligochaetes and chironomids. Animal tracks at this location were abundant along the shoreline and mainly included raccoon and deer.

The last area evaluated was approximately 8.5 miles downstream from Lake Kildeer near the crossing at Highway 335 east of Norphlet. At this point, the creek is named Haynes Creek. The unnamed creek merges with Flat Creek, Salt Creek and numerous unnamed tributaries upstream of this point to form Haynes Creek. The creek is wide and tannin stained with habitat consisting of rock piles and submerged woody structure. Sunfish (*Lepomis spp.*) and mosquito fish (*Gambusia affinis*) were present along the shoreline and near the bridge abutments. Indicators of wildlife included deer, muskrat, fox and raccoon tracks along the banks.

4.4.1 **Potential Ecological Receptors**

The creek downstream of Lake Kildeer is only about 1.5 feet deep and 5 feet wide for approximately 600 feet downstream of Lake Kildeer. The flow of the creek in this reach is primarily flow from outfall 001.

Groundwater discharge, if any, to the creek in this area should be minimal compared to the total flow in the creek. Consequently, establishment of groundwater TMLs for nitrate should not be necessary to protect aquatic organisms, mammals, or fowl.

4.4.2 **Pollution Prevention**

EDC is currently conducting investigations for pollution prevention programs and an upgraded wastewater treatment system at the El Dorado site. Once completed, it is anticipated this will improve the water quality in the creek receiving water from outfall 001.

5.0 FATE AND TRANSPORT MODELING OF CONTAMINANTS

The technical approach for the contaminant fate and transport modeling is described in the *Development of Risk-Based Target Monitoring Levels Work Plan* (WC 1996). The modeling is summarized in the Sections 5.1 and 5.2 below. More detailed discussion of the modeling is presented in Appendix C (domestic well) and Appendix D (commercial well).

5.1 HORIZONTAL TRANSPORT

The horizontal transport modeling was used to evaluate the transport of nitrate in the groundwater to potential groundwater use locations. The International Ground Water Modeling Center's (IGWMC) Solute Program Package, Analytical Model for Transport of a Solute Plume from Point Sources in a Uniform Two-Dimensional Groundwater Flow Field (Plume2D) was used to simulate the transport of the nitrate horizontally with groundwater to the receptor locations.

The source configuration for the nitrate used within the contaminant fate and transport modeling grid was trial-and-error fit to represent current site conditions. Site-specific values for the saturated monitoring interval thickness and saturated hydraulic conductivity were used in the base case model. Hydraulic gradient of the Cockfield formation in the site vicinity was obtained from an Arkansas Geological Commission Information Circular (1988).

The nitrate horizontal transport scenario developed for the EDC site was non-steady state and the nitrate concentration in the groundwater changes with time. As time increases, the nitrate moves farther from the initial source location at the site. A maximum nitrate concentration of 1.1 mg/L is simulated to reach the nearest downgradient receptor domestic well in approximately 7,250 years. At times greater than 7,250 years, the concentration of nitrate at the nearest downgradient receptor domestic well decreases. A maximum nitrate concentration of 2.8 mg/L is simulated to reach the nearest downgradient receptor commercial well in approximately 3,000 years. At times greater than 3,000 years, the concentration of nitrate at the nearest downgradient commercial well receptor decreases. Based on the horizontal transport

modeling, the nitrate MCL of 10 mg/L will not be exceeded at either of the identified receptor locations.

The only attenuation mechanism modeled in the base case simulations was dispersion. A sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation (denitrification or incorporation in biomass). The degradation (or decay) mechanisms were modeled in the sensitivity analysis using a first-order rate equation.

- <u>Sorption</u>: As sorption increases (modeled by increase in the retardation factor, R), the maximum concentration which could reach the nearest downgradient receptor domestic well decreases from the base case maximum concentration of 1.1 mg/L (R=1) to a concentration of 0.22 mg/L (R=5). The maximum concentration which could reach the nearest downgradient receptor commercial well decreases from the base case of 2.8 mg/L (R=1) to a concentration of 0.54 mg/L (R=5).
 - <u>Degradation:</u> As the decay rate increases, the maximum concentration which could reach the nearest downgradient receptor domestic well decreases from the base case maximum concentration of 1.1 mg/L (no decay) to a maximum concentration of 0.0000076 mg/L with the halflife equal to 190 years. The maximum concentration which could reach the nearest downgradient receptor commercial well decreases from the base case maximum concentration of 2.8 mg/L (no decay) to a maximum concentration of 0.002 mg/L with the half life equal to 190 years.

Therefore, any attenuation through decay or sorption which is occurring insitu will further decrease the concentration in the groundwater below the 1.1 mg/L (domestic well) or 2.8 mg/L (commercial well) concentration predicted by the base case model, which included no attenuation mechanisms other than dispersion.

Sensitivity analyses were also conducted for hydraulic conductivity and dispersivity. Increasing the hydraulic conductivity by one order of magnitude increases the seepage velocity by one order of magnitude. The maximum concentration predicted to reach the receptor point did not change; however, the time for the maximum concentration to occur decreases by one order of magnitude. That is, it decreases from 7,250 to 725 years for the domestic well and from 3,000 to 300 years for the commercial well. When the hydraulic conductivity was decreased by one order of magnitude, to 72,500 years for the domestic well and 30,000 years for the commercial well, but the maximum concentration was not changed. The longitudinal dispersivity was decreased to one-fifth of the base case value. The lateral dispersivity was calculated to be 10 percent of the longitudinal dispersivity. Decreasing the dispersivity increases the maximum concentration at the receptor point from 1.1 mg/L (base case) to 3.5 mg/L for the domestic well and from 2.8 to 4.1 mg/L for the commercial well. The time to reach the maximum concentration increased from 7,250 to 8,500 years for the domestic well and from 3,000 to 3,500 years for the commercial well.

In the base case scenario and all sensitivity analyses, the maximum concentrations at the receptor domestic well and at the receptor commercial well were predicted to remain below the MCL of 10 mg/L. The results of the nitrate horizontal fate and transport modeling are conservative and the modeled concentrations which have been generated by the simulations are expected to be higher than the concentrations which will actually occur.

5.2 VERTICAL TRANSPORT

The generalized modeling cross-section for the EDC site is shown in Figure 5.1. The local geology beneath the EDC site to the base of the Cook Mountain formation consists of the following:

- A thin veneer of Quaternary-aged alluvial sediments
- Tertiary-aged Cockfield formation (part of Claiborne Group)
- Cook Mountain formation (clay confining unit)

The geology below the Cook Mountain formation includes the following:

- Sparta Sand (contains Greensand aquifer, Sparta middle confining bed and El Dorado aquifer)
- Cane River formation (clay confining unit)

Using values of hydraulic conductivity by McWreath *et al.* and Fitzpatrick *et al.* of 9×10^{-6} feet/day, a formation thickness of 95 feet, an effective porosity of 0.35, a vertical gradient of 0.9474 feet/feet, the travel time for water through the Cook Mountain formation is approximately 10,680 years. This travel time calculation is for water to reach the top of the Greensand aquifer interval of the Sparta aquifer at approximately 300 feet below ground surface. The potential receptor well, the city of El Dorado public supply well, is completed approximately 400 feet deeper in the El Dorado aquifer interval of the Sparta aquifer. The Greensand aquifer is separated from the El Dorado aquifer by the Sparta aquifer middle confining bed. Therefore, additional travel time would be required if the nitrate could migrate vertically through the Cook Mountain formation (100 feet) and the uppermost 400 feet of the Sparta aquifer.

Based on the fate and transport model developed for the shallow Cockfield formation, the maximum concentration of nitrate that could migrate horizontally in the shallow Cockfield formation to the location of the nearest downgradient public supply well is 4.3 mg/L and requires approximately 3,000 years. If the nitrate could migrate vertically through the lower portions of the Cockfield formation, through 95 feet of the Cook Mountain formation, and then through 400 feet of the Sparta Sand to the El Dorado aquifer, additional attenuation of the nitrate would occur through dispersion, degradation and sorption. If the nitrate reaches the top of the Sparta Sand, it would be further attenuated as it migrates vertically and horizontally through the Greensand aquifer and the Sparta middle confining unit before reaching the El Dorado aquifer. Throughout this vertical travel distance (to a depth of 700 feet below ground surface), dispersion and attenuation mechanisms would further reduce the concentration of the nitrate in groundwater below 4.3 mg/L.

6.0 TARGET MONITORING LEVEL DEVELOPMENT

For this project, human health risk-based target monitoring levels (TMLs) were calculated. The TML incorporates carcinogenic and noncarcinogenic hazards. However, since nitrate is noncarcinogenic, carcinogenic risks are not applicable. In general, TMLs are calculated by performing a risk assessment in reverse. Acceptable risk and hazard levels are identified and media concentrations that will not result in exposures exceeding the acceptable levels are calculated. A TML is the concentration of a chemical in each exposure medium that corresponds to the appropriate risk or hazard. In general, TMLs for noncarcinogens are calculated as follows:

Chronic Daily Intake = Target Hazard Quotient x Reference Dose (or reference concentration)

and

TML (mg/L) = Chronic Daily Intake ÷ Intake Factor

EPA policy was used to establish noncarcinogenic hazard quotients used in the TML calculation. Under the EPA Proposed Corrective Action Rule (55 FR 30798, July 27, 1990), for noncarcinogens, sites with a hazard index (i.e., the sum of all hazard quotients) of 1.0 or less, typically do not require remediation. A hazard index consistent with the EPA guidance document referenced above was used to develop noncarcinogenic TMLs. The TML calculations utilized a target hazard index (THI) of 1.0.

Reference doses (estimates of noncarcinogenic toxicity in mg/kg-day) were obtained from the EPA's Integrated Risk Information Systems (IRIS) (EPA, 1995a), Health Effects Assessment Summary Tables (HEAST) (EPA, 1995b) and other EPA references (1995c).

6.1 GROUNDWATER TARGET MONITORING LEVELS

For groundwater exposures, ingestion and dermal pathways were incorporated, as appropriate, into the TML calculations. TMLs for groundwater were calculated using the following equations:

Noncarcinogens:

$$\frac{TML}{(mg/L)} = \frac{THI}{(IF_{dw} \div RfD_d) + (IF_{ow} \div RfD_o)}$$

where:

THI	==	Target hazard index (unitless)
IF _{dw}	=	Dermal intake factor (L/kg-day)
IF _{ow}	=	Oral intake factor (L/kg-day)
RfD _d	=	Dermal reference dose (mg/kg-day)
RfD _o		Oral reference dose (mg/kg-day)

The TML spreadsheets are presented in Appendix B. It should be noted that ingestion accounts for the vast majority of exposure to nitrate in groundwater. The dermal exposure route is included; however, it contributes only a small fraction of the exposure to nitrate in groundwater.

6.2 COMPARISON OF TMLS WITH MODELING RESULTS

The groundwater TMLs calculated for adult off-site resident and child off-site resident exposures at the EDC site are presented in Table 6.1. The final TMLs are presented in Table 6.2 along with the predicted maximum concentrations of COCs in the groundwater modeled to the appropriate exposure location for the individual receptor. A review of Table 6.2 shows that predicted concentrations in groundwater are lower than the corresponding TMLs for all compounds and for all receptors. However, the TMLs calculated at the receptors were not used to calculate a TML for on-site monitor wells because they exceeded the MCL of 10 mg/L established by EPA. Use of the MCL at the receptor to calculate a TML for on-site monitor wells is more conservative.

The TML development and the contaminant fate and transport modeling are based on very conservative assumptions that, independently and in combination, may overestimate the potential risk posed by the site. As discussed in Sections 5.1 and 7.0, conservative assumptions and approach were consistently utilized throughout this assessment.

The uncertainty attributed to the route-to-route extrapolation and to the difference in subchronic and chronic exposure durations produces rather low (conservative) RfDs. Correspondingly, the TMLs are also conservative (i.e., protective of human health).

It should be noted that the TMLs presented in this report are based on site-specific assumptions which are unique to the EDC site. The TMLs calculated for the EDC site must be viewed in the light of the conservative assumptions made in the risk assessment as well as the groundwater modeling efforts. These TMLs should not be used for any other purpose than that intended during this project.

The calculated TMLs (58 mg/L-adults and 24 mg/L-child) for nitrate at the receptor point were compared to the MCL(as shown in Table 6.2). The MCL is lower than the TMLs. The predicted groundwater concentrations are also lower than the MCL for nitrate (10 mg/L). For risk assessment purposes, the MCL was utilized to be conservative, since it is lower than the TMLs calculated at the off-site receptor for adult and child residents.

6.3 CALCULATION OF ACCEPTABLE ON-SITE MONITORING LEVELS

To monitor changes in nitrate concentration in the groundwater at the EDC site, a groundwater monitoring system is proposed. Target Monitoring Levels (TMLs) will be established for onsite monitor wells. The TMLs for the monitor wells will be set so that the nitrate MCL of 10 mg/L will not be exceeded if nitrate in groundwater migrates to the exposure point (nearest downgradient receptor well).

As described in Section 5.1, analytical transport modeling simulated the maximum nitrate concentration for the nearest downgradient domestic water well receptor to be 1.1 mg/L and to

be 2.8 mg/L for the nearest downgradient commercial water well receptor. Therefore, transport modeling predicts that the concentration of nitrate in groundwater will not exceed the MCL at the receptor well. Fate and transport modeling was then performed as an aid in selecting an appropriate nitrate TML for the selected on-site monitor wells.

Currently, the maximum concentration measured at a monitor well on-site is 1010 mg/L at monitor well MW-EDC-8. Using the maximum on-site concentration and the maximum concentration simulated to reach the receptor, a site-specific nitrate attenuation factor can be developed. The attenuation factor, AF, may be calculated as follows:

$$AF = \frac{MAXIMUM CONCENTRATION ONSITE}{MAXIMUM CONCENTRATION AT RECEPTOR}$$

Based on the domestic well the
$$AF_{Dom} = \frac{1010}{1.1} = 918$$

Based on the commercial well the
$$AF_{Com} = \frac{1010}{2.8} = 360.7$$

The MCL for nitrate of 10 mg/L is the risk-based TML at the receptor.

The site-specific AFs developed from the horizontal transport modeling may be used to calculate nitrate TMLs for on-site monitor wells which will be protective of human health at the respective points of exposure. The MCL is the regulatory standard for drinking water. Based on the results of the site-specific horizontal transport modeling described in Section 5.1, the on-site nitrate groundwater monitoring levels that will be protective of human health at the identified receptor locations are calculated as follows:

Acceptable Monitoring Level (TML for on - site monitor wells) = MCL • Nitrate AF

where:

Use of this equation gives a nitrate TML for on-site monitor wells of 9,180 mg/L based on the domestic water well receptor, and of 3,607 mg/L based on the commercial water well receptor.

The TML for on-site monitoring wells is the concentration at the on-site monitoring points below which the MCL should not be exceeded for the potential receptors at the point of exposure.

7.0 CONSERVATIVE RISK FACTORS

The EPA guidance for risk assessment provides a systematic means for organizing, analyzing, and presenting information on the nature and magnitude of potential risks to public health and the environment from chemical exposures. Despite the advanced state of the current methodology, uncertainties and limitations associated with assumptions are inherent in the risk assessment process. Available data quality, assumptions regarding existing conditions and future circumstances, as well as other factors discussed below contribute to these uncertainties and limitations. To avoid underestimating the risk of exposure, risk assessment methodology applies conservative approximations of risk to uncertainties and limitations, which can result in an overestimation of the risk of exposure. This section discusses the following sources of uncertainties and limitations associated with this risk assessment:

- Data collection and evaluation
- Exposure assessment
- Toxicity assessment
- TML comparison
- Contaminant fate and groundwater modeling

It is important to carefully examine each of these sources of uncertainty and limitation to understand how conservatively the risk of exposure has been estimated.

7.1 DATA COLLECTION AND EVALUATION

Data used in this TML development were obtained from the site assessments conducted at the EDC site. The data collected are subject to uncertainty associated with sampling and analysis. It was assumed that samples collected were representative of conditions at the site. However, the collected samples may not be perfectly representative, due to biases in sampling and to random variability of samples. Therefore, some data gaps may exist. To evaluate risk of exposure, the amount of nitrate present was estimated from the site assessment data using

conservative interpretations of extent of concentrations which are consistent with the existing data but may overestimate the amount of nitrate in the groundwater.

7.2 EXPOSURE ASSESSMENT

The exposure assessment is based on a series of assumptions concerning patterns of behavior leading to exposure or intake of chemicals (exposure scenarios). The site is assumed to remain industrial in the future. Use of the site for other purposes is unlikely and would not be expected to result in significant change in risks since the shallow groundwater would be unlikely to be used for drinking water.

The existing groundwater nitrate concentrations were used. Reductions in groundwater concentrations are anticipated due to pollution prevention measures and a future wastewater treatment plant; however, these measures were not considered in this assessment. These measures and processes are anticipated to reduce the chemical concentrations from the source, and therefore those actually present in the media (groundwater) and at the points of exposure during the exposure periods considered in the TML development. The use of existing chemical concentrations and exposure periods projected into the future may result in an overestimation of the potential health risk.

The exposure assessment utilized the RME scenario that incorporates upper-bound (90th percentile) assumptions in every case. In fact, this approach exceeds the guidance requirement which indicates that an RME scenario should incorporate upper bound exposure factors for a limited number of inputs rather than all exposure factors. The conservative nature of the approach in choosing RME factors for each input is indicative of the conservative approach utilized in all areas of this assessment. It should also be noted that the conservative approach associated with each part of the project and each series of assumptions is multiplicative in nature producing an end result which is far more conservative than each individual assumption.

The residential exposure scenario for both adult and child residents have been quantitatively evaluated in this risk assessment. However, the assumption that the exposure pathway for adult and child residents using potentially contaminated groundwater for household use is a complete pathway incorporates two hypothetical factors. One of these factors assumes that the direction

of groundwater flow is in a straight line toward a receptor well location which may not be the case. Based on regional hydrogeology, the groundwater flows to the southeast with the nearest downgradient domestic well approximately 4.7 miles southeast of the site and the nearest downgradient commercial well approximately 1.3 miles southeast of the site. The second factor is the assumption that groundwater from a domestic well completed in the Cockfield formation is used for drinking water. Based on the date of the receptor domestic well installation (1973) and its location (near the city limits of El Dorado), it is not known whether the well is currently in use for drinking water. In addition, water from commercial water wells is not used for drinking water. However, for consideration of TMLs, the nearest commercial water well was evaluated as though it was also used for drinking water. This is a very conservative assumption which results in a lower TML than is necessary to protect drinking water receptors.

Based upon previous interviews with the El Dorado municipal water supply company, coverage for municipal water supply is provided to residents within the city of El Dorado. All residents are supplied with municipal water service from municipal wells in El Dorado, Arkansas, the closest of which is approximately 1.4 miles south of the EDC site. The municipal supply well is 700 feet deep and is located in the El Dorado aquifer. The El Dorado aquifer is separated from the Cockfield formation by two thick clay layers and the Greensand aquifer. Additionally, there are several factors that impact the probability that an individual within the city limits would install a well at his/her residence to use groundwater as the primary source for household water. First is the cost of well installation versus the cost of hookup to the municipal water supply. The following is a summary of the cost comparison:

Shallow Private Well	Municipal Hookup
≈ \$2,000 plus operation and maintenance costs	1 \$65 installation plus \$6.20 per month.

Based upon previous site reports and interviews with El Dorado Public Works personnel and the Arkansas Department of Health, there are currently no known private wells used for drinking water within the city of El Dorado. It is unlikely that any wells for drinking water supply would be installed in the Cockfield formation in this area.
Second, the quality of the water is also a factor when considering the probability of using groundwater as a household water source. Municipal water systems must adhere to strict water quality standards to provide the assurance that the water is safe and pleasant to drink. In contrast, there are no such continuous water quality measurements that are required of private wells. However, the groundwater of the Cockfield formation in the area of the site is generally potable in regards to salinity, total dissolved solids, taste, and odor; however, iron concentrations are sometimes high and may make the water undesirable for domestic supply.

The third factor to consider in the comparison of municipal water versus well water is the difficulty in hookup and installation. The hookup to municipal water requires only a call to make an appointment for city personnel to complete the hookup at the needed location. In contrast, well installation would require much more homeowner involvement in both planning and development of the well.

The assumed probability that groundwater would be used as a household water source rather than municipal water is very low.

7.3 TOXICITY ASSESSMENT

In general, the available body of scientific information is insufficient to provide a thorough understanding of all the potential toxic properties of chemicals to which humans are potentially exposed. Consequently, varying degrees of uncertainty surround the assessment of adverse health effects in exposed populations. Sources of uncertainty related directly to toxicity data include:

- Use of dose-response data from experiments on homogenous, sensitive animal populations to predict effects in heterogeneous human populations with a wide range of sensitivities.
- Extrapolation of data from 1) high-dose animal studies to low dose human exposures; 2) acute or subchronic exposure to chronic exposure;
 3) one exposure route to another (e.g., from ingestion to dermal

absorption); and 4) use of low and no observed adverse effect levels (LOAELs and NOAELs) to arrive at a reference dose.

Provisional toxicity data from EPA Region IX were used to supplement available toxicity values. The best and most appropriate available quantitative toxicity information was chosen in an effort to reduce the uncertainties. This results in an overestimation of potential hazards and is conservative from a human health perspective.

7.4 TML COMPARISON

Because there are uncertainties in each step of the risk assessment process, these uncertainties are often magnified in the final results. The final quantitative estimates of human health risk may be one or several orders of magnitude different from the potential risk associated with a given exposure. In an attempt to minimize the consequences of uncertainty, EPA guidance typically relies upon use of conservative estimates of risks and hazards in the absence of strong scientific data. The overall result is that noncarcinogenic TMLs presented in this report are not likely to be exceeded even with the conservative assumptions incorporated into the assessment.

7.5 CONTAMINANT FATE AND TRANSPORT MODELING

The contaminant fate and transport modeling, as summarized in Section 5.0 and presented in full in Appendices C and D, incorporated a number of conservative assumptions. The conservative assumptions produce modeling results that may overestimate the potential for site-related constituents to migrate to the identified receptor locations.

The results of the nitrate horizontal fate and transport modeling are conservative and the modeling results from the simulations are expected to predict higher concentrations than will actually occur. Several conservative assumptions were used to develop the base case model scenario:

• The base case scenario simulated no attenuation of the nitrate due to sorption or degradation mechanisms. The transport of nitrate in groundwater is likely to be attenuated by sorption (most probably by ion

exchange). Additionally, nitrate is subject to degradation (denitrification or incorporation in biomass). As shown in the sensitivity analysis, both of these insitu attenuation mechanisms will further decrease the concentrations of nitrate in groundwater as it is transported.

The analytical model selected for the simulation, Plume2D, is a twodimensional model. Dispersion was only simulated in the longitudinal and lateral (or transverse) directions. No vertical dispersion of the nitrate to the lower portions of the Cockfield formation was simulated. Dispersion is an anisotropic process and some vertical dispersion will occur as the nitrate migrates. Any amount of vertical dispersion, within the Cockfield formation, will further decrease the concentrations of nitrate in groundwater.

Groundwater flow directions in the Cockfield formation are influenced by topographic surface features. As a conservative estimate, the shortest path (distance) between the EDC site and the nearest downgradient receptor domestic or commercial well was modeled as the groundwater flow direction. The actual flow path is probably longer, giving more time for attenuation due to dispersivity, degradation, and sorption effects.

8.0 PROJECT CONCLUSIONS AND RECOMMENDATIONS

Site-specific human health risk assessment procedures have been performed to develop a Target Monitoring Level (TML) for nitrate in groundwater at the El Dorado Chemical Company site in El Dorado, Arkansas. TMLs are concentrations of constituents of concern below which adverse effects to the exposed receptor are not expected to occur based on site-specific inputs.

The Phase II groundwater investigation conducted at the site concluded that, based on nitrate concentrations in excess of the EPA MCL of 10 mg/L at ten monitoring locations in the monitoring interval of the Cockfield formation, nitrate in groundwater is a potential concern for the EDC site. As nitrate was the only constituent determined to be present in the groundwater above primary MCLs, it was the only constituent of concern identified for the risk assessment.

TML development is conducted by performing a risk assessment in reverse. Potential receptor populations identified in the site vicinity were off-site adult and child residents. These populations could potentially be exposed if nitrate in on-site groundwater migrates off-site to a well used for drinking water. The nearest downgradient domestic water well (4.7 miles downgradient of the EDC site) and the nearest commercial water well (1.3 miles downgradient of the EDC site) were identified as the potential exposure points. Noncarcinogenic Reasonable Maximum Exposure (RME) intake variables were used to describe the potentially exposed populations. Based on these exposure factors, calculated nitrate TMLs at the exposure point of 58 mg/L for off-site adult residents and 24 mg/L for off-site child residents were developed. These TMLs are both higher than the nitrate MCL of 10 mg/L. To be conservative the MCL rather than the calculated values was used as the TML at the receptor for the development of the site-specific TML for on-site monitor wells.

Horizontal fate and transport modeling of nitrate in site groundwater was performed. The objective of the groundwater modeling was two-fold:

- Evaluate the potential for nitrate to migrate to the nearest downgradient domestic water well or the nearest downgradient commercial water well at concentrations which exceed the MCL for nitrate.
- Develop site-specific attenuation factors based on (1) the nearest downgradient domestic water well (AF_{Dom}) and (2) the nearest downgradient commercial water well (AF_{Com}). The AFs are used to calculate nitrate monitoring levels for on-site groundwater monitoring wells based on the MCL at off-site receptor exposure locations.

The groundwater modeling indicated that the MCL for nitrate of 10 mg/L should not be reached at any of the potential receptors. The risk-based TMLs are calculated at the point of exposure. This point of exposure for the horizontal transport modeling scenario was the nearest downgradient receptor domestic well. Using the maximum on-site concentration in groundwater and the maximum concentration simulated to reach the receptor location, a site-specific nitrate attenuation factor based on the domestic water well (AF_{Dom}) of 918 was calculated. A site-specific nitrate attenuation factor based on the commercial water well (AF_{Com}) of 360.7 was calculated. The site-specific attenuation factors developed from the horizontal transport modeling were then used to calculate on-site nitrate groundwater monitoring levels which will be protective of human health at the point of exposure. The MCL is the regulatory standard for drinking water. The acceptable on-site nitrate groundwater monitoring level or TML calculated using the MCL and the site-specific attenuation factors are 9,180 mg/L based on the domestic water well and 3,607 mg/L based on the commercial water well.

The nitrate TML for on-site monitoring wells is the concentration on-site which would not result in exceeding the MCL for the potential receptors at the point of exposure.

It is concluded that the estimated human health risks are acceptable for all receptor populations evaluated. It is also recommended that a 5-year semiannual groundwater monitoring program for nitrate be initiated for selected on-site monitor wells. Annual monitoring reports would be prepared and submitted to the ADPC&E. After this 5-year period, a data review report would be prepared and submitted to the ADPC&E. The

suggested approach also includes semiannual measurement of groundwater levels for all monitoring wells. The proposed monitoring well sampling locations include the following:

- Monitor Well MW-EDC-17 which is downgradient of Lake Kildeer
- Monitor Well MW-EDC-18 which is downgradient of Lake Kildeer
- Monitor Well MW-EDC-8 which had the highest nitrate concentration
- Monitor Well MW-EDC-2 which is at the upgradient portion of the EDC site

Annual reports to the ADPC&E would include analytical results and water level data. If onsite nitrate concentrations increase to or above the site-specific on-site TML for nitrate, corrective actions would be investigated. However, EDC is in the process of implementing Best Management Practices (BMPs) and upgrading its Waste Water Treatment Plant (WWTP) at the El Dorado facility which should mitigate future releases of nitrate to the shallow groundwater, resulting in decreasing nitrate concentrations. With the anticipated decrease in groundwater nitrate concentrations due to BMPs and the future WWTP project, it is likely that no further action will be necessary.

9.0 REFERENCES

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TABLES

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TABLE 3.1

CRITICAL TOXICITY VALUES FOR CONSTITUENTS OF CONCERN EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Constituent	Oral* (mg/kg/day)	Inhalation (mg/kg/day)	Dermal* (mg/kg/day)	Carcinogenic Classification
Nitrate	1.6 ^{(A)(B)}	NA	1.6 ^{(A) (B)}	NC

NOTES:

(A) USEPA, 1995c; LDEQ, August 1995

1997 1997 - 1997 1997 - 1997 - 1997

^(B) EPA, 1992b

NA = Not available

NC = Not Classified as a Human Carcinogen; consequently slope factors are not applicable.
 * Due to lack of a published dermal RfD, the oral RfD was used as a surrogate for quantification of dermal exposures.

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EXPOSURE PARAMETERS FOR THE DERMAL EXPOSURE TO GROUNDWATER USED FOR DOMESTIC PURPOSES BY OFF-SITE ADULT RESIDENTS (REASONABLE MAXIMUM EXPOSURE) EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Intake Factor = $\frac{SAxETxEFxEDxPCxCF}{BWxAT}$

Abbreviation	Description	RME
C A	Surface $Ame \left(am^2\right)(1)$	20.000
DA ET	Exposure Time (brs/day) ⁽²⁾	20,000
	Exposure Frequency (days/yr) ⁽³⁾	350
ED	Exposure Duration (vears) ⁽⁴⁾	30
PC	Permeability Constant (cm/hr) ⁽⁵⁾	0.0015
CF	Conversion Factor (L/cm ³)	0.001
BW	Body Weight (kg) ⁽⁶⁾	70
AT	Averaging Time (days) ⁽⁷⁾	
	Noncarcinogenic	10,950

- ¹ The surface area for adult residents (20,000 cm²) represents the average total body surface area for the respective adult receptors (EPA, 1992a).
- ² The exposure time of 0.25 hr (15 min.) corresponds to the RME assumption of time spent bathing each day by adult residents (EPA, 1992a).
- ³ An exposure time of 350 days/year assumes that the resident spends approximately two weeks away from home per year (EPA, 1992a).
- ⁴ The exposure duration of 30 years is the upper-bound estimate of time spent living in one residence (EPA, 1989b).
- ⁵ As a surrogate for compound-specific permeability coefficients (PC), the default for water (0.0015) is used (EPA, 1992a).
- ⁶ The body weight of 70 kg is the average body weight of adult males (EPA, 1989b).
- ⁷ The averaging time is the time (in days) over which the exposure is assumed to occur: that is, 10,950 days (30 years) for noncarcinogenic effects (EPA, 1989a).

EXPOSURE PARAMETERS FOR INGESTION OF GROUNDWATER USED FOR DOMESTIC PURPOSES BY OFF-SITE <u>ADULT</u> RESIDENTS (REASONABLE MAXIMUM EXPOSURE) EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Intake Factor = $\frac{IRxEFxED}{BWxAT}$

Abbreviation	Description	RME
IR EF ED BW AT	Ingestion Rate (L/day) ⁽¹⁾ Exposure Frequency (days/yr) ⁽²⁾ Exposure Duration (years) ⁽³⁾ Body Weight (kg) ⁽⁴⁾ Averaging Time (days) ⁽⁵⁾ Noncarcinogenic	2.0 350 30 70 10,950

- ¹ The ingestion rate of 2.0 L/day corresponds to the RME estimate of the amount of water ingested per day by the adult receptor (EPA, 1991b).
- ² An exposure time of 350 days/year assumes that the resident spends approximately two weeks away from home per year (EPA, 1991b).
- 3 The exposure duration of 30 years is the average time spent living in one residence (EPA, 1989b).
- ⁴ The body weight of 70 kg is the average body weight of adult males (EPA, 1989b).
- ⁵ The averaging time is the time (in days) over which the exposure is assumed to occur: that is, 10,950 days (30 years) for noncarcinogenic effects (EPA, 1989a).

EXPOSURE PARAMETERS FOR THE DERMAL EXPOSURE TO GROUNDWATER USED FOR DOMESTIC PURPOSES BY OFF-SITE CHILD RESIDENTS (REASONABLE MAXIMUM EXPOSURE) EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Intake Factor = $\frac{SAxETxEFxEDxPCxCF}{BWxAT}$

Abbreviation	Description	RME
	2 (1)	
SA	Surface Area (cm ²) ⁽¹⁾	6,947
ET	Exposure Time (hrs/day) ⁽²⁾	0.5
EF	Exposure Frequency (days/yr) ⁽³⁾	350
ED	Exposure Duration (years) ⁽⁴⁾	6
PC	Permeability Constant (cm/hr) ⁽⁵⁾	0.0015
CF	Conversion Factor (L/cm ³)	0.001
BW	Body Weight (kg) ⁽⁶⁾	14.5
AT	Averaging Time (days) ⁽⁷⁾	
	Noncarcinogenic	2,190

- ¹ The surface area for child residents (6,947 cm²) represents the average total body surface area for the male child receptor (EPA, 1989b).
- ² The exposure time of 0.5 hr (30 min.) corresponds to the RME assumption of time spent bathing each day by the child receptor (EPA, 1992a).
- ³ An exposure time of 350 days/year assumes that the resident spends approximately two weeks away from home per year (EPA, 1992a).
- ⁴ The exposure duration of 6 years for the child receptor (0 to 6 years) (EPA, 1989a).
- ⁵ As a surrogate for compound-specific permeability coefficients (PC), the default PC for water (0.0015) is used (EPA, 1992a).
- ⁶ The body weight of 14.5 kg is the averaged RME body weights of male children 0 to 6 years old (EPA, 1989a).
- ⁷ The averaging time is the time (in days) over which the exposure is assumed to occur: that is, 2,190 days (6 years) for noncarcinogenic effects (EPA, 1989a). USE THE CONTRACT OF THE CONTRACT. THE CONTRACT OF THE CONTRACT OF THE CONTRACT OF THE CONTRACT OF THE CONTRACT. THE CONTRACT OF THE CONTRACT OF THE CONTRACT OF THE CONTRACT OF THE CONTRACT. THE CONTRACT OF THE CONTRACT OF THE CONTRACT OF THE CONTRACT. THE CONTRACT OF

EXPOSURE PARAMETERS FOR INGESTION OF GROUNDWATER USED FOR DOMESTIC PURPOSES BY OFF-SITE CHILD RESIDENTS (REASONABLE MAXIMUM EXPOSURE) EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Intake Factor = $\frac{IRxEFxED}{BWxAT}$

Abbreviation	Description	RME
IR EF ED BW AT	Ingestion Rate (L/day) ⁽¹⁾ Exposure Frequency (days/yr) ⁽²⁾ Exposure Duration (years) ⁽³⁾ Body Weight (kg) ⁽⁴⁾ Averaging Time (days) ⁽⁵⁾ Noncarcinogenic	1.0 350 6 14.5 2,190

- ¹ The ingestion rate of 1.0 L/day corresponds to the RME estimate of the amount of water ingested per day by the child receptor (EPA, 1989b).
- ² An exposure time of 350 days/year assumes that the resident spends approximately two weeks away from home per year (EPA, 1991b).
- ³ The exposure duration of 6 years is the time spent living in one residence for the child receptor (0 to 6 years) (EPA, 1989a).
- ⁴ The body weight of 14.5 kg is the averaged RME body weights of male children 0 to 6 years old (EPA, 1989b).
- ⁵ The averaging time is the time (in days) over which the exposure is assumed to occur; that is, 2,190 days (6 years) for noncarcinogenic effects (EPA, 1980a).

TABLE 6.1

ESTIMATED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

	Off-site A	dult Resident	Off-site Child Resident		
Groundwater (mg/L)	Carcinogenic	Noncarcinogenic	Carcinogenic Noncarcinoge		
Nitrate	NA	58	NA	24	

Notes:

NA = Not Applicable (nitrate is not considered a carcinogen).

TABLE 6.2

FINAL TARGET MONITORING LEVELS AND ESTIMATED GROUNDWATER CONCENTRATIONS FOR POTENTIALLY EXPOSED POPULATIONS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Constituent	Predicted Maximum Groundwater Concentration at Domestic Water Well (mg/L)	Predicted Maximum Groundwater Concentration at Commercial Water Well (mg/L)	Calculated Groundwater TML ⁽¹⁾ (mg/L)	EPA MCL (mg/L)		
ADULT OFF-SITE RESIDENT						
Nitrate	1.1	2.8	58.	10.		
CHILD OFF-SITE RESIDENT						
Nitrate	1.1	2.8	24.	10.		

.

NOTES:

⁽¹⁾ Represents noncarcinogenic hazard of 1.

FIGURES



LEGEND

- Shallow Domestic Well in Cockfield Formation
- Public Supply 700' Deep Well in Sparta Aquifer
- Shallow Commercial Well in Cockfield Formation



ELDORADO	Woodward-Clyde Image: Sciences applied to the earth & its environment POTENTIAL RECEPTOR WELLS FILE Baton Rouge, Louisiana IN SITE VICINITY FIG. SCALE: DRAWN BY: D.OLSON DATE: 10/24/97 AS SHOWN CHKD. BY: D. REECE DATE: 10/27/97 4.				FILE NO. 978061-13 FIG. NO.
CHEMICAL COMPANY	SCALE: AS SHOWN	DRAWN BY: D.OLSON CHKD. BY: D. REECE	DATE: 10/24/97 DATE: 10/27/97		4,1





11.

APPENDIX A

TOXICITY PROFILES

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NITRATE

Nitrate accumulation in the environment likely results from changing patterns in agriculture, food processing, urbanization, and industrialization. All of these have had an impact on the accumulation of nitrate in the environment. Nitrate levels in groundwater have increased over the past two decades because of the use of nitrogenous fertilizers. Nitrogenous wastes from livestock and poultry production, as well as urban sewage treatment, have also contributed nitrogenous wastes to the soil and water environments. In addition, nitrate and nitrite are used extensively for color enhancement and preservation of processed meat products. These practices inevitably lead to increased exposure of man and animals to significant nitrate levels in food, feed, and water (National Academy of Sciences, 1981).

In adults, vegetables are the main dietary source of nitrate exposure, accounting for more than 70 percent of the total intake. Water, the second most important source of nitrates, provides approximately 21 percent. Meat products contribute about 6 percent, because sodium nitrate is used as a preservative and color-enhancing agent in cured meats (Vogtman and Biederman, 1985).

Nitrate is relatively nontoxic, but when reduced to nitrite, toxicity greatly increases. Nitrate can be reduced to nitrite by bacteria in the upper gastrointestinal tract. In the human body, nitrate is rapidly absorbed from the proximal small intestine and distributed throughout the body. Approximately 60 to 70 percent of an oral nitrate dose is excreted in urine in the first 24 hours. About 25 percent of ingested nitrate is excreted in saliva through an active blood nitrate transport system (Kross et al., 1992).

The primary environmental health impact of nitrate is its conversion to nitrite, which interferes with the normal oxygen-carrying capacity of hemoglobin. The mechanism of nitrite toxicity is the oxidation of the ferrous iron in deoxyhemoglobin to the ferric iron valence state, producing methemoglobin (Greenberg et al., 1943; Marshall and Marshall, 1945; Bodandky, 1951. Kross et al., 1992). Methemoglobin is unable to carry oxygen, resulting in cyanosis and anoxemia if the level of methemoglobin becomes sufficiently high. The risk of nitrite toxicity is greatest in infants under four months of age. Infants are particularly susceptible to nitrite poisoning because fetal hemoglobin are more readily oxidized to methemoglobin. Affected infants may have asymptomatic cyanosis, which can progress to dyspnea, lethargy, coma, and death.

Animal studies suggest that nitrite may traverse the placenta (Globus and Samuel, 1978; Gruener et al., 1973.) or exert a transplacental effect (Inui et al., 1979a; Inui et al., 1979b). The possibility of infant

death as a consequence of methemoglobinemia in the mother has been suggested by several authors (Askari and Hodas, 1952; Schmitz, 1961.). Studies in Australia found an increased risk of congenital malformations with consumption of high-nitrate groundwater (Scragg et al., 1982; Dorsch et al., 1984). Nitrate levels were found positively associated with increased risk of congenital malformations.

Besides the methemoglobinemia causing effects, nitrate and nitrite are known also as contributors to the exogenous formation of N-nitroso compounds. It has been hypothesized that nitrite and nitrate also have a role in the endogenous formation of N-nitroso compounds. Secondary amines and nitrites, capable of forming nitrosamines, are also found in many foods. (Ishidate et al., 1972). Work by several researchers has demonstrated that certain N-nitroso compounds can induce cancer of the stomach in several animal species (Herrold, 1966.). Evidence that animal experiments may reflect the response of humans to the same agents is discussed by Weisburger and Raineri (1975).

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APPENDIX B

TML CALCULATIONS

CALCULATION OF INTAKE FACTORS (IFs) OFF-SITE ADULT RESIDENT (REASONABLE MAXIMUM EXPOSURE (RME) SCENARIO) GROUNDWATER EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

A. INGESTION

Noncarcinogens

Equation:	IForal = (IR x EF x ED)/(BW x AT)	e jagen (* 1990) Maria
Where:	IForal = Ingestion Intake Factor (L/kg-day)-1 EF = Exposure Frequency (days/yr) BW = Body Weight (kg)	 IR = Groundwater Ingestion Rate (L/day) ED = Exposure Duration (years) AT = Averaging Time (days)

	IForal	IR	EF	ED	BW	AT
	(L/kg-day)-1	(L/daγ)	(days/year)	(yr)	(kg)	(days)
NITRATE	2.74E-02 -	2	350	30	70	10950

B. DERMAL CONTACT

<u>Noncarcinogens</u>

Equation:	IFderm =	(SA x ET x EF x ED x PC x CF) / (BW x AT)	1. Co	
Where:	IFderm =	Intake Factor For Dermal Contact (L/kg-day)-1		PC = Permeability Constant (cm/hr)
	SA =	Surface Area (cm2)		CF = Conversion Factor (L/cm3)
	ET =	Exposure Time (hrs/day)		AT = Averaging Time (days)
	EF =	Exposure Frequency (days/yr)	[BW = Body Weight (kg)
	ED =	Exposure Duration (years)		

....

	lFderm	SA	ET	EF	ED	PC	CF	BW	AT
	(L/kg-day)-1	(cm2)	(hrs/day)	(days/yr)	(yrs)	(cm/hr)	(L/cm3)	(kg)	(days)
NITRATE	1.03E-04	20000	0.25	350	30	1.50E-03	1.00E-03	70	10950

TARGET MONITORING LEVELS BASED ON OFF-SITE ADULT RESIDENT RME SCENARIO (Non Carcinogenic Compounds) EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

	Equation:		TML = Hazard Index / ((IForal x 1/RfDoral) + (IFderm x 1/RfDderm))						
	Where:								
		TML=	Target monit	toring levelof	chemical in gr	oundwate	er (mg/L)		
		iForal =	Intake factor	for ingestion	(L/kg-day)-1				
		IFderm =	Intake factor	for dermal e	xposure (L/kg-	day)-1			
		RfDoral =	Reference do	ose for ingest	ion or dermal	contact (n	ng/kg-day)		
		RfDderm ⇒	Reference do	ose for derma	l exposure (m	g/kg-day)			
Chemical Name		RfDoral	RFDderm	IForal	IFderm	Target	TML	TML	
		(mg/kg-day)	(mg/kg-day)	(L/kg-day)-1	(L/kg-day)-1	HI	(mg/L)	(ug/L)	
NITRATE		1.60E+00	1.60E+00	2.74E-02	1.03E-04	1	5.82E+01	58181.82	

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CALCULATION OF INTAKE FACTORS (IFs) OFF-SITE CHILD RESIDENT REASONABLE MAXIMUM EXPOSURE (RME) SCENARIO GROUNDWATER EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

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A. INGESTION

Noncarcinogens

Equation:	IForal =	(IR x EF x ED)/(BW x AT)	
Where: iF	oral = Ingestion I	ntake Factor (L/kg-day)-1	IR = Groundwater Ingestion Rate (L/day)
	EF = Exposure f	Frequency (days/yr)	ED = Exposure Duration (years)
	BW = Body Weig	iht (kg)	AT = Averaging Time (days)

	lForal	IR	EF	ED	BW	AT
	(L/kg-day)-1	(L/day)	(days/year)	(yr)	(kg)	(days)
NITRATE	6.61E-02 -	1	350	6	14.5	2190

B. DERMAL CONTACT

Noncarcinogens

 Equation:
 IFderm =
 (SA x ET x EF x ED x PC x CF) / (BW x AT)

 Where:
 IFderm =
 Intake Factor For Dermal Contact (L/kg-day)-1
 PC = Permeability Constant (cm/hr)

 SA =
 Surface Area (cm2)
 CF = Conversion Factor (L/cm3)

 ET =
 Exposure Time (hrs/day)
 AT = Averaging Time (days)

 EF =
 Exposure Frequency (days/yr)
 BW = Body Weight (kg)

 ED =
 Exposure Duration (years)
 EX

	IFderm	SA	ET	EF	ED	PC	CF	BW	AT
	(L/kg-day)-1	(cm2)	(hrs/day)	(days/yr)	(yrs)	(cm/hr)	(L/cm3)	(kg)	(days)
NITRATE	3.45E-04 [°]	6947	0.5	350	6	1.50E-03	1.00E-03	14.5	2190

TARGET MONITORING LEVELS BASED ON OFF-SITE CHILD RESIDENT RME SCENARIO (Non Carcinogenic Compounds)

Equation:	IML=	Hazard Index	1 / ((IForal x 1/	/RfDoral) +	(IFderm x 1	/RfDderm})		
Where:								
TML =	Target monitoring level of chemical in groundwater (mg/L)							
Foral =	Intake factor	for ingestion	(L/kg-day)-1		-			
IFderm =	Intake factor	for dermal e	xposure (L/kg-	day)-1				
RfDoral =	= Reference dose for ingestion or dermal contact (mg/kg-day)							
RfDderm =	Reference do	se for derma	i exposure (m	g/kg-day)				
RfDoral	RFDderm	IForal	IFderm	Target	TML	TML		
(mg/kg-day)	(mg/kg-day)	(L/kg-day)-1	(L/kg-day)-1	нĨ	(mg/L)	(ug/L)		
-	Where: IForal = IFderm = RfDoral = RfDderm = RfDoral (mg/kg-day)	Where: TML = Target monit IForal = Intake factor IFderm = Intake factor RfDoral = Reference do RfDderm = Reference do RfDoral RFDderm (mg/kg-day) (mg/kg-day)	Where: TML = Target monitoring level of IForal = Intake factor for ingestion IFderm = Intake factor for dermal ex- RfDoral = Reference dose for ingesti RfDderm = Reference dose for derma RfDoral RFDderm IForal (mg/kg-day) (mg/kg-day) (L/kg-day)-1	Where: TML = Target monitoring level of chemical in g IForal = Intake factor for ingestion (L/kg-day)-1 IFderm = Intake factor for dermal exposure (L/kg- RfDoral = Reference dose for ingestion or dermal RfDderm = Reference dose for dermal exposure (mg RfDoral RFDderm IForal IFderm (mg/kg-day) (mg/kg-day) (L/kg-day)-1 (L/kg-day)-1	Where: TML = Target monitoring level of chemical in groundwate IForal = Intake factor for ingestion (L/kg-day)-1 IFderm = Intake factor for dermal exposure (L/kg-day)-1 RfDoral = Reference dose for ingestion or dermal contact (mg/RfDderm = Reference dose for dermal exposure (mg/kg-day) RfDoral RFDderm IForal IFderm Target (mg/kg-day) (mg/kg-day) (L/kg-day)-1 (L/kg-day)-1 HI	Where: TML = Target monitoring level of chemical in groundwater (mg/L) IForal = Intake factor for ingestion (L/kg-day)-1 IFderm = Intake factor for dermal exposure (L/kg-day)-1 RfDoral = Reference dose for ingestion or dermal contact (mg/kg-day) RfDderm = Reference dose for dermal exposure (mg/kg-day) RfDoral RFDderm IForal IFderm Target TML (mg/kg-day) (L/kg-day)-1		

NITRATE	1.60E+00	1.60E+00	6.61E-02	3.45E-04	1	2.41E+01	24068.88

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APPENDIX C

CONTAMINANT FATE AND TRANSPORT MODELING DOMESTIC WATER WELL RECEPTOR

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APPENDIX C

CONTAMINANT FATE AND TRANSPORT MODELING DOMESTIC WATER WELL RECEPTOR (DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS)

EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Prepared for El Dorado Chemical Company El Dorado, Arkansas

December 1997

WCC File 97B061



Woodward-Clyde Three Financial Centre 900 S. Shackleford, Suite 412 Little Rock, AR 72211 501-223-2583

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Attachment C-1 Slug Test Results

1.0 INTRODUCTION

The objective of this section is to present the results of fate and transport modeling the domestic water well receptor, which was conducted as part of the development of risk-based target monitoring levels for the El Dorado Chemical Company (EDC) site. The contaminant fate and transport modeling was used to evaluate the potential for the identified constituent of concern, nitrate, to reach the identified receptors exposure point via groundwater movement and to calculate a nitrate attenuation factor for migration of nitrate from the site to the receptor. The technical approach for the contaminant fate and transport modeling is described in the *Development of Risk-Based Target Monitoring Levels Work Plan (Work Plan)* (WCC 1996).
2.0 TECHNICAL APPROACH

2.1 CONSTITUENT OF CONCERN: NITRATE

As described in the *Phase II Groundwater Investigation: Final Report* (WCC 1996), nitrate concentrations in excess of the EPA Maximum Contaminant Level (MCL) of 10 mg/L were observed at 10 of 22 monitor well locations tested during the Phase II investigation. The nitrate concentrations at those ten monitor wells ranged from 11.9 mg/L (MW-EDC-14) to 1,010 mg/L (MW-EDC-8). These wells are completed in the upper saturated interval of the Cockfield formation and concentrated in two distinct areas at the EDC site:

- The north side of the acid and nitrate process areas known as the Production Area
- The vicinity of Lake Kildeer

The Phase II investigation concluded that, based on nitrate concentrations in excess of the EPA MCL at ten monitoring locations, nitrate in groundwater remains a potential concern in these two areas. Nitrate was the only constituent determined to be present above primary MCLs in on-site monitor wells.

Contaminant fate and transport modeling of the nitrate was performed to evaluate the potential for nitrate to reach receptors via groundwater movement. Identification of exposure points for receptors is described in the following section.

2.2 **RECEPTOR POPULATION IDENTIFICATION**

As described in the Exposure Assessment (Section 4.0) of the *Development of Risk-Based Target Monitoring Levels Report*, off-site residents could have the potential for exposure if nitrate from the site migrates in the groundwater to a water well used for drinking water. According to El Dorado's city engineer, residents within the city limits of El Dorado are

Woodward-Clyde

supplied with drinking water by the El Dorado Public Works Department. However, some rural area residential domestic wells have reportedly been completed in the Cockfield formation. El Dorado's public supply wells are completed in the deeper El Dorado aquifer.

2.2.1 Wells in Cockfield Formation

A well search was made of the Arkansas Geological Commission Well Drilling Report files. The search indicated that the nearest downgradient well is located in Section 26 of Township 17 South, Range 15 West, approximately 4.7 miles southeast from the EDC site as shown in Figure C-3.2. The well is reported to be 40 feet deep and completed in the Cockfield formation. Although this well was reportedly installed for domestic use in 1973. It is not known if this well is still in use and is currently used for drinking water. This nearest downgradient domestic well has been identified as the receptor point for the horizontal fate and transport modeling presented in Appendix C.

2.2.2 Wells Completed in Deeper Units

The closest downgradient city of El Dorado public supply well is located (see Figure C-3.2) approximately 1.4 miles south of the EDC site in Section 16, Township 17 South, Range 15 West. This well is 700 feet deep and is completed in the El Dorado aquifer. The El Dorado aquifer is separated from the Cockfield formation by two thick clay layers (the Cook Mountain formation and the middle confining bed of the Sparta aquifer). This well has been identified as the potential receptor point for vertical migration of nitrate from the Cockfield formation through the Cook Mountain formation into the deeper aquifers. Vertical migration will be addressed qualitatively using travel time calculations.

3.0 HORIZONTAL TRANSPORT MODEL

This section discusses the selection of the analytical transport model, the assumptions used to develop the analytical model, and the grid definition used to apply the model to the EDC site.

3.1 HORIZONTAL MODELING OBJECTIVES

The objectives of the horizontal modeling are to evaluate if current nitrate concentrations in the groundwater may, over time, produce concentrations at various receptor locations which exceed the Target Monitoring Levels (TML) determined using risk assessment procedures and to develop an attenuation factor for calculating acceptable on-site nitrate concentration.

3.2 SELECTION OF SOLUTE PLUME2D MODEL

The International Ground Water Modeling Center's (IGWMC) Solute Program Package, Analytical Model for Transport of a Solute Plume from Point Sources in a Uniform Two-Dimensional Groundwater Flow Field (Plume2D) was used to simulate the transport of the nitrate horizontally in groundwater to the receptor location. Solute uses analytical solutions of the advective dispersive transport equation for a non-conservative tracer solution. Solute contains four groups of analytical solutions for 1-, 2- and 3-dimensional transport of a solute in uniform groundwater flow. For this work, the solution module for 2-dimensional transport, Plume2D, was used.

The Plume2D model calculates the concentration distribution from point sources in twodimensional regional flow. Plume2D has two analytical solutions based on different types of sources. The specified mass instantaneous source release analytical solution, Slug2D, was utilized for all horizontal fate and transport modeling.

3.3 ANALYTICAL MODEL ASSUMPTIONS

This Plume2D solution assumes the solute to be well-mixed over the constant thickness of the aquifer resulting in an areal concentration distribution which is uniform with depth. Each point source is a vertical line source extending from the top to the base of the aquifer. The Plume2D model is based on the following assumptions:

- Uniformly porous aquifer
- The aquifer is homogeneous and isotropic with respect to its hydraulic and transport characteristics
- The aquifer is infinite in areal extent and of constant thickness
- A source fully penetrates the aquifer
- The groundwater flow regime is fully-saturated
- One-dimensional steady-state uniform regional flow in the x-direction (recharge rates from constituent source are small and do not influence flow field)
- Constituents are distributed instantaneously over the entire aquifer thickness beneath the source
- Release of specified mass of solute is instantaneous
- The density and viscosity of the solute in the source and in the aquifer are identical and do not change in time
- There is no solute advection or dispersion into or out of the confining layers
- Dirichlet, Neumann, or Cauchy boundaries

3.4 **DEFINITION OF PLUME2D GRID**

Solute Plume2D uses the convention that the regional one-dimensional flow is in the positive x-direction. Groundwater flow beneath the site is southeast as shown in Figure C-3.1. Therefore, the model grid is orientated so that the positive x-axis is to the southeast. For modeling purposes, a localized coordinate system was developed for the base map of the EDC site and surrounding area (see Figure C-3.2). From the base map, a consistent set of coordinates for the receptors and sources was developed using Cartesian coordinate (x,y) pairs based on the model coordinate grid system.

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3.5 GENERALIZED MODELING CROSS-SECTION

The generalized modeling cross-section for the EDC site is shown in Figure 5.1 of the report to which this appendix is attached. The local geology beneath the EDC site to the base of the Cook Mountain formation consists of the following:

- A thin veneer of Quaternary-aged alluvial sediments
- Tertiary-aged Cockfield formation (part of Claiborne Group)
- Cook Mountain formation (clay confining unit)

The Cook Mountain formation overlies the following:

- Sparta Sand (contains Greensand aquifer, Sparta middle confining bed and El Dorado aquifer)
- Cane River formation (clay confining unit)

Table C-3.1 provides a description of hydrogeologic units in the study area.

3.5.1 Quaternary-Aged Sediments

A thin veneer of quaternary-aged alluvial sediments overlay the Cockfield formation along the Ouachita River and its tributaries.

3.5.2 Cockfield Formation

The Tertiary-aged Cockfield formation (part of the Claiborne Group) crops out over most of Union County and underlies the EDC site. This formation consists predominantly of sands, silts, and carbonaceous (calcitic) clays with minor amounts of interbedded lignite and gypsum. The formation can contain lenticular beds of lignitic sands in some areas. The formation thickness is approximately 200 feet in most of Union County.

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Water levels in area wells range in depth from near land surface in low-lying areas to as much as 50 feet on the highest hills and ridges. Discharge is primarily base flow to streams with lesser amounts of evapotranspiration. Water table configuration within the aquifer generally exhibits a subdued reflection of the local topography with flow toward surface drains (i.e., the valleys of the principal streams).

The horizontal transport model developed for the EDC site will model the uppermost saturated monitoring interval of the Cockfield formation at the site. The average saturated thickness of the monitoring interval is 13.83 feet thick for the 22 monitor wells at the site. The modeled interval is shown in Figure 5.1 of the report to which this appendix is attached.

3.5.3 Cook Mountain Formation

The Cook Mountain formation underlies the Cockfield formation in all areas of the region except where the younger sediments have been removed by erosion. The formation consists of low permeability clays and silty clays with lesser amounts of very fine sands. The formation acts as a lower confining unit (aquitard) for groundwater of the Cockfield formation and an upper confining unit for the underlying Greensand aquifer.

Thickness of the confining unit is variable from approximately 50 feet to as much as 200 feet across the region. In the vicinity of the EDC facility, the thickness of the clays comprising the confining unit is estimated to be between 75 and 100 feet (McWreath *et al.* 1991).

3.5.4 Sparta Aquifer

The Sparta aquifer is overlain by the Cook Mountain formation in Union County and overlies the Cane River formation. The Tertiary-aged Sparta aquifer is the main source of municipal and industrial water supplies throughout the region. Heavy pumping stresses placed on the aquifer in the past decades have created large cones of depression within the potentiometric surface surrounding the pumping centers. One such cone of depression is centered around El Dorado, Arkansas. Large quantities of groundwater withdrawn from the aquifer have altered, and in some cases reversed, flow directions in the aquifer (McWreath *et al.* 1991).

In Union County, the Sparta aquifer is hydrogeologically separated into three hydrostratigraphic zones based on lithologic character and water production capacities. These zones, in descending order, are the Greensand aquifer, the Sparta aquifer middle confining bed, and the El Dorado aquifer. The El Dorado aquifer is the most heavily used portion of this hydrostratigraphic sequence.

3.5.4.1 Greensand Aquifer

The Greensand aquifer occupies the upper portion of the Sparta aquifer. This sequence consists of fine-grained to very fine-grained glauconitic sands with lesser amounts of silts and clays. Groundwater within the aquifer is under confined conditions. Confining units are the Cook Mountain confining unit above and a clay-rich horizon (the Sparta aquifer middle confining bed) of the El Dorado aquifer below.

The Greensand aquifer thickness in the Union County area is approximately 200 feet (Leidy and Taylor, 1992). The regional flow direction within the aquifer is south-southeast (Broom *et al.* 1984).

The Greensand aquifer is generally less productive than the deeper El Dorado aquifer. The aquifer is used as a potable water supply, but less extensively than the deeper, more productive El Dorado aquifer.

3.5.4.2 Sparta Aquifer Middle Confining Bed

In separate investigations by Fitzpatrick *et al.* (1990) and McWreath *et al.* (1991), the Sparta aquifer has been treated as a single aquifer for the purposes of finite-difference modeling of the effects of pumping stresses. However, as stated by Broom *et al.* (1984), sufficient evidence exists to support the conceptualization that in Union County, Arkansas a predominantly marine clay horizon in the middle portion of the Sparta aquifer serves as a confining unit. Hydraulic conductivity, both horizontal and vertical, is low in comparison to the overlying and underlying sediments. This zone serves as a confining bed between the upper and lower portions of the Sparta aquifer and allows them to function separately as individual aquifers. This zone primarily consists of clays and silty clays. McWreath *et al.* (1991) support the designation of

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this clay horizon as a confining unit on a local scale. The confining bed is between 40 and 160 feet thick in Union County. (McWreath *et al.* 1991).

3.5.4.3 El Dorado Aquifer

The El Dorado aquifer is more productive and, thus, more heavily targeted for placement of high yield wells. This sequence consists of a thickly bedded medium to coarse sand. The thickness of this sequence of the El Dorado aquifer in Union County is approximately 300 feet (Leidy and Taylor 1992). The city of El Dorado public supply water wells are completed in the El Dorado aquifer.

4.0 PLUME2D INPUTS

The identification of receptors and exposure points was described in Section 2 and the selection of the analytical model was described in Section 3. This section discusses the site-specific hydrogeologic inputs in Plume2D.

The variables necessary for input into the model include: groundwater (seepage) velocity, aquifer thickness, porosity of the aquifer, longitudinal dispersivity, lateral dispersivity, retardation factor, half-life of the source constituent, number of point sources, source strength, elapsed time, coordinates of the source and coordinates of the grid. The coordinate grid was discussed in Section 3.4. The site-specific hydraulic and matrix-dependent transport properties used in the Solute Plume2D transport simulations are shown in Table C-4.1. The following sections provide a brief description of how each input variable was evaluated.

4.1 SEEPAGE VELOCITY

The groundwater (seepage) velocity is the rate of groundwater movement. This value was evaluated using Darcy's law and estimates of soil water holding capacity typical of soils at the site. Darcy's Law states that:

$$v = K \frac{dh}{dl}$$

where:

ν	=	Darcy Velocity
Κ	=	Saturated Hydraulic Conductivity
dh/dl	=	Groundwater Gradient

The seepage velocity is :

$$\overline{v} = \frac{v}{\theta}$$

where:

$$\overline{v}$$
 = Seepage Velocity
 θ = Water Holding Capacity of the Soil (Effective Porosity)

Determination of hydraulic conductivity, gradient, and effective porosity are discussed below.

4.1.1 Hydraulic Conductivity of Cockfield Formation

The saturated hydraulic conductivity which was used to calculate the seepage velocity for the horizontal transport model was calculated from slug tests. In accordance with the *Work Plan*, slug tests were conducted in monitor wells MW-EDC-4, MW-EDC-13, and MW-EDC-18, which are located at the EDC site. The results of the slug tests are shown in Attachment C-1. The hydraulic conductivity calculated for the Cockfield formation from these slugs tests ranged from 4.0×10^{-4} cm/sec to 8.26×10^{-4} cm/sec. The arithmetic average hydraulic conductivity calculated for the formation from these slugs tests ranged solution these slugs tests was 1.87 ft/day (6.61 x 10^{-4} cm/sec).

4.1.2 Regional Hydraulic Gradient of Cockfield

A water table contour map was presented in the *Phase II Groundwater Investigation Final Report* (Woodward-Clyde 1996) for the uppermost saturated monitoring interval at the EDC site. This map is reproduced in this report as Figure C-3.1. Static groundwater levels in the 22 monitor wells ranged from approximately 2 feet above ground surface (artesian conditions) at MW-2 in the northern portion of the EDC site to approximately 27 feet below grade at MW-17 in the southern portion of the site. In general, groundwater flow beneath the site is southeast with the exception of areas locally influenced by ground surface topography and the presence of Lake Kildeer. The regional groundwater gradient for Union County is also to the southeast towards the Ouachita River.

Figure C-4.1 presents a potentiometric surface of the Cockfield formation in the south Arkansas area as presented in the Arkansas Geological Commission Information Circular 28-D (1988). The groundwater flow direction near El Dorado is generally southeast. However, this potentiometric surface appears to be locally influenced by ground surface topography. Based on this potentiometric surface, a regional groundwater gradient of 1.42×10^{-3} feet/feet was calculated in the vicinity of El Dorado.

4.1.3 Porosity

Based on effective porosity values determined by Freeze and Cherry (1979), a value of 0.30 will be utilized for the effective porosity of the uppermost saturated monitoring interval at the EDC site, as was presented in the approved Work Plan.

4.1.4 Saturated Thickness

Based on Phase II field measurements, the saturated thickness has been evaluated to be 13.83 feet from the average saturated thickness of the uppermost saturated monitoring interval. Tabulated Phase II data used in the calculation are presented in Table C-4.2.

4.1.5 Seepage Velocity Calculation

The groundwater seepage velocity was calculated as follows:

$$\overline{v} = \frac{K}{\theta} \frac{dh}{dl} = \left(\frac{1.87}{0.3}\right) \ 1.42E - 3 \ \frac{feet}{day} = 0.00885 \ \frac{feet}{day}$$

4.2 **DISPERSIVITY**

The dispersivity, reported in dimensions of length, represents the effects of porous medium properties on dispersion of the solute mass in the longitudinal and lateral (or transverse) directions.

4.2.1 Longitudinal Dispersivity

The longitudinal dispersivity, when multiplied by the seepage velocity, yields the longitudinal dispersion coefficient. Woodward-Clyde used a conservative value calculated by taking ten percent of the transport distance to the receptor location as was presented in the approved Work Plan. The source was 28,000 feet from the receptor and the longitudinal dispersivity used in the Plume2D model was 2,800 feet. A sensitivity analysis was performed on this parameter as described in Section 6.2.

4.2.2 Lateral Dispersivity

The lateral dispersivity (reported in dimensions of length), was estimated to be 10 percent of the longitudinal dispersivity as was presented in the approved Work Plan. A sensitivity analysis was performed on this parameter as described in Section 6.2.

4.3 ATTENUATION MECHANISMS

The transport of a dissolved solute such as nitrate is by means of advective transport with the groundwater and varying degrees of retardation of the solute transport relative to the water due to attenuation processes such as sorption (most probably by ion exchange) and degradation. Consequently, the solute is expected to move at a slower velocity than the groundwater and some of the solute is expected to be retained on the soil particles of the aquifer matrix or destroyed by degradation reactions (such as denitrification or incorporation in biomass).

The only attenuation mechanism modeled in the base case simulations was dispersion. As discussed in Section 6.3, a sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation. The results of these sensitivity analyses are described below.

4.4 SOURCE DEFINITION

The initial concentration conditions for the contaminant fate and transport modeling were evaluated from the results of the Phase I and II groundwater investigations. An estimate of the mass of nitrate in the groundwater of the uppermost saturated monitoring interval beneath the EDC site was interpreted from the groundwater sampling results. The source areas defined in the analytical model contained a mass of nitrate consistent with the mass indicated by the groundwater sampling results. A Plume2D simulation utilizing no mechanisms for source decay (model scenario was conservative) was performed and the mass in the system measured to further confirm the conservative nature of the base-case model. The source configuration used within the contaminant fate and transport modeling grid was trial-and-error fit to represent current site conditions.

4.5 ELAPSED TIME

The elapsed time represents the time period for which the model was run. This elapsed time period was evaluated by trial and error to obtain the maximum concentration of nitrate that could reach the identified receptor location.

5.0 TRANSPORT SIMULATION RESULTS

Solute Plume2D fate and transport modeling results are presented in this section. Concentrations of nitrate at both downgradient and upgradient receptor locations are discussed. Following these discussions, the horizontal transport model is used to develop target monitoring levels (TMLs) for the groundwater monitoring system at the EDC site. Finally, a discussion of vertical transport of nitrate to deeper aquifers such as the Greensand or El Dorado aquifers is addressed.

5.1 PLUME2D SIMULATION RESULTS

The Plume2D fate and transport model was used to predict the areal distribution of nitrate in the groundwater. The base case model scenario developed for the EDC site was non-steady state and the nitrate concentration in the groundwater continues to change with time. Figure C-5.1 shows the location of the 0.5 mg/L and 1.0 mg/L nitrate concentrations in the leading edge of the plume as it migrates downgradient of the EDC site. As time increases, the nitrate plume moves farther from the initial source location at the site. As noted on Figure C-5.1, a maximum nitrate concentration of 1.1 mg/L is simulated to reach the nearest downgradient receptor domestic well in approximately 7,250 years. At times greater than 7,250 years, the concentration of nitrate at the nearest downgradient receptor domestic well decreases. Based on the horizontal transport modeling, the nitrate MCL of 10 mg/L will not be exceeded at the identified receptor location.

5.2 CALCULATION OF ACCEPTABLE ON-SITE CONCENTRATIONS

To monitor changes in nitrate concentration in the groundwater at the EDC site, a groundwater monitoring system is proposed. A Target Monitoring Level (TML) will be established for these wells. The TML for the on-site monitor wells will be set so that the nitrate MCL of 10 mg/L will not be exceeded if nitrate in groundwater migrates to the exposure point (nearest downgradient domestic receptor well).

As described in Section 5.1, the base case analytical transport modeling simulated the maximum nitrate concentration for the nearest identified receptor, a downgradient domestic water well, to be 1.1 mg/L. Therefore, transport modeling predicts that the concentration of nitrate in groundwater will not exceed the MCL at the receptor well. Fate and transport modeling was then performed as an aid in selecting an appropriate nitrate TML for the on-site monitor wells.

Currently, the maximum concentration measured at a monitor well on-site is 1010 mg/L at monitor well MW-EDC-8. Using the maximum on-site concentration and the maximum concentration simulated to reach the receptor, a site-specific nitrate attenuation factor can be developed. The attenuation factor, AF, may be calculated as follows:

$$AF = \frac{Maximum \ Concentration \ On-site}{Maximum \ Concentration \ at \ Receptor} = \frac{1010}{1.1} = 918$$

The site-specific TML at the receptor is the MCL of 10 mg/L. The MCL is the regulatory standard for drinking water.

TMLs are concentrations below which adverse health effects are not expected to occur based on site-specific conditions. The point of exposure for the horizontal transport modeling scenario was the nearest downgradient receptor domestic well. The site-specific AF developed from the horizontal transport modeling may be used to calculate on-site nitrate groundwater monitoring levels for on-site monitor wells which will be protective of human health at the point of exposure. Based on the results of the site-specific horizontal transport modeling as described in Section 5.1, the on-site nitrate groundwater monitoring levels that will be protective of human health at the identified receptor location are calculated as follows:

Use of this equation gives a TML of 9,180 mg/L as the site specific on-site TML.

The on-site nitrate TML is the concentration at the on-site monitoring wells below which the MCL should not be exceeded for the potential receptors at the point of exposure.

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6.0

SENSITIVITY ANALYSIS OF INPUT PARAMETERS ON MODEL RESULTS

As stated in the *Work Plan*, a sensitivity analysis was conducted on four of the modeling input parameters. Woodward-Clyde conducted sensitivity analyses for:

- hydraulic conductivity,
- longitudinal and lateral dispersivity,
- retardation factor and half-life.

The purpose of the sensitivity analyses is to evaluate how sensitive the model is to a particular input parameter. For each parameter evaluated, the change in the model result was compared to the relative amount by which the parameter was changed. A general evaluation of the uncertainty of the modeled results based on the sensitivity to the identified input parameters is discussed below.

6.1 HYDRAULIC CONDUCTIVITY SENSITIVITY ANALYSIS

A sensitivity analysis was conducted for the saturated hydraulic conductivity.

6.1.1 Increase Hydraulic Conductivity

The hydraulic conductivity was increased by an order of magnitude. Increasing the hydraulic conductivity one order of magnitude increases the seepage velocity of the groundwater by one order of magnitude. Because dispersion is the only attenuation mechanism that was modeled in the simulation, increasing the hydraulic conductivity only decreases the time (from 7,250 to 725 years) at which the maximum concentration of nitrate is predicted to reach the receptor point, but the maximum concentration of 1.1 mg/L is not changed.

6.1.2 Decrease Hydraulic Conductivity

Similarly, as described in Section 6.1.1, decreasing the hydraulic conductivity one order of magnitude increases the time (from 7,250 to 72,500 years) at which the maximum concentration of nitrate is predicted to reach the receptor point, but the maximum concentration is still 1.1 mg/L.

6.2 DISPERSIVITY SENSITIVITY ANALYSIS

A sensitivity analysis was also performed on longitudinal dispersivity. The longitudinal dispersivity was decreased to one-fifth of the base case value. When longitudinal dispersivity was changed, lateral dispersivity was also changed accordingly because it is calculated to be 10 percent of the longitudinal dispersivity term. Decreasing the dispersivity increases the time (from 7,250 to 8,500 years) at which the maximum concentration of nitrate is predicted to reach the receptor point. The maximum concentration at the receptor point increased from a base case value of 1.1 mg/L to a sensitivity analysis modeled value of 3.5 mg/L which is also below the MCL of 10 mg/L.

6.3 ATTENUATION FACTORS SENSITIVITY ANALYSIS

The transport of a dissolved solute such as nitrate is by means of advective transport with the groundwater and varying degrees of retardation of the solute transport relative to the water due to attenuation by mechanisms such as sorption (most probably by ion exchange) and degradation. Consequently, the solute is expected to move at a slower velocity than the groundwater and some of the solute is expected to be retained on the soil particles of the aquifer matrix or destroyed by degradation reactions (such as denitrification or incorporation in biomass).

The only attenuation mechanism modeled in the base case simulations was dispersion. A sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation. The results of these sensitivity analyses are described below.

6.3.1 Retardation Factor

Sorption is described in the Solute Plume2D model by the retardation factor, R. The retardation factor is a ratio of the average linear groundwater velocity to the velocity of the contaminant. Therefore, an R value of 1 indicates no retardation due to sorption and R was set equal to one in the base case simulations. As the value of the retardation factor in the model increases, sorption of the contaminant decreases the velocity of the contaminant relative to the groundwater. To evaluate the effect of sorption on the predicted maximum concentrations of nitrate reaching the receptor well, the retardation factor was increased over the range from 1 to 5. Tabulated results of the retardation sensitivity analysis are presented below and in Figure C-6.4. As shown in Figure C-6.4, as the retardation factor is increased, the maximum concentration which could reach the nearest downgradient receptor domestic well decreases.

Retardation Factor	Maximum Concentration at Nearest Downgradient Receptor Domestic Well (mg/L)		
1	1.1		
2	0.55		
3	0.36		
5	0.22		

Results of Retardation Factor Sensitivity Analysis

Therefore, any sorption which is occurring insitu will further decrease the concentration of nitrate in the groundwater below the 1.1 mg/L concentration predicted by the base case model which included no retardation due to sorption mechanisms.

6.3.2 Decay Rate

Attenuation due to decay (degradation) is described in the Solute Plume2D model using a first-order decay constant, λ , so that:

$$\frac{dc}{dt} = \lambda c$$

where c is the concentration of the contaminant and t is time. In the above equation, $\lambda = \ln(2)/t_{1/2} = 0.693/t_{1/2}$, where $t_{1/2}$ is the half-life of the contaminant.

The base case simulation was performed assuming no degradation of the nitrate in groundwater. To evaluate the effect of degradation on the predicted maximum concentrations of nitrate reaching the receptor well, the decay rate, λ , was increased over the range from 0 to 0.00001 days⁻¹ (half-life from infinity to 190 years). Tabulated results of the retardation sensitivity analysis are presented below and in Figure C-6.5. As shown in Figure C-6.5, as the decay rate is increased, the maximum concentration which could reach the nearest downgradient receptor domestic well decreases substantially.

Decay Rate (days ⁻¹)	Maximum Concentration at Nearest Downgradient Receptor Domestic Well (mg/L)		
0	1.1		
0.0000001	0.85		
0.000001	0.13		
0.00001	0.0000076		

Results of Decay Rate Sensitivity Analysis

Therefore, any degradation which is occurring insitu will further decrease the concentration of nitrate in the groundwater below the 1.1 mg/L concentration predicted by the base case model which included no attenuation due to first-order decay mechanisms.

6.4 CONCLUSIONS FROM SENSITIVITY ANALYSIS

Based on the results of the sensitivity analysis, the input parameter which had the greatest effect on the horizontal model results was the saturated hydraulic conductivity because it linearly increased or decreased the time required for transport of nitrate. However, it did not increase the maximum concentration of nitrate predicted to reach the nearest downgradient receptor domestic well.

Finally, in all of the simulations performed during the sensitivity analysis, the maximum concentration at the receptor domestic well was predicted to remain below the MCL of 10 mg/L. The maximum concentration predicted to reach the receptor well was 3.1 mg/L at 8500 years in the dispersivity sensitivity analysis.

The only attenuation mechanism modeled in the base case simulations was dispersion. Sensitivity analyses were performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation. As sorption increases (modeled by increase in the retardation factor, R), the maximum concentration which could reach the nearest downgradient receptor domestic well decreases from the base case maximum concentration of 1.1 mg/L (R=1) to a maximum concentration of 0.22 mg/L (R=5). Nitrate may also be destroyed by degradation reactions such as denitrification. These degradation mechanisms were modeled in the sensitivity analysis using a first-order rate equation. In the base case simulation, the decay constant was equal to zero so no decay of the nitrate was modeled. In the sensitivity analysis, the decay constant was increased from 0 to 0.00001 days⁻¹. As the decay rate increases (modeled by decreasing the half-life of the nitrate), the maximum concentration which could reach the nearest downgradient receptor domestic well decreases from the base case maximum concentration of 1.1 mg/L (no decay) to a maximum concentration of 0.0000076 mg/L with the decay constant equal to 0.00001 days⁻¹ (a half-life of 190 years). Therefore, any attenuation through decay or sorption which is occurring insitu will further decrease the concentration in the groundwater below the 1.1 mg/L concentration predicted by the base case model which included no attenuation mechanisms other than dispersion.

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7.0 CONCLUSIONS

The technical approach for the contaminant fate and transport modeling is described in the Development of Risk-Based Target Monitoring Levels Work Plan (WCC 1996).

Horizontal transport modeling was used to evaluate the potential transport of nitrate in the groundwater to potential groundwater use locations. The International Ground Water Modeling Center's (IGWMC) Solute Program Package, Analytical Model for Transport of a Solute Plume from Point Sources in a Uniform Two-Dimensional Groundwater Flow Field (Plume2D) was used to simulate the transport of the nitrate horizontally with groundwater to the receptor locations. The horizontal transport modeling was also used to calculate a nitrate attenuation factor for transport of nitrate from the site to a receptor. The attenuation factor was then used to calculate the TML for on-site monitor wells.

The Phase II groundwater investigation conducted at the site concluded that, based on nitrate concentrations in excess of the EPA MCL at ten monitoring locations in the monitoring interval of the Cockfield formation, nitrate in groundwater remains a potential concern for the EDC site. As nitrate was the only constituent determined to be present in the groundwater above primary MCLs, it was the only constituent of concern identified for fate and transport modeling. The source configuration for the nitrate used within the contaminant fate and transport modeling grid was trial-and-error fit to represent current site conditions. Site-specific values for the saturated monitoring interval thickness and saturated hydraulic conductivity were used in the model. Hydraulic gradient of the Cockfield formation in the site vicinity was obtained from an Arkansas Geological Commission document (1988).

As described in the *Work Plan*, off-site residents could have the potential for exposure to siterelated groundwater if nitrate from the site migrates in the groundwater to a well used for drinking water. A well search was made of the Arkansas Geological Commission Well Drilling report files. The search identified the nearest domestic well downgradient from the site to be located approximately 4.7 miles from the EDC site as shown in Figure C-3.2. This nearest downgradient domestic well was identified as the receptor point for the horizontal fate and transport modeling.

The base case nitrate horizontal transport scenario developed for the EDC site was non-steady state and the nitrate concentration in the groundwater continues to change with time. As time increases, the nitrate plume moves farther from the initial source location at the site. A maximum nitrate concentration of 1.1 mg/L is simulated to reach the nearest downgradient receptor domestic well in approximately 7,250 years. At times greater than 7,250 years, the concentration of nitrate at the nearest downgradient receptor domestic well decreases. Based on the horizontal transport modeling, the nitrate MCL of 10 mg/L will not be exceeded at the identified receptor location.

The only attenuation mechanism modeled in the base case simulations was dispersion. A sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation (denitrification or incorporation in biomass).

- <u>Sorption</u>: As sorption increases (modeled by increase in the retardation factor, R), the maximum concentration which could reach the nearest downgradient receptor domestic well decreases from the base case maximum concentration of 1.1 mg/L (no sorption) to a concentration of 0.22 mg/L (R=5).
- <u>Degradation</u>: As the decay rate increases, the maximum concentration which could reach the nearest downgradient receptor domestic well decreases from the base case maximum concentration of 1.1 mg/L (no decay) to a maximum concentration of 0.0000076 mg/L with the half life equal to 190 years.

Therefore, any attenuation through decay or sorption which is occurring insitu will further decrease the concentration in the groundwater below the 1.1 mg/L concentration predicted by the base case model which included no attenuation mechanisms other than dispersion.

The generalized modeling cross-section for the EDC site is shown in Figure 5.1 of the report to which this appendix is attached. The local geology beneath the EDC site to the base of the Cook Mountain formation consists of the following:

- A thin veneer of Quaternary-aged alluvial sediments
- Tertiary-aged Cockfield formation (part of Claiborne Group)
- Cook Mountain formation (clay confining unit)

The geology below the Cook Mountain formation includes the following:

- Sparta Sand (contains Greensand aquifer, middle confining bed and El Dorado aquifer)
- Cane River formation (clay confining unit)

The horizontal transport model was developed for the EDC monitoring interval of the Cockfield formation. The location of the nearest downgradient City of El Dorado public supply well is shown in Figure C-3.2. This well is 700 feet deep and completed in the El Dorado aquifer which is below the Greensand aquifer. This public supply well has been identified as the potential receptor point for vertical migration of nitrate from the Cockfield formation through the Cook Mountain formation confining unit into the Greensand aquifer. Vertical migration was addressed qualitatively using travel time calculations.

Using values of hydraulic conductivity by McWreath *et al.* and Fitzpatrick *et al.* of $9 \ge 10^{-6}$ feet/day, a formation thickness of 95 feet, an effective porosity of 0.35, a vertical gradient of 0.9474 feet/feet, the travel time for water through the Cook Mountain formation is approximately 10,680 years. This travel time calculation is for water to reach the top of the Greensand aquifer interval of the Sparta Sand at approximately 300 feet below ground surface. The potential receptor well, the city of El Dorado public supply well, is completed approximately 400 feet deeper in the El Dorado aquifer interval of the Sparta Sand. The Greensand aquifer is separated from the El Dorado aquifer by the Sparta aquifer middle confining bed. Therefore, additional travel time would be required if the nitrate migrated

vertically through the Cook Mountain formation (100 feet) and the uppermost 400 feet of the Sparta aquifer.

Based on the fate and transport model developed for the Cockfield formation, the maximum concentration of nitrate that would migrate horizontally in the shallow Cockfield formation to the location of the nearest downgradient public supply well is 2.8 mg/L. If the nitrate migrated through the lower portions of the Cockfield formation, through 95 feet of the Cook Mountain formation, and then through 400 feet of the Sparta Sand to the El Dorado aquifer, additional attenuation of the nitrate would occur through degradation and sorption. If the nitrate reached the top of the Sparta Sand, it would be further attenuated as it migrated vertically through the Greensand aquifer and the Sparta middle confining unit before reaching the El Dorado aquifer. Throughout this vertical travel distance (to a depth of 700 feet below ground surface), dispersion and attenuation mechanisms would further reduce the concentration of the nitrate in groundwater below 2.8 mg/L.

The results of the nitrate horizontal fate and transport modeling are conservative and the modeled concentrations which have been generated by the simulations are expected to be higher than the concentrations which will actually occur. Several conservative assumptions were used to develop the base case model scenario:

• The base case scenario simulated no attenuation of the nitrate due to sorption or degradation mechanisms. The transport of nitrate in groundwater is likely to be retarded by sorption (most probably by ion exchange). Additionally, nitrate is subject to degradation (denitrification or incorporation in biomass). As shown in the sensitivity analysis, both of these insitu attenuation mechanisms will further decrease the concentrations of nitrate in groundwater as it is transported.

The analytical model selected for the simulation, Plume2D, is a twodimensional model. Dispersion was only simulated in the longitudinal and lateral (or transverse) directions. No vertical dispersion of the nitrate to the lower portions of the Cockfield formation was simulated. Dispersion is an anisotropic process and some vertical dispersion will occur as the nitrate

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migrates. Any amount of vertical dispersion, within the Cockfield formation, will further decrease the concentrations of nitrate in groundwater.

Groundwater flow directions in the Cockfield formation are influenced by topographic surface features. As a conservative estimate, the shortest path (distance) between the EDC site and the nearest downgradient receptor domestic well was modeled as the groundwater flow direction. The actual flow path is probably longer, giving more time for attenuation due to dispersivity, degradation, and sorption effects.

In the base case scenario and all sensitivity analyses, the maximum concentration at the receptor domestic well was predicted to remain below the MCL of 10 mg/L.

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TABLES

TABLE C-3.1

DESCRIPTION OF HYDROGEOLOGIC UNITS IN THE STUDY AREA DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

System	Series	Group	Formation	Hydrogeologic Unit	Hydrogeologic Properties
Quaternary	Holocene and Pleistocene		Alluvial and terrace deposits		Clay, silt, sand, and gravel. Present only in bottomlands of most streams. Generally not used. As much as 100 feet thick.
Tertiary		Claiborne	Cockfield Formation	Cockfield aquifer	Lignitic sand with interbedded clay. Principal aquifer for rural domestic supply. Approximately 200 feet thick where present.
			Cook Mountain Formation	Cook Mountain confining unit	Clay with interbedded fine sand. Not an aquifer. Thickness ranges from 50 to 200 feet.
	Eocene		Sparta Sand	Greensand aquifer	Thinly bedded fine glauconitic sand with interbedded clay. Source of municipal and industrial water supply principally in southeast part of county. Water withdrawals approximately 0.5 million gallons per day. Approximately 200 feet thick.
				Middle confining bed	Clay and silt. Not an aquifer. Thickness ranges from 40 to 160 feet.
				El Dorado aquifer	Thickly bedded medium to coarse sand. Source of municipal and industrial water supply throughout the county. Water withdrawals approximately 14 million gallons per day. Approximately 300 feet thick.
			Cane River Formation	Cane River confining unit	Clay and silty clay. Not an aquifer. Approximately 300 feet thick.

From Leidy and Taylor, 1992

TABLE C-4.1

SOLUTE PLUME 2D TRANSPORT MODEL BASE CASE INPUT DATA DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY, EL DORADO, ARKANSAS

PARAMETER		VALUE	UNITS	REFERENCE
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Groundwater (Seepage) velocity	0.008867	feet/day	
eters	Saturated monitoring interval thickness	18.83	feet	Arithmetic average of site data
am	Effective porosity	0.3		Work Plan
Par	Longitudinal dispersivity	2800	feet	Work Plan (10% of travel distance)
ical	Lateral dispersivity	280	feet	Work Plan (10% of longitudinal dispersivity)
hys	Retardation factor	1		No retardation
Half-life		0		No decay
	X-coordinate of origin	0	feet	
S	Y-coordinate of origin	0	feet	
id nete	D x	1000	feet	
ran G	D y	1000	feet	
L Å	nodes in x direction	35		·
	nodes in y direction	14		

## TABLE C-4.2

# SATURATED THICKNESS DETERMINATION DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Monitoring Well No.	Total Well Depth (ft)	Depth to Groundwater (ft)	Saturated Zone Thickness (ft)		
MW-EDC-1	22.1	10.07	12.03		
MW-EDC-2	20.2	0.45	19.75		
MW-EDC-3	27.1	9.31	17.79		
MW-EDC-4	22.1	7.64	14.46		
MW-EDC-5	17.7	5.22	12.48		
MW-EDC-6	22.0	4.79	17.21		
MW-EDC-7	23.9	7.81	16.09		
MW-EDC-8	29.9	8.06	21.84		
MW-EDC-9	30.0	9.11	20.89		
MW-EDC-10	22.6	13.18	9.42		
MW-EDC-11	19.8	10.65	9.15		
MW-EDC-12	19.9	6.70	13.20		
MW-EDC-13	19.8	10.30	9.50		
MW-EDC-14	18.2	8.23	9.97		
MW-EDC-15	17.0	5.13	11.87		
MW-EDC-16	19.3	5.60	13.70		
MW-EDC-17	34.7	26.92	7.78		
MW-EDC-18	17.2	5.41	11.79		
	ARITHMETIC AVERAGE 13.83				

**FIGURES** 





# EL DORADO CHEMICAL COMPANY

Contour Interval: 10 feet except where shown.						
Woodward-Clyde Consultants Engineering & sciences applied to the earth & its environment 900 S Shacklefore Suite ±12 Little Rock Arkansas 72211						
Development of Risk Based Target Monitoring Levels						
SCALE	MADE BY GAT	DATE 04/01/96	FILE NO			
1" = 1.000'	97B061					
	WATER TABL	E MAP	FIGURE C-3.1			



LEGEND

- Shallow Domestic Well in Cockfield Formation
- Public Supply 700' Deep Well in Sparta Aquifer
- Shallow Commercial Well in Cockfield Formation



	dward-Clyc & sciences applied to the earth &	HORIZONTAL TRANSPORT	FILE NO. 978061-13	
SCALE: AS SHOWN	DRAWN BY: D.OLSON CHKD. BY: D. REECE	DATE: 10/24/97 DATE: 10/27/97		HG. NO. C-3.2



#### FIGURE C-5.1

#### NITRATE TRANSPORT MODEL RESULTS DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS


### SENSITIVITY ANALYSIS: INCREASE HYDRAULIC CONDUCTIVITY DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



### SENSITIVITY ANALYSIS: DECREASE HYDRAULIC CONDUCTIVITY DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



### SENSITIVITY ANALYSIS: DECREASE DISPERSIVITY DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



### SENSITIVITY ANALYSIS: RETARDATION FACTOR DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



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FIGURE C-6.5





# **ATTACHMENT C-1**

# **SLUG TEST RESULTS**

Noodward-Clyde 🐓	Project Notes
onsultants	Project Name:EDC
biea: EUC AQUIFER LESTING	Project No.: 958165
EJF Date: 12-20-96	Task No.: <u>KA</u> File No.: Sheet { of <b>3</b>
ecked By: Date:	
MW-18; Test #1	······································
Screen Length (Ft) Depth to Bottom of Well (Ft.) Depth to Water Table (Ft.) Depth to Bottom of Aquifer (Ft.)	- 10.0 - 17 16 - 5.79 - 17.16
Casing radius (in.) Well radius (in.)	- H.o
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Ye: 0.188 Ft	
$r_{a} = \frac{1}{2} \frac{1}$	
$\frac{y_{F}}{F} = \frac{12.0 \text{ min}}{12.0 \text{ min}}$	
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Transmissivity (Ft2/doy) =	.244 E + 02
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MW-18 (TEST =1)



Consultants	Project Notes
EDC Aguifer Testing	Project Name: EDC
	Project No.: <u>95165+KA</u>
CJFDate: 12/20156	task No.:
Pecked By: Date:	······································
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	- 10 A
- Screen Length	
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Depth to water lagie (FT.)	
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Well radius (in.)	= 10,0
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<u>rw * 8.333 E-001 Ft.</u>	
L[w = 12.0000	· · · · · · · · · · · · · · · · · · ·
1. 1903030 - 4 2.16	210 2 -001 - 8
N. = 0.359 CH	
$t_{2} = 2.0$ min.	
NE = 0.107 Ft.	
te_= 10.0 min.	
Re = .576 = +01	
- • • • • • • • • • • • • • • • • • • •	
Hydraulic Conductivity (co	x (sec) = 826 E-03
	+ day)=234 E+01
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Woo Con	dwar sultar	d-Clyde 🌑 nts	
Subject: _	EDC	AQUIFER TESTING	
8y:	ESF	Date: 12-20 -96	

Checked By: _____ Date: _____

# **Project Notes**

 Project Name:
 EDC

 Project No.:
 958165

 Task No.:
 2A

 File No.:
 3

MW-13: TEST #1
Screen Length (Ft.) - 10.0
Depth To Bottom of Well [Ft.) - 19,8
Derth To Weter Table (FT.) - 1.02
Depth to pottem of Aquiter (Ft) = 17.8
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$\frac{Casing}{ A  } = \frac{Casing}{ A  } = \frac{100}{ A  } = \frac{100}{ A  }$
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ta 7 26 min
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TOF **H S. BERKER CONNERSERS** FILSE

MW - 3 (TEST #2)



### **APPENDIX D**

# CONTAMINANT FATE AND TRANSPORT MODELING COMMERCIAL WATER WELL RECEPTOR

## APPENDIX D

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# CONTAMINANT FATE AND TRANSPORT MODELING COMMERICAL WATER WELL RECEPTOR (DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS)

# EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Prepared for El Dorado Chemical Company El Dorado, Arkansas

December 1997

WC File 97B061 -13



Woodward-Ciyde Three Financial Centre 900 S. Shackleford, Suite 412 Little Rock, AR 72211 501-223-2583

# Woodward-Clyde

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Attachment D-1 Slug Test Results

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# 1.0 INTRODUCTION

The objective of this section is to present the results of fate and transport modeling for the commercial water well receptor, which was conducted as part of the development of risk-based target monitoring levels for the El Dorado Chemical Company (EDC) site. The contaminant fate and transport modeling was used to evaluate the potential for the identified constituent of concern, nitrate, to reach the identified receptor exposure point via groundwater movement and to calculate a nitrate attenuation factor for migration of nitrate from the site to the receptor. The technical approach for the contaminant fate and transport modeling is described in the *Development of Risk-Based Target Monitoring Levels Work Plan (Work Plan)* (WCC 1996).

# 2.0 TECHNICAL APPROACH

# 2.1 CONSTITUENT OF CONCERN: NITRATE

As described in the *Phase II Groundwater Investigation: Final Report* (WCC 1996), nitrate concentrations in excess of the EPA Maximum Contaminant Level (MCL) of 10 mg/L were observed at 10 of 22 monitor well locations tested during the Phase II investigation. The nitrate concentrations at those ten monitor wells ranged from 11.9 mg/L (MW-EDC-14) to 1,010 mg/L (MW-EDC-8). These wells are completed in the upper saturated interval of the Cockfield formation and concentrated in two distinct areas at the EDC site:

- The north side of the acid and nitrate process areas known as the Production Area
- The vicinity of Lake Kildeer

The Phase II investigation concluded that, based on nitrate concentrations in excess of the EPA MCL at ten monitoring locations, nitrate in groundwater remains a potential concern in these two areas. Nitrate was the only constituent determined to be present above primary MCLs in on-site monitor wells.

Contaminant fate and transport modeling of the nitrate was performed to evaluate the potential for nitrate to reach receptors via groundwater movement. Identification of exposure points for receptors is described in the following section.

#### 2.2 **RECEPTOR POPULATION IDENTIFICATION**

As described in the Exposure Assessment (Section 4.0) of the *Development of Risk-Based Target Monitoring Levels Report*, off-site residents could have the potential for exposure if nitrate from the site migrates in the groundwater to a water well used for drinking water. According to El Dorado's city engineer, residents within the city limits of El Dorado are supplied with drinking water by the El Dorado Public Works Department. However, some rural area residential domestic wells have reportedly been completed in the Cockfield formation. El Dorado's public supply wells are completed in the deeper El Dorado aquifer.

### 2.2.1 Wells in Cockfield Formation

A well search was made of the Arkansas Geological Commission Well Drilling Report files.

The search indicated that the nearest downgradient commercial well is located in Section 16 of Township 17 South, Range 15 West, approximately 1.3 miles southeast from the EDC site as shown in Figure D-3.2. The well is reported to be 37 feet deep and completed in the Cockfield formation. This nearest downgradient commercial water well has been identified as the receptor point for the horizontal fate and transport modeling presented in Appendix D. Water from commercial water wells is not used for drinking water. Consequently, consideration of a commercial water well as a receptor location at which a drinking water MCL is applied is very conservative.

## 2.2.2 Wells Completed in Deeper Units

The closest downgradient city of El Dorado public supply well is located (see Figure D-3.2) approximately 1.4 miles south of the EDC site in Section 16, Township 17 South, Range 15 West. This well is 700 feet deep and is completed in the El Dorado aquifer. The El Dorado aquifer is separated from the Cockfield formation by two thick clay layers (the Cook Mountain formation and the middle confining bed of the Sparta aquifer). This well has been identified as the potential receptor point for vertical migration of nitrate from the Cockfield formation

through the Cook Mountain formation into the deeper aquifers. Vertical migration will be addressed qualitatively using travel time calculations.

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# 3.0 HORIZONTAL TRANSPORT MODEL

This section discusses the selection of the analytical transport model, the assumptions used to develop the analytical model, and the grid definition used to apply the model to the EDC site.

## 3.1 HORIZONTAL MODELING OBJECTIVES

The objectives of the horizontal modeling are to evaluate if current nitrate concentrations in the groundwater may, over time, produce concentrations at various receptor locations which exceed the Target Monitoring Levels (TML) determined using risk assessment procedures and to develop an attenuation factor for calculating acceptable on-site nitrate concentration.

## 3.2 SELECTION OF SOLUTE PLUME2D MODEL

The International Ground Water Modeling Center's (IGWMC) Solute Program Package, Analytical Model for Transport of a Solute Plume from Point Sources in a Uniform Two-Dimensional Groundwater Flow Field (Plume2D) was used to simulate the transport of the nitrate horizontally in groundwater to the receptor location. Solute uses analytical solutions of the advective dispersive transport equation for a non-conservative tracer solution. Solute contains four groups of analytical solutions for 1-, 2- and 3-dimensional transport of a solute in uniform groundwater flow. For this work, the solution module for 2-dimensional transport, Plume2D, was used.

The Plume2D model calculates the concentration distribution from point sources in twodimensional regional flow. Plume2D has two analytical solutions based on different types of sources. The specified mass instantaneous source release analytical solution, Slug2D, was utilized for all horizontal fate and transport modeling.

## 3.3 ANALYTICAL MODEL ASSUMPTIONS

This Plume2D solution assumes the solute to be well-mixed over the constant thickness of the aquifer resulting in an areal concentration distribution which is uniform with depth. Each point source is a vertical line source extending from the top to the base of the aquifer. The Plume2D model is based on the following assumptions:

- Uniformly porous aquifer
- The aquifer is homogeneous and isotropic with respect to its hydraulic and transport characteristics
- The aquifer is infinite in areal extent and of constant thickness
- A source fully penetrates the aquifer
- The groundwater flow regime is fully-saturated
- One-dimensional steady-state uniform regional flow in the x-direction (recharge rates from constituent source are small and do not influence flow field)
- Constituents are distributed instantaneously over the entire aquifer thickness beneath the source
- Release of specified mass of solute is instantaneous
- The density and viscosity of the solute in the source and in the aquifer are identical and do not change in time
- There is no solute advection or dispersion into or out of the confining layers
- Dirichlet, Neumann, or Cauchy boundaries

## 3.4 DEFINITION OF PLUME2D GRID

Solute Plume2D uses the convention that the regional one-dimensional flow is in the positive x-direction. Groundwater flow beneath the site is southeast as shown in Figure D-3.1. Therefore, the model grid is orientated so that the positive x-axis is to the southeast. For modeling purposes, a localized coordinate system was developed for the base map of the EDC site and surrounding area (see Figure D-3.2). From the base map, a consistent set of coordinates for the receptors and sources was developed using Cartesian coordinate (x,y) pairs based on the model coordinate grid system.

## 3.5 GENERALIZED MODELING CROSS-SECTION

The generalized modeling cross-section for the EDC site is shown in Figure 5.1 of the report to which this appendix is attached. The local geology beneath the EDC site to the base of the Cook Mountain formation consists of the following:

- A thin veneer of Quaternary-aged alluvial sediments
- Tertiary-aged Cockfield formation (part of Claiborne Group)
- Cook Mountain formation (clay confining unit)

The Cook Mountain formation overlies the following:

- Sparta Sand (contains Greensand aquifer, Sparta middle confining bed and El Dorado aquifer)
- Cane River formation (clay confining unit)

Table D-3.1 provides a description of hydrogeologic units in the study area.

## 3.5.1 Quaternary-Aged Sediments

A thin veneer of quaternary-aged alluvial sediments overlay the Cockfield formation along the Ouachita River and its tributaries.

### 3.5.2 Cockfield Formation

The Tertiary-aged Cockfield formation (part of the Claiborne Group) crops out over most of Union County and underlies the EDC site. This formation consists predominantly of sands, silts, and carbonaceous (calcitic) clays with minor amounts of interbedded lignite and gypsum. The formation can contain lenticular beds of lignitic sands in some areas. The formation thickness is approximately 200 feet in most of Union County.

Water levels in area wells range in depth from near land surface in low-lying areas to as much as 50 feet on the highest hills and ridges. Discharge is primarily base flow to streams with lesser amounts of evapotranspiration. Water table configuration within the aquifer generally exhibits a subdued reflection of the local topography with flow toward surface drains (i.e., the valleys of the principal streams).

The horizontal transport model developed for the EDC site will model the uppermost saturated monitoring interval of the Cockfield formation at the site. The average saturated thickness of the monitoring interval is 13.83 feet thick for the 22 monitor wells at the site. The modeled interval is shown in Figure 5.1 of the report to which this appendix is attached.

#### 3.5.3 Cook Mountain Formation

The Cook Mountain formation underlies the Cockfield formation in all areas of the region except where the younger sediments have been removed by erosion. The formation consists of low permeability clays and silty clays with lesser amounts of very fine sands. The formation acts as a lower confining unit (aquitard) for groundwater of the Cockfield formation and an upper confining unit for the underlying Greensand aquifer.

Thickness of the confining unit is variable from approximately 50 feet to as much as 200 feet across the region. In the vicinity of the EDC facility, the thickness of the clays comprising the confining unit is estimated to be between 75 and 100 feet (McWreath *et al.* 1991).

### 3.5.4 Sparta Aquifer

The Sparta aquifer is overlain by the Cook Mountain formation in Union County and overlies the Cane River formation. The Tertiary-aged Sparta aquifer is the main source of municipal and industrial water supplies throughout the region. Heavy pumping stresses placed on the aquifer in the past decades have created large cones of depression within the potentiometric surface surrounding the pumping centers. One such cone of depression is centered around El Dorado, Arkansas. Large quantities of groundwater withdrawn from the aquifer have altered, and in some cases reversed, flow directions in the aquifer (McWreath *et al.* 1991).

In Union County, the Sparta aquifer is hydrogeologically separated into three hydrostratigraphic zones based on lithologic character and water production capacities. These zones, in descending order, are the Greensand aquifer, the Sparta aquifer middle confining bed, and the El Dorado aquifer. The El Dorado aquifer is the most heavily used portion of this hydrostratigraphic sequence.

#### 3.5.4.1 Greensand Aquifer

The Greensand aquifer occupies the upper portion of the Sparta aquifer. This sequence consists of fine-grained to very fine-grained glauconitic sands with lesser amounts of silts and clays. Groundwater within the aquifer is under confined conditions. Confining units are the Cook Mountain confining unit above and a clay-rich horizon (the Sparta aquifer middle confining bed) of the El Dorado aquifer below.

The Greensand aquifer thickness in the Union County area is approximately 200 feet (Leidy and Taylor, 1992). The regional flow direction within the aquifer is south-southeast (Broom *et al.* 1984).

The Greensand aquifer is generally less productive than the deeper El Dorado aquifer. The aquifer is used as a potable water supply, but less extensively than the deeper, more productive El Dorado aquifer.

### 3.5.4.2 Sparta Aquifer Middle Confining Bed

In separate investigations by Fitzpatrick *et al.* (1990) and McWreath *et al.* (1991), the Sparta aquifer has been treated as a single aquifer for the purposes of finite-difference modeling of the effects of pumping stresses. However, as stated by Broom *et al.* (1984), sufficient evidence exists to support the conceptualization that in Union County, Arkansas a predominantly marine clay horizon in the middle portion of the Sparta aquifer serves as a confining unit. Hydraulic conductivity, both horizontal and vertical, is low in comparison to the overlying and underlying sediments. This zone serves as a confining bed between the upper and lower portions of the Sparta aquifer and allows them to function separately as individual aquifers. This zone primarily consists of clays and silty clays. McWreath *et al.* (1991) support the designation of this clay horizon as a confining unit on a local scale. The confining bed is between 40 and 160 feet thick in Union County. (McWreath *et al.* 1991).

#### 3.5.4.3 El Dorado Aquifer

The El Dorado aquifer is more productive and, thus, more heavily targeted for placement of high yield wells. This sequence consists of a thickly bedded medium to coarse sand. The thickness of this sequence of the El Dorado aquifer in Union County is approximately 300 feet (Leidy and Taylor 1992). The city of El Dorado public supply water wells are completed in the El Dorado aquifer.

The identification of receptors and exposure points was described in Section 2 and the selection of the analytical model was described in Section 3. This section discusses the site-specific hydrogeologic inputs in Plume2D.

The variables necessary for input into the model include: groundwater (seepage) velocity, aquifer thickness, porosity of the aquifer, longitudinal dispersivity, lateral dispersivity, retardation factor, half-life of the source constituent, number of point sources, source strength, elapsed time, coordinates of the source and coordinates of the grid. The coordinate grid was discussed in Section 3.4. The site-specific hydraulic and matrix-dependent transport properties used in the Solute Plume2D transport simulations are shown in Table D-4.1. The following sections provide a brief description of how each input variable was evaluated.

## 4.1 SEEPAGE VELOCITY

The groundwater (seepage) velocity is the rate of groundwater movement. This value was evaluated using Darcy's law and estimates of soil water holding capacity typical of soils at the site. Darcy's Law states that:

$$v = K \frac{dh}{dl}$$

where :

v = Darcy Velocity K = Saturated Hydraulic Conductivity dh/dl = Groundwater Gradient The seepage velocity is :

$$\bar{v} = \frac{v}{\theta}$$

where :

v=Seepage Velocityq=Water Holding Capacity of the Soil (Effective Porosity)

Determination of hydraulic conductivity, gradient, and effective porosity are discussed below.

### 4.1.1 Hydraulic Conductivity of Cockfield Formation

The saturated hydraulic conductivity which was used to calculate the seepage velocity for the horizontal transport model was calculated from slug tests. In accordance with the *Work Plan*, slug tests were conducted in monitor wells MW-EDC-4, MW-EDC-13, and MW-EDC-18, which are located at the EDC site. The results of the slug tests are shown in Attachment D-1. The hydraulic conductivity calculated for the Cockfield formation from these slugs tests ranged from  $4.0 \times 10^{-4}$  cm/sec to  $8.26 \times 10^{-4}$  cm/sec. The arithmetic average hydraulic conductivity calculated for the Start (6.61  $\times 10^{-4}$  cm/sec).

#### 4.1.2 Regional Hydraulic Gradient of Cockfield

A water table contour map was presented in the *Phase II Groundwater Investigation Final Report* (Woodward-Clyde 1996) for the uppermost saturated monitoring interval at the EDC site. This map is reproduced in this report as Figure D-3.1. Static groundwater levels in the 22 monitor wells ranged from approximately 2 feet above ground surface (artesian conditions) at MW-2 in the northern portion of the EDC site to approximately 27 feet below grade at MW-17 in the southern portion of the site. In general, groundwater flow beneath the site is southeast with the exception of areas locally influenced by ground surface topography and the presence of Lake Kildeer. The regional groundwater gradient for Union County is also to the southeast towards the Ouachita River.

Figure D-4.1 presents a potentiometric surface of the Cockfield formation in the south Arkansas area as presented in the Arkansas Geological Commission Information Circular 28-D (1988). The groundwater flow direction near El Dorado is generally southeast. However, this potentiometric surface appears to be locally influenced by ground surface topography. Based on this potentiometric surface, a regional groundwater gradient of  $1.42 \times 10^{-3}$  feet/feet was calculated in the vicinity of El Dorado.

### 4.1.3 Porosity

Based on effective porosity values determined by Freeze and Cherry (1979), a value of 0.30 will be utilized for the effective porosity of the uppermost saturated monitoring interval at the EDC site, as was presented in the approved Work Plan.

### 4.1.4 Saturated Thickness

Based on Phase II field measurements, the saturated thickness has been evaluated to be 13.83 feet from the average saturated thickness of the uppermost saturated monitoring interval. Tabulated Phase II data used in the calculation are presented in Table D-4.2.

## 4.1.5 Seepage Velocity Calculation

The groundwater seepage velocity was calculated as follows:

$$\overline{v} = \frac{K}{\theta} \frac{dh}{dl} = \left(\frac{1.87}{0.3}\right) 1.42E - 3 \frac{feet}{day} = 0.00885 \frac{feet}{day}$$

## 4.2 DISPERSIVITY

The dispersivity, reported in dimensions of length, represents the effects of porous medium properties on dispersion of the solute mass in the longitudinal and lateral (or transverse) directions.

#### 4.2.1 Longitudinal Dispersivity

The longitudinal dispersivity, when multiplied by the seepage velocity, yields the longitudinal dispersion coefficient. Woodward-Clyde used a conservative value calculated by taking ten percent of the transport distance to the receptor location as was presented in the approved Work Plan. The source was 9,800 feet from the receptor and the longitudinal dispersivity used in the Plume2D model was 980 feet. A sensitivity analysis was performed on this parameter as described in Section 6.2.

### 4.2.2 Lateral Dispersivity

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The lateral dispersivity (reported in dimensions of length), was estimated to be 10 percent of the longitudinal dispersivity as was presented in the approved Work Plan. A sensitivity analysis was performed on this parameter as described in Section 6.2.

#### 4.3 ATTENUATION MECHANISMS

The transport of a dissolved solute such as nitrate is by means of advective transport with the groundwater and varying degrees of retardation of the solute transport relative to the water due to attenuation processes such as sorption (most probably by ion exchange) and degradation. Consequently, the solute is expected to move at a slower velocity than the groundwater and some of the solute is expected to be retained on the soil particles of the aquifer matrix or destroyed by degradation reactions (such as denitrification or incorporation in biomass).

The only attenuation mechanism modeled in the base case simulations was dispersion. As discussed in Section 6.3, a sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation. The results of these sensitivity analyses are described below.

#### 4.4 SOURCE DEFINITION

The initial concentration conditions for the contaminant fate and transport modeling were evaluated from the results of the Phase I and II groundwater investigations. An estimate of the mass of nitrate in the groundwater of the uppermost saturated monitoring interval beneath the EDC site was interpreted from the groundwater sampling results. The source areas defined in the analytical model contained a mass of nitrate consistent with the mass indicated by the groundwater sampling results. A Plume2D simulation utilizing no mechanisms for source decay (model scenario was conservative) was performed and the mass in the system measured to further confirm the conservative nature of the base-case model. The source configuration used within the contaminant fate and transport modeling grid was trial-and-error fit to represent current site conditions.

### 4.5 ELAPSED TIME

The elapsed time represents the time period for which the model was run. This elapsed time period was evaluated by trial and error to obtain the maximum concentration of nitrate that could reach the identified receptor location.

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# 5.0 TRANSPORT SIMULATION RESULTS

Solute Plume2D fate and transport modeling results are presented in this section. Concentrations of nitrate at both downgradient and upgradient receptor locations are discussed. Following these discussions, the horizontal transport model is used to develop target monitoring levels (TMLs) for the groundwater monitoring system at the EDC site. Finally, a discussion of vertical transport of nitrate to deeper aquifers such as the Greensand or El Dorado aquifers is addressed.

### 5.1 PLUME2D SIMULATION RESULTS

The Plume2D fate and transport model was used to predict the areal distribution of nitrate in the groundwater. The base case model scenario developed for the EDC site was non-steady state and the nitrate concentration in the groundwater continues to change with time. Figure D-5.1 shows the location of the 0.5 mg/L and 1.0 mg/L nitrate concentrations in the leading edge of the plume as it migrates downgradient of the EDC site. As time increases, the nitrate plume moves farther from the initial source location at the site. As noted on Figure D-5.1, a maximum nitrate concentration of 2.8 mg/L is simulated to reach the nearest downgradient commercial well in approximately 3,000 years. At times greater than 3,000 years, the concentration of nitrate at the nearest downgradient commercial well decreases. Based on the horizontal transport modeling, the nitrate MCL of 10 mg/L will not be exceeded at the nearest downgradient commercial well.

#### 5.2 CALCULATION OF ACCEPTABLE ON-SITE CONCENTRATIONS

To monitor changes in nitrate concentration in the groundwater at the EDC site, a groundwater monitoring system is proposed. A Target Monitoring Level (TML) will be established for these wells. The TML for the on-site monitor wells will be set so that the nitrate MCL of 10 mg/L will not be exceeded if nitrate in groundwater migrates to the exposure point (nearest downgradient commercial well).

As described in Section 5.1, the base case analytical transport modeling simulated the maximum nitrate concentration for the nearest identified receptor, a downgradient commercial well, to be 2.8 mg/L. Therefore, transport modeling predicts that the concentration of nitrate in groundwater will not exceed the MCL at the receptor well. Fate and transport modeling was then performed as an aid in selecting an appropriate nitrate TML for the on-site monitor wells.

Currently, the maximum concentration measured at a monitor well on-site is 1010 mg/L at monitor well MW-EDC-8. Using the maximum on-site concentration and the maximum concentration simulated to reach the receptor, a site-specific nitrate attenuation factor can be developed. The attenuation factor, AF, may be calculated as follows:

$$AF = \frac{Maximum Concentration On - site}{Maximum Concentration at Receptor} = \frac{1010}{2.8} = 360.7 \approx 361$$

The site-specific TML at the receptor is the MCL of 10 mg/L. The MCL is the regulatory standard for drinking water.

TMLs are concentrations below which adverse health effects are not expected to occur based on site-specific conditions. The point of exposure for the horizontal transport modeling scenario was the nearest downgradient commercial well. The site-specific AF developed from the horizontal transport modeling may be used to calculate on-site nitrate groundwater monitoring levels for on-site monitor wells which will be protective of human health at the point of exposure. Based on the results of the site-specific horizontal transport modeling as described in Section 5.1 of the report to which this appendix is attached, the on-site nitrate groundwater monitoring levels that will be protective of human health at the identified receptor location are calculated as follows:

On - Site Acceptable Monitoring Level (TML) = MCL • Nitrate AF

Use of this equation gives a TML of 3,607 mg/L as the site specific on-site TML.

The on-site nitrate TML is the concentration at the on-site monitoring wells below which the MCL should not be exceeded for the potential receptors at the point of exposure.

## 5.3 VERTICAL TRANSPORT TO GREENSAND AQUIFER

The United States Geological Survey, in cooperation with the Arkansas Department of Health, published a report which specifically addressed the susceptibility of aquifers of Union County, Arkansas to contamination (Leidy and Taylor 1992). The purposes of this investigation were to:

- "Describe the general hydrogeology and groundwater flow system of Union County;
- 2) Identify potential sources of contamination; and
- 3) Provide an overview of the susceptibility of major aquifers to contamination."

The susceptibility of the deeper aquifers to contamination was addressed in part by computational estimates of the vertical rate of movement of water through confining units. Specifically, derivations of Darcy's law were used, along with available information on confining unit thicknesses and characteristics and potentiometric surface data for the aquifers, to estimate the rates at which water moves vertically through the Cook Mountain formation and the Sparta Sand confining bed. The key variables used in making these estimates are:

- The thickness of the confining unit(s);
- The vertical hydraulic conductivity of the confining unit(s);
- The potentiometric or hydrostatic head difference between the aquifer above and the aquifer below the confining unit(s); and
- The effective porosity of the confining unit(s).

Based on information presented by Leidy and Taylor (1992), the thickness of the Cook Mountain formation in the vicinity of the EDC site is 95 feet. This thickness is based on a geophysical well log for an unspecified well that is reported to be located near the city of El Dorado's Water Supply Well No. 16. The referenced well location is approximately 8,000 feet

# Woodward-Clyde

(1.5 miles) southeast of the EDC Production Area. Based on water level measurements, Leidy and Taylor reported a hydrostatic head difference between the Cockfield formation and the Greensand aquifer in the vicinity of this same well of 90 feet. Leidy and Taylor used an effective porosity value of 0.35 for the Cook Mountain formation. The final variable used in Leidy and Taylor's travel time estimates is the vertical hydraulic conductivity of the Cook Mountain formation: this was assigned a value of  $3.0 \times 10^{-4}$  feet per day (1.06 x  $10^{-7}$  cm/sec).

Using Leidy and Taylor's Equation 2 and the above values, Woodward-Clyde estimates the travel time for water to move vertically through the Cook Mountain formation in the vicinity of the EDC plant to be approximately 320 years. However, Woodward-Clyde notes that the vertical hydraulic conductivity value used by Leidy and Taylor is in the very upper end of values used by McWreath *et al.* and Fitzpatrick *et al.* in their models. These authors used a much lower vertical hydraulic conductivity value of  $9 \times 10^{-6}$  feet per day (3.18 x  $10^{-9}$  cm/sec) for the areas in and around Union County, Arkansas. With this conductivity value and the other variables assigned as above, Woodward-Clyde estimates that the travel time for water to move through the Cook Mountain formation increases to 10,680 years.

The above information on the time required for groundwater to move from the Cockfield formation through the Cook Mountain formation aquitard to the Sparta aquifer is such that movement of dissolved constituents from the Cockfield formation to the Sparta aquifer should not be of concern.

The location of the nearest downgradient city of El Dorado public supply well is shown in Figure D-3.2. This well is 700 feet deep and completed in the El Dorado aquifer as discussed in Section 2.2.2. The travel time calculations above are to the top of the Greensand aquifer in the Sparta Sand at approximately 300 feet below ground surface. The public supply well is completed approximately 400 feet deeper in the El Dorado aquifer of the Sparta Sand which is separated from the Greensand aquifer by the Sparta aquifer middle confining bed. Therefore, additional travel time will be required if the nitrate migrates vertically through the Cook Mountain formation (100 feet) and the uppermost 400 feet of the Sparta aquifer. Based on the fate and transport model developed for the Cockfield formation, the maximum concentration of nitrate that could migrate horizontally in the shallow Cockfield formation to the location of the

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nearest downgradient public supply well is 4.3 mg/L and would require approximately 3,000 years. Throughout the vertical travel distance of 700 feet, dispersion and attenuation mechanisms would further reduce the concentration of the nitrate in groundwater below 4.3 mg/L.

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## Woodward-Clyde

### 6.0

### SENSITIVITY ANALYSIS OF INPUT PARAMETERS ON MODEL RESULTS

As stated in the *Work Plan*, a sensitivity analysis was conducted on four of the modeling input parameters. Woodward-Clyde conducted sensitivity analyses for:

- hydraulic conductivity,
- longitudinal and lateral dispersivity,
- retardation factor and half-life.

The purpose of the sensitivity analyses is to evaluate how sensitive the model is to a particular input parameter. For each parameter evaluated, the change in the model result was compared to the relative amount by which the parameter was changed. A general evaluation of the uncertainty of the modeled results based on the sensitivity to the identified input parameters is discussed below.

### 6.1 HYDRAULIC CONDUCTIVITY SENSITIVITY ANALYSIS

A sensitivity analysis was conducted for the saturated hydraulic conductivity.

### 6.1.1 Increase Hydraulic Conductivity

The hydraulic conductivity was increased by an order of magnitude. Increasing the hydraulic conductivity one order of magnitude increases the seepage velocity of the groundwater by one order of magnitude. Because dispersion is the only attenuation mechanism that was modeled in the simulation, increasing the hydraulic conductivity only decreases the time (from 3,000 to 300 years) at which the maximum concentration of nitrate is predicted to reach the receptor point, but the maximum concentration of 2.8 mg/L is not changed.

### 6.1.2 Decrease Hydraulic Conductivity

Similarly, as described in Section 6.1.1, decreasing the hydraulic conductivity one order of magnitude increases the time (from 3,000 to 30,000 years) at which the maximum concentration of nitrate is predicted to reach the receptor point, but the maximum concentration is still 2.8 mg/L.

### 6.2 DISPERSIVITY SENSITIVITY ANALYSIS

A sensitivity analysis was also performed on longitudinal dispersivity. The longitudinal dispersivity was decreased to one-fifth of the base case value. When longitudinal dispersivity was changed, lateral dispersivity was also changed accordingly because it is calculated to be 10 percent of the longitudinal dispersivity term. Decreasing the dispersivity increases the time (from 3,000 to 3,500 years) at which the maximum concentration of nitrate is predicted to reach the receptor point. The maximum concentration at the receptor point increased from a base case value of 2.8 mg/L to a sensitivity analysis modeled value of 4.1 mg/L which is also below the MCL of 10 mg/L.

### 6.3 ATTENUATION FACTORS SENSITIVITY ANALYSIS

The transport of a dissolved solute such as nitrate is by means of advective transport with the groundwater and varying degrees of retardation of the solute transport relative to the water due to attenuation by mechanisms such as sorption (most probably by ion exchange) and degradation. Consequently, the solute is expected to move at a slower velocity than the groundwater and some of the solute is expected to be retained on the soil particles of the aquifer matrix or destroyed by degradation reactions (such as denitrification or incorporation in biomass).

The only attenuation mechanism modeled in the base case simulations was dispersion. A sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of

sorption (most probably by ion exchange) and degradation. The results of these sensitivity analyses are described below.

### 6.3.1 Retardation Factor

Sorption is described in the Solute Plume2D model by the retardation factor, R. The retardation factor is a ratio of the average linear groundwater velocity to the velocity of the contaminant. Therefore, an R value of 1 indicates no retardation due to sorption and R was set equal to one in the base case simulations. As the value of the retardation factor in the model increases, sorption of the contaminant decreases the velocity of the contaminant relative to the groundwater. To evaluate the effect of sorption on the predicted maximum concentrations of nitrate reaching the receptor well, the retardation factor was increased over the range from 1 to 5. Tabulated results of the retardation sensitivity analysis are presented below and in Figure D-6.4. As shown in Figure D-6.4, as the retardation factor is increased, the maximum concentration which could reach the nearest downgradient commercial well decreases.

Retardation Factor	Maximum Concentration at Nearest Downgradient Commercial Well (mg/L)
1	2.8
2	1.28
3	0.93
5	0.54

**Results of Retardation Factor Sensitivity Analysis** 

Therefore, any sorption which is occurring insitu will further decrease the concentration of nitrate in the groundwater below the 2.8 mg/L concentration predicted by the base case model which included no retardation due to sorption mechanisms.

### 6.3.2 Decay Rate

Attenuation due to decay (degradation) is described in the Solute Plume2D model using a firstorder decay constant, l, so that:

$$\frac{dc}{dt} = \lambda c$$

where c is the concentration of the contaminant and t is time. In the above equation,  $1 = \ln(2)/t_{1/2} = 0.693/t_{1/2}$ , where  $t_{1/2}$  is the half-life of the contaminant.

The base case simulation was performed assuming no degradation of the nitrate in groundwater. To evaluate the effect of degradation on the predicted maximum concentrations of nitrate reaching the receptor well, the decay rate, l, was increased over the range from 0 to 0.00001 days⁻¹ (half-life from infinity to 190 years). Tabulated results of the retardation sensitivity analysis are presented below and in Figure D-6.5. As shown in Figure D-6.5, as the decay rate is increased, the maximum concentration which could reach the nearest downgradient commercial well decreases substantially.

Decay Rate (days ⁻¹ )	Maximum Concentration at Nearest Downgradient Commercial Well (mg/L)
0	2.8
0.0000001	2.5
0.000001	0.94
0.00001	0.002

### **Results of Decay Rate Sensitivity Analysis**

Therefore, any degradation which is occurring insitu will further decrease the concentration of nitrate in the groundwater below the 2.8 mg/L concentration predicted by the base case model which included no attenuation due to first-order decay mechanisms.

#### 6.4 CONCLUSIONS FROM SENSITIVITY ANALYSIS

Based on the results of the sensitivity analysis, the input parameter which had the greatest effect on the horizontal model results was the saturated hydraulic conductivity because it linearly increased or decreased the time required for transport of nitrate. However, it did not increase the maximum concentration of nitrate predicted to reach the nearest downgradient commercial well.

Finally, in all of the simulations performed during the sensitivity analysis, the maximum concentration at the commercial well was predicted to remain below the MCL of 10 mg/L. The maximum concentration predicted to reach the receptor well was 4.1 mg/L at 3,500 years in the dispersivity sensitivity analysis.

The only attenuation mechanism modeled in the base case simulations was dispersion. Sensitivity analyses were performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation. As sorption increases (modeled by increase in the retardation factor, R), the maximum concentration which could reach the nearest downgradient commercial well decreases from the base case maximum concentration of 2.8 mg/L (R=1) to a maximum concentration of 0.54 mg/L (R=5). Nitrate may also be destroyed by degradation reactions such as denitrification. These degradation mechanisms were modeled in the sensitivity analysis using a first-order rate equation. In the base case simulation, the decay constant was equal to zero so no decay of the nitrate was modeled. In the sensitivity analysis, the decay constant was increased from 0 to 0.00001 days⁻¹. As the decay rate increases (modeled by decreasing the half-life of the nitrate), the maximum concentration which could reach the nearest downgradient commercial well decreases from the base case maximum concentration of 2.8 mg/L (no decay) to a maximum concentration of 0.002 mg/L with the decay constant equal to  $0.00001 \text{ days}^{-1}$  (a half-life of 190 years). Therefore, any attenuation through decay or sorption which is occurring insitu will further decrease the concentration in the groundwater below the 2.8 mg/L concentration predicted by the base case model which included no attenuation mechanisms other than dispersion.

### 7.0 CONCLUSIONS

The technical approach for the contaminant fate and transport modeling is described in the Development of Risk-Based Target Monitoring Levels Work Plan (WCC 1996).

Horizontal transport modeling was used to evaluate the potential transport of nitrate in the groundwater to potential groundwater use locations. The International Ground Water Modeling Center's (IGWMC) Solute Program Package, Analytical Model for Transport of a Solute Plume from Point Sources in a Uniform Two-Dimensional Groundwater Flow Field (Plume2D) was used to simulate the transport of the nitrate horizontally with groundwater to the receptor locations. The horizontal transport modeling was also used to calculate a nitrate attenuation factor for transport of nitrate from the site to a receptor. The attenuation factor was then used to calculate the TML for on-site monitor wells.

The Phase II groundwater investigation conducted at the site concluded that, based on nitrate concentrations in excess of the EPA MCL at ten monitoring locations in the monitoring interval of the Cockfield formation, nitrate in groundwater remains a potential concern for the EDC site. As nitrate was the only constituent determined to be present in the groundwater above primary MCLs, it was the only constituent of concern identified for fate and transport modeling. The source configuration for the nitrate used within the contaminant fate and transport modeling grid was trial-and-error fit to represent current site conditions. Site-specific values for the saturated monitoring interval thickness and saturated hydraulic conductivity were used in the model. Hydraulic gradient of the Cockfield formation in the site vicinity was obtained from an Arkansas Geological Commission document (1988).

As described in the *Work Plan*, off-site residents could have the potential for exposure to siterelated groundwater if nitrate from the site migrates in the groundwater to a well used for drinking water. A well search was made of the Arkansas Geological Commission Well Drilling report files. The search identified the nearest commercial well downgradient from the site to be located approximately 1.3 miles from the EDC site as shown in Figure D-3.2. This nearest downgradient commercial well was identified as a receptor point for the horizontal fate and transport modeling.

The base case nitrate horizontal transport scenario developed for the EDC site was non-steady state and the nitrate concentration in the groundwater continues to change with time. As time increases, the nitrate plume moves farther from the initial source location at the site. A maximum nitrate concentration of 2.8 mg/L is simulated to reach the nearest downgradient commercial well in approximately 3,000 years. At times greater than 3,000 years, the concentration of nitrate at the nearest downgradient commercial well decreases. Based on the horizontal transport modeling, the nitrate MCL of 10 mg/L will not be exceeded at the identified receptor location.

The only attenuation mechanism modeled in the base case simulations was dispersion. A sensitivity analysis was performed on the inclusion of additional attenuation mechanisms in the simulation. Separate simulations were performed with the addition of the mechanisms of sorption (most probably by ion exchange) and degradation (denitrification or incorporation in biomass).

- <u>Sorption</u>: As sorption increases (modeled by increase in the retardation factor, R), the maximum concentration which could reach the nearest downgradient commercial well decreases from the base case maximum concentration of 2.8 mg/L (no sorption) to a concentration of 0.54 mg/L (R=5).
- <u>Degradation</u>: As the decay rate increases, the maximum concentration which could reach the nearest downgradient commercial well decreases from the base case maximum concentration of 2.8 mg/L (no decay) to a maximum concentration of 0.002 mg/L with the half life equal to 190 years.

Therefore, any attenuation through decay or sorption which is occurring insitu will further decrease the concentration in the groundwater below the 2.8 mg/L concentration predicted by the base case model which included no attenuation mechanisms other than dispersion.

The generalized modeling cross-section for the EDC site is shown in Figure 5.1 of the report to which this appendix is attached. The local geology beneath the EDC site to the base of the Cook Mountain formation consists of the following:

- A thin veneer of Quaternary-aged alluvial sediments
- Tertiary-aged Cockfield formation (part of Claiborne Group)
- Cook Mountain formation (clay confining unit)

The geology below the Cook Mountain formation includes the following:

- Sparta Sand (contains Greensand aquifer, middle confining bed and El Dorado aquifer)
- Cane River formation (clay confining unit)

The horizontal transport model was developed for the EDC monitoring interval of the Cockfield formation. The location of the nearest downgradient City of El Dorado public supply well is shown in Figure D-3.2. This well is 700 feet deep and completed in the El Dorado aquifer which is below the Greensand aquifer. This public supply well has been identified as the potential receptor point for vertical migration of nitrate from the Cockfield formation through the Cook Mountain formation confining unit into the Greensand aquifer. Vertical migration was addressed qualitatively using travel time calculations.

Using values of hydraulic conductivity by McWreath *et al.* and Fitzpatrick *et al.* of  $9 \ge 10^{-6}$  feet/day, a formation thickness of 95 feet, an effective porosity of 0.35, a vertical gradient of 0.9474 feet/feet, the travel time for water through the Cook Mountain formation is approximately 10,680 years. This travel time calculation is for water to reach the top of the Greensand aquifer interval of the Sparta Sand at approximately 300 feet below ground surface. The potential receptor well, the city of El Dorado public supply well, is completed approximately 400 feet deeper in the El Dorado aquifer interval of the Sparta Sand. The Greensand aquifer is separated from the El Dorado aquifer by the Sparta aquifer middle confining bed. Therefore, additional travel time would be required if the nitrate migrated

vertically through the Cook Mountain formation (100 feet) and the uppermost 400 feet of the Sparta aquifer.

Based on the fate and transport model developed for the Cockfield formation, the maximum concentration of nitrate that would migrate horizontally in the shallow Cockfield formation to the location of the nearest downgradient public supply well is 2.8 mg/L. If the nitrate migrated through the lower portions of the Cockfield formation, through 95 feet of the Cook Mountain formation, and then through 400 feet of the Sparta Sand to the El Dorado aquifer, additional attenuation of the nitrate would occur through degradation and sorption. If the nitrate reached the top of the Sparta Sand, it would be further attenuated as it migrated vertically through the Greensand aquifer and the Sparta middle confining unit before reaching the El Dorado aquifer. Throughout this vertical travel distance (to a depth of 700 feet below ground surface), dispersion and attenuation mechanisms would further reduce the concentration of the nitrate in groundwater below 2.8 mg/L.

The results of the nitrate horizontal fate and transport modeling are conservative and the modeled concentrations which have been generated by the simulations are expected to be higher than the concentrations which will actually occur. Several conservative assumptions were used to develop the base case model scenario:

- The base case scenario simulated no attenuation of the nitrate due to sorption or degradation mechanisms. The transport of nitrate in groundwater is likely to be retarded by sorption (most probably by ion exchange). Additionally, nitrate is subject to degradation (denitrification or incorporation in biomass). As shown in the sensitivity analysis, both of these insitu attenuation mechanisms will further decrease the concentrations of nitrate in groundwater as it is transported.
- The analytical model selected for the simulation, Plume2D, is a twodimensional model. Dispersion was only simulated in the longitudinal and lateral (or transverse) directions. No vertical dispersion of the nitrate to the lower portions of the Cockfield formation was simulated. Dispersion is an anisotropic process and some vertical dispersion will occur as the nitrate

migrates. Any amount of vertical dispersion, within the Cockfield formation, will further decrease the concentrations of nitrate in groundwater.

• Groundwater flow directions in the Cockfield formation are influenced by topographic surface features. As a conservative estimate, the shortest path (distance) between the EDC site and the nearest downgradient commercial well was modeled as the groundwater flow direction. The actual flow path is probably longer, giving more time for attenuation due to dispersivity, degradation, and sorption effects.

In the base case scenario and all sensitivity analyses, the maximum concentration at the commercial well was predicted to remain below the MCL of 10 mg/L.

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**TABLES** 

### TABLE D-3.1

### DESCRIPTION OF HYDROGEOLOGIC UNITS IN THE STUDY AREA **DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS**

System	Series	Group	Formation	Hydrogeologic Unit	Hydrogeologic Properties
Quaternary	Holocene and Pleistocene		Alluvial and terrace deposits		Clay, silt, sand, and gravel. Present only in bottomlands of most streams. Generally not used. As much as 100 feet thick.
	Co		Cockfield Formation	Cockfield aquifer	Lignitic sand with interbedded clay. Principal aquifer for rural domestic supply. Approximately 200 feet thick where present.
			Cook Mountain Formation	Cook Mountain confining unit	Clay with interbedded fine sand. Not an aquifer. Thickness ranges from 50 to 200 feet.
Tertiary Eocene C	ne Claiborne		Greensand aquifer	Thinly bedded fine glauconitic sand with interbedded clay. Source of municipal and industrial water supply principally in southeast part of county. Water withdrawals approximately 0.5 million gallons per day. Approximately 200 feet thick.	
			Sparta Sand	Middle confining bed	Clay and silt. Not an aquifer. Thickness ranges from 40 to 160 feet.
				El Dorado aquifer	Thickly bedded medium to coarse sand. Source of municipal and industrial water supply throughout the county. Water withdrawals approximately 14 million gallons per day. Approximately 300 feet thick.
			Cane River Formation	Cane River confining unit	Clay and silty clay. Not an aquifer. Approximately 300 feet thick.
					From Leidy and Taylor, 1992

12/4/97

### TABLE D-4.1

## SOLUTE PLUME 2D TRANSPORT MODEL BASE CASE INPUT DATA DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY, EL DORADO, ARKANSAS

	PARAMETER	VALUE	UNITS	REFERENCE
	Groundwater (Seepage) velocity	0.008867	feet/day	
oter	Saturated monitoring interval thickness	18.83	feet	Arithmetic average of site data
ame	Effective porosity	0.3		Work Plan
Par	Longitudinal dispersivity	980	feet	Work Plan (10% of travel distance)
ical	Lateral dispersivity	98	feet	Work Plan (10% of longitudinal dispersivity)
hys	Retardation factor	1		No retardation
	Half-life	0		No decay
	X-coordinate of origin	0	feet	
2	Y-coordinate of origin	0	feet	
id	D x	1000	feet	
ran G	D y	1000	feet	
Pa	nodes in x direction	35		
	nodes in y direction	14		

### TABLE D-4.2

### SATURATED THICKNESS DETERMINATION DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Monitoring Well No.	Total Well Depth (ft)	Depth to Groundwater (ft)	Saturated Zone Thickness (ft)
MW-EDC-1	22.1	10.07	12.03
MW-EDC-2	20.2	0.45	19.75
MW-EDC-3	27.1	9.31	17.79
MW-EDC-4	22.1	7.64	14.46
MW-EDC-5	17.7	5.22	12.48
MW-EDC-6	22.0	4.79	17.21
MW-EDC-7	23.9	7.81	16.09
MW-EDC-8	29.9	8.06	21.84
MW-EDC-9	30.0	9.11	20.89
MW-EDC-10	22.6	13.18	9.42
MW-EDC-11	19.8	10.65	9.15
MW-EDC-12	19.9	6.70	13.20
MW-EDC-13	19.8	10.30	9.50
MW-EDC-14	18.2	8.23	9.97
MW-EDC-15	17.0	5.13	11.87
MW-EDC-16	19.3	5.60	13.70
MW-EDC-17	34.7	26.92	7.78
MW-EDC-18	17.2	5.41	11.79
	13.83		

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**FIGURES** 





# EL DORADO CHEMICAL COMPANY

Contour Interval: 10 feet except where shown.							
Wooc Engineening & s	Woodward-Clyde Consultants Engineering & sciences applied to the earth & its environment 900 S. Shacklefore Suite 412 Little Rock. Arkansas 72211						
	Development of Risk Based Target Monitoring Levels						
SCALE	SCALE MADE BY GAT DATE 04/01/96 FILE NO						
1" = 1.000'	CHECKED BY EF	DATE	978061				
	FIGURE D-3.1						



LEGEND

- Shallow Domestic Well in Cockfield Formation
- Public Supply 700' Deep Well in Sparta Aquifer
- Shallow Commercial Well in Cockfield Formation



	Woodward-Clyde Engineering & sciences applied to the earth & its environment			HORIZONTAL TRANSPORT MODEL GRID	FILE NO. 97B061-13
ELID <b>O</b> IR/AIDO	Baton Rouge, Louisiana				FIG. NO.
CHEMICAL COMPANY	SCALE:	DRAWN BY: D.OLSON	DATE: 10/24/97		
	AS SHOWN	CHKD. BY: D. REECE	DATE: 10/27/97		D-3.2







### SENSITIVITY ANALYSIS: INCREASE HYDRAULIC CONDUCTIVITY DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



### SENSITIVITY ANALYSIS: DECREASE HYDRAULIC CONDUCTIVITY DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



### SENSITIVITY ANALYSIS: DECREASE DISPERSIVITY DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



### SENSITIVITY ANALYSIS: RETARDATION FACTOR DEVELOPMENT OF RISK-BASED TARGET MONITORING LEVELS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS



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## ATTACHMENT D-1

# SLUG TEST RESULTS

# Woodward-Clyde **Consultants**

SUBJECT: EDC AQUIFER TESTING

by: EJF Date: 12-20-96

# **Project Notes**

Project Name: EDC Project No.: 958165 Task No.: RA File No.: Sheet 1 of 3

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MW-18 (TEST =1)



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# Woodward-Clyde C

# **Project Notes**

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