

**NUMERICAL GROUNDWATER FATE AND TRANSPORT  
MODELING REPORT**

**Interim Certification Application Support  
Omya Inc., Verpol Plant TMAs  
Florence, Vermont**

*Prepared for*  
**Omya Inc.**

*Prepared by*  
**Sanborn, Head & Associates, Inc.**

File 2461.01  
December 2005  
Revised June 2006

## TABLE OF CONTENTS

1.0	INTRODUCTION .....	1
1.1	Background .....	1
1.2	Objective .....	2
1.3	Scope of Services .....	3
2.0	MODELING APPROACH.....	4
3.0	SCREENING AND SELECTION OF CONSTITUENTS.....	5
4.0	SELECTION OF MODEL PARAMETERS.....	7
4.1	Flow and Transport Parameters .....	7
4.1.1	Hydraulic Gradient.....	8
4.1.2	Hydraulic Conductivity.....	8
4.1.3	Total and Effective Porosity .....	8
4.1.4	Seepage Velocity.....	9
4.1.5	Longitudinal and Transverse Dispersivity .....	9
4.2	Species Parameters.....	10
4.2.1	Initial Concentration .....	11
4.2.2	Diffusion Coefficient .....	11
4.2.3	Retardation Factor.....	12
4.2.4	First-Order Decay Rate .....	13
5.0	ANALYTICAL MODELING .....	14
6.0	NUMERICAL MODELING .....	15
6.1	Model Development.....	16
6.1.1	Governing Equations.....	16
6.1.2	Discretization .....	17
6.1.3	Boundary Conditions .....	18
6.2	Model Simulations .....	18
6.2.1	Base Case Results .....	20
6.2.2	Sensitivity Analysis Results.....	20
7.0	SUMMARY OF FINDINGS .....	21
8.0	LIMITATIONS.....	22

## TABLE OF CONTENTS (cont.)

### TABLES

Table 1	Evaluation of Numerical Modeling Constituents
Table 2	Summary of Numerical Modeling Parameters

### FIGURES

Figure 1	Decision Tree: Constituents for Fate and Transport Modeling
Figure 2	Base Case Model Layout
Figure 3	Sensitivity Analysis Model Layout
Figure 4a	Acetone Base Case
Figure 4b	Acetone Base Case: Centerline of Steady State Plume
Figure 5a	Acrylamide Base Case
Figure 5b	Acrylamide Base Case: Centerline of Steady State Plume
Figure 6a	TOHI Base Case
Figure 6b	Amine Acetate Base Case
Figure 6c	AEEA Base Case
Figure 6d	Custamine 51D Flotation Reagent Base Case: Centerline of Steady State Plume
Figure 7a	Acetone Sensitivity Analysis
Figure 7b	Acetone Sensitivity Analysis: Centerline of Steady State Plume
Figure 8a	Acrylamide Sensitivity Analysis
Figure 8b	Acrylamide Sensitivity Analysis: Centerline of Steady State Plume
Figure 9a	TOHI Sensitivity Analysis
Figure 9b	Amine Acetate Sensitivity Analysis
Figure 9c	AEEA Sensitivity Analysis
Figure 9d	Custamine 51D Flotation Reagent Sensitivity Analysis: Centerline of Steady State Plume

## **1.0 INTRODUCTION**

On behalf of Omya Inc. (Omya), Sanborn, Head & Associates, Inc. (SHA) prepared this report to summarize our services and findings related to three-dimensional numerical groundwater flow and transport modeling completed in support of the Interim Certification Application (Application) for the tailings management areas (TMAs) at the Omya Verpol Plant in Florence, Vermont. We understand that this report will be submitted to the Vermont Department of Environmental Conservation (VTDEC), Solid Waste Program, and possibly to a third-party, for technical evaluation as part of the Application review process.

Our numerical modeling effort was based on our understanding of site conditions related to groundwater flow and transport, which was developed in consideration of the site characterization data, information, and inferences presented by Heindel & Noyes, Consulting Scientists and Engineers (Heindel & Noyes) in their August 15, 2005 Site Characterization Report submitted as part of the Application (i.e., Volume II).

### **1.1 Background**

The TMAs are used to store tailings product generated from ground calcium carbonate production processes at the Omya Verpol Plant. The tailings product has been stockpiled directly on the carbonate bedrock underlying the site in former quarry areas since the late 1970s. Groundwater is found at the site in the underlying Ordovician Age Shelburne Limestone, which is reported to exhibit dissolution-enlarged fractures in localized areas. Groundwater monitoring wells are located over an approximately 250-acre area between two topographic ridges that run roughly north to south on the east and west borders of the site. The site wells are constructed as open holes in bedrock that intersect fractures at varying depths from about 20 to 420 feet below grade in various locations, including within and hydraulically downgradient of the TMAs. The hydraulically downgradient wells are situated between the TMAs and surface drainage features located as far as 2,000 to 4,000 feet north of the TMAs, which are considered points of groundwater discharge according to Heindel & Noyes' conceptual hydrogeologic model of the site.

As further discussed in Section 3.0 of this report, the tailings product constituents of interest relative to groundwater flow and transport are Omya's organic flotation reagent "Custamine 51D" (Custamine), as well as Acetone and Acrylamide, which may be present in the TMAs as incidental/refractory constituents. The organic constituents of Custamine include: (i) Tall Oil Hydroxyethyl Imidazoline [TOHI - 91 percent by mass]; (ii) Amine Acetate [AA - 7.5 percent by mass]; and (iii) Aminoethyl-Ethanolamine [AEEA - 1.5 percent by mass]. TOHI, AA, AEEA, Acetone, and Acrylamide are collectively referred to herein as the "species of interest."

A limited assessment of environmental fate of the Custamine compounds performed by Golder Associates, Inc. (Golder)<sup>1</sup> indicates that TOHI, AA, AEEA are readily biodegradable in the subsurface with half-lives of less than 30 days. TOHI and AA were indicated to readily sorb onto geologic materials with reported retardation factors in the site environment of about 1,600 to 1,800. Golder's findings indicated the potential for sorption and degradation of the compounds to significantly limit groundwater transport downgradient of the TMAs. Golder's findings are supported by several years of water quality monitoring data at the site that indicate the general absence of the Custamine flotation reagent (and the other species of interest) in groundwater and surface water samples collected from monitoring locations at and near the site despite over 25 years of similar on-site tailings product storage.

## 1.2 Objective

The VTDEC, Solid Waste Program requested that Omya perform numerical groundwater flow and transport modeling to assess possible subsurface transport of tailings product constituents in groundwater from the TMAs at the Omya Verpol Plant. The purpose of the numerical modeling is to assess potential "fate and transport of the chemicals present in [potential] leachate"<sup>2</sup> relative to the Design Management Zone (DMZ)<sup>3</sup> boundary. Under VTDEC Solid Waste Management Procedures (Procedures) such modeling is a normal requirement to "demonstrate that the design of the solid waste unit ensures compliance with the ground water quality standards...at the Design Management Zone ("DMZ") boundary."<sup>4</sup> The specific performance goal established in the Procedures is no exceedance of "any groundwater quality standard at the DMZ boundary at any point in time" for the base condition of the model.<sup>5</sup> The spatial relationship between the TMAs, the DMZ, and the site monitoring well network is indicated on the figure provided as Page 1 of Appendix 8 of Volume II of the Application.

The objective of our services was to develop and apply a numerical groundwater flow and transport model to simulate advective solute transport of the species of interest in consideration of the possible effects of physical/chemical sorption, biochemical degradation, and variable hydrodynamic dispersion. The intent of the modeling effort was to augment Golder's previous analytical modeling while further supplementing Heindel & Noyes' field-based assessment of groundwater chemistry that indicates the general absence of the species of interest in

---

<sup>1</sup> Golder Associates, Inc., "Report on Custamine 51D Flotation Reagent Use at the Omya Verpol Plant", August 2005, which was included in Appendix 8 of Volume II of the Application.

<sup>2</sup> Procedure, Solid Waste Landfill Design, Section III.

<sup>3</sup> For solid waste landfills, the DMZ is defined as having a distance no greater than one-third the distance from the waste facility boundary to the property line (Groundwater Protection Rule and Strategy, Section 12-802), but no more than 150 meters (about 492 feet) (Procedure, Solid Waste Landfill Design, Section III).

<sup>4</sup> Procedure, Solid Waste Landfill Design, Section III.

<sup>5</sup> Ibid, Step 6.

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

groundwater and surface water downgradient of the existing TMAs. Our approach to the modeling, as outlined in more detail below, was developed in consideration of the available site characterization data collected by Heindel & Noyes, VTDEC requirements, and our understanding of the nature of the chemical constituents and the anticipated scale of transport relative to the DMZ boundary.

### **1.3 Scope of Services**

To meet the above-stated objective, SHA completed the following scope of services:

- Review of the site characterization data and hydrogeologic inferences compiled by Heindel & Noyes for adequacy in supporting the modeling effort and to independently assess the range of probable hydraulic/aquifer properties and physical/chemical properties pertinent to groundwater flow and transport.
- Development of a modeling approach consistent with VTDEC requirements. The modeling approach is described under Section 2.0 of this report and in our interim memorandum dated August 10, 2005, which was submitted to the VTDEC for review and approval.
- Development of a screening process to select model constituents. The selection of model constituents is described under Section 3.0 of this report and in our interim memorandum dated September 14, 2005, which was submitted to the VTDEC for review and approval.
- Selection of flow and transport model parameters and completion of preliminary analytical modeling. The selection of model parameters and preliminary analytical modeling are described under Sections 4.0 and 5.0 of this report and in our interim memoranda dated October 14, 2005 and November 15, 2005, which were submitted to the VTDEC for review and approval.
- Development and application of a numerical groundwater flow and transport model using “Base Case” and “Sensitivity Range” parameter assumptions. The development and application of the numerical model is described under Section 6.0 of this report and in our interim memorandum dated November 21, 2005, which was submitted to the VTDEC for review and approval.
- Preparation of this final report to summarize our services and findings related to the numerical groundwater flow and transport modeling. The information contained in this final report supercedes the information presented in our interim memoranda.

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

In addition, SHA met with VTDEC representatives in Waterbury, Vermont on:

- September 7, 2005 to discuss our modeling approach and selected model constituents.

Based on the information contained in our interim memoranda dated August 10 and September 14, 2005 and our discussions during the September 7, 2005 meeting, the VTDEC concurred with our modeling approach and the selected model constituents as documented in the VTDEC's October 3, 2005 letter to Omya.

- November 7, 2005 to discuss our selected flow and transport model parameters and preliminary analytical modeling.

Based on the information contained in our interim memoranda dated October 14 and November 15, 2005 and our discussions during the November 7, 2005 meeting, the VTDEC concurred with our selected flow and transport model parameters as documented in the VTDEC's November 22, 2005 letter to Omya.

- December 5, 2005 to discuss our development and application of the numerical model and our associated findings.

Based on the information contained in our interim memorandum dated November 21, 2005 and our discussions during the December 5, 2005 meeting, the VTDEC acknowledged its understanding of the model and our findings, and orally agreed that SHA should proceed with the preparation of this final report.

## **2.0 MODELING APPROACH**

SHA constructed and applied a 'parametric' model to simulate numerically the possible groundwater transport of the organic components of the tailings product present in the TMAs, including the organic constituents of Custamine (TOHI, AA, and AEEA), Acetone, and Acrylamide (i.e., the species of interest). The term 'parametric' is used to denote that the modeling was performed to assess possible transport distance in groundwater considering the range of probable hydrogeologic properties indicated by the available site characterization data and a range of geochemical properties relevant to fate and transport of the key constituents ('parameters'). In addition, a sensitivity analysis was performed to assess the potential magnitude of transport in groundwater under a broader set of parameters in accordance with our understanding of VTDEC requirements. The VTDEC concurred with our modeling approach in a letter to Omya dated October 3, 2005.

Our approach to modeling was developed in consideration of the following:

- The available site characterization data, including: (i) Heindel & Noyes' interpretation of a lateral groundwater flow field with a principally northerly direction of flow; (ii) the apparent lateral hydraulic gradients observed from the existing groundwater monitoring well network; and (iii) the range of hydraulic properties as estimated and measured in site characterization work performed by Heindel & Noyes.
- The probable scale of groundwater transport, with degradation and sorption significantly limiting groundwater transport downgradient of the TMAs, including the need to provide sufficient spatial model discretization where the transport solution was expected to vary considerably with distance. In other words, we constructed a tightly divided model grid system to allow for simulation of steep concentration gradients.
- The need to simulate advective solute transport of the species of interest in consideration of the possible effects of physical/chemical sorption, biochemical degradation, and variable hydrodynamic dispersion.
- The need to perform a sensitivity analysis considering the apparent variability of aquifer properties and uncertainties associated with physical and chemical properties pertinent to the modeling objectives.

### 3.0 SCREENING AND SELECTION OF CONSTITUENTS

SHA developed and implemented the screening process outlined on Figure 1 to select tailings product constituents to model based on the available site characterization data and in the context of the aforementioned modeling objectives and VTDEC requirements. The resulting list of constituents selected for numerical flow and transport modeling included: Acetone, Acrylamide, TOHI, AA, and AEEA, or the "species of interest". The VTDEC concurred with our selected model constituents in a letter to Omya dated October 3, 2005. Analytical data and toxicological information supporting our selection of model constituents are summarized in Appendices 3, 5, 6, and 7 of Volume II of the Application, and analytical laboratory data reports are provided in Addenda A, B, and C of Volume II of the Application.

Mass balance<sup>6</sup> and analytical data available for samples of tailings product solids, tailings product pore water, and liquid from the tailings product were used to generate an initial list of substances identified and/or potentially present in the TMAs as shown in Table 1. The initial list was reviewed against analytical data available for samples of the tailings product pore water;

---

<sup>6</sup> "Mass balance" data refer to estimated concentrations calculated by Omya based on the actual usage of the constituent in production processes. Our understanding is that Omya will provide the VTDEC with a copy of the mass balance calculations, but due to the confidentiality of this information, these calculations are not provided in the Application.

**\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\***

liquid extracted from the tailings product (i.e., 'leachate', which was extracted using modified TCLP procedures [pH=7.8]); groundwater; and surface water because these data are considered to indicate the constituents that may be subject to groundwater transport rather than those that are strongly sorbed to the tailings product itself and/or insoluble.

Constituents identified and/or considered to be potentially present in the TMAs began as candidates for numerical flow and transport modeling. The first constituents removed from further consideration were those that were not expected to be typically present in the tailings product, but rather were related to an isolated incident, such as an historic accidental release. Ortho-phenylphenol (OPP) and methyl isothiocyanate (MITC) were eliminated on this basis. It is noted, nonetheless, that OPP and MITC are expected to exhibit fate and transport properties within the range of those of the constituents retained for modeling.

OPP is not typically associated with the tailings product, but was present in some of the tailings product as a result of an accidental release in 2000. The OPP release was remediated in 2001 as part of a State-approved monitoring and remediation program. OPP has not been detected in groundwater since the remediation of the spill in 2001. MITC is not typically associated with the tailings product, but was present in some of the tailings product as a result of an accidental release of thione in 2003. An investigation was completed following the MITC release in collaboration with both the VTDEC Wastewater Management Division and Water Quality Division. Concentrations in the receiving on-site quarry were calculated to be below the allowable standards and acceptable for discharge. MITC has not been detected in groundwater.

The second level of screening included retaining those remaining substances with established groundwater or drinking water quality criteria and/or known or perceived toxicity. Phosphoric acid, polyacrylamide, polyacrylates, and stearic acid were therefore eliminated. Phosphoric acid and stearic acid are "Generally Recognized As Safe" (GRAS) food ingredients by the USFDA, and mass balance calculations for phosphorus suggest that its potential presence in the TMAs related to use of phosphoric acid would be at levels in the range of typical background concentrations in the natural environment. Polyacrylamide is a nontoxic polymer commonly added to drinking water systems for use as a flocculant, and is also widely used in cosmetics. Polyacrylates are nontoxic polymers commonly used in water treatment processing, contact lenses, denture materials, and textile coatings.

The third level of screening was based on the historic presence of the remaining constituents in samples of groundwater, surface water, tailings product pore water, or tailings product 'leachate', which would suggest potential mobility in groundwater. Methylamine and free chlorine were eliminated on this basis because there are no data supporting their presence in these media. In addition to being a GRAS food ingredient, stearic acid was not present in these media as well.

The fourth level of screening was based on the observed concentrations of the remaining constituents in samples of groundwater, surface water, tailings product pore water, and/or tailings product 'leachate' relative to established or estimated groundwater and/or drinking water standards. If the constituent concentrations in these media were below relevant standards, then the constituent was eliminated from further consideration because groundwater quality standards are already being met, and as such would be met at the DMZ boundary. Barium, trihalomethanes (THMs), isopropanol (IPA), and toluene were eliminated on this basis because the available data indicate that the concentrations of these constituents in the groundwater, surface water, tailings product pore water, or tailings product 'leachate' are below (i.e., satisfy) groundwater quality standards. In addition, the observed concentrations of barium are at levels consistent with naturally occurring background conditions in groundwater.

#### **4.0 SELECTION OF MODEL PARAMETERS**

To select model parameter values for use in the numerical modeling effort, SHA reviewed the available site characterization data, information, and inferences developed by Heindel & Noyes, as presented in their August 15, 2005 Site Characterization Report. In addition, SHA reviewed readily available published data and estimation methods to augment the available site characterization data, where appropriate. Site-specific data generally are preferred over literature values and were used where available. The VTDEC concurred with our selected model parameters in a letter to Omya dated November 22, 2005.

A summary of "Base Case" and "Sensitivity Range" values selected as model parameters is provided in Table 2. The "Base Case" values represent the baseline conditions, or probable values for model parameters, selected based on the available information. The "Base Case" reflects values believed to be generally representative of site conditions as inferred from direct measurements in the field or laboratory and scientific estimates developed through accepted procedures. The "Sensitivity Range" represents the broader range in values over which the sensitivity of the transport solution was evaluated. For discussion purposes, the model parameters have been separated into flow and transport parameters and species parameters as outlined below.

##### **4.1 Flow and Transport Parameters**

To model the flow and transport of dissolved species in groundwater, estimates of the following flow and transport parameters are required: hydraulic gradient, hydraulic conductivity, total and effective porosity, seepage velocity, and longitudinal and transverse dispersivity. A discussion of each of these parameters is provided below.

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

#### **4.1.1 Hydraulic Gradient**

Hydraulic gradient is the driving force in groundwater flow, as expressed as the decline in hydraulic head per distance along a flow path, commonly given in units of feet per foot (ft/ft) or meters per meter (m/m). Groundwater elevation contour plans developed by Heindel & Noyes based on measurements recorded on various dates ranging from 2001 to 2005 were reviewed to develop a “Base Case” value for hydraulic gradient (see Appendix 1 of Volume II of the Application). Particular attention was focused in the area encompassed by the DMZ, because that was the area of interest for the numerical modeling effort. A review of these data suggest an arithmetic mean hydraulic gradient of approximately 0.03 m/m in the area encompassed by the DMZ, with a range of approximately 0.02 to 0.04 m/m. As such, a “Base Case” value of 0.03 m/m was selected. The “Sensitivity Range” for this parameter is addressed under Seepage Velocity (Section 4.1.4 of this report).

#### **4.1.2 Hydraulic Conductivity**

Hydraulic conductivity is a measure of the ability of a geologic material to transmit water. Hydraulic conductivity is a constant of proportionality relating discharge per unit area to the hydraulic gradient, and is expressed in dimensions of length per unit time, commonly feet per day (ft/day) or meters per second (m/sec). Hydraulic conductivity estimates derived by Heindel & Noyes from pumping tests completed at wells 2, 5, C-2, G, and H were reviewed to develop a “Base Case” value for hydraulic conductivity (see Appendix 4 of Volume II of the Application). These estimates ranged from approximately  $3 \times 10^{-8}$  m/s to  $5 \times 10^{-6}$  m/s, and include those derived from pumping tests performed at wells within which Heindel & Noyes reported dissolution-enlarged fractures. Because hydraulic conductivity has been commonly shown to be approximately log-normally distributed, the geometric mean is considered to be a reasonable estimate of ‘average’ hydraulic conductivity. As such, the approximate geometric mean of hydraulic conductivity estimates derived by Heindel & Noyes ( $4 \times 10^{-7}$  m/s) was selected as the “Base Case” value. The “Sensitivity Range” for this parameter is addressed under Seepage Velocity (Section 4.1.4 of this report).

#### **4.1.3 Total and Effective Porosity**

Total porosity is defined as the portion of the geologic material that is void space irrespective of pore connections, whereas effective porosity is defined as the portion of the geologic material that is interconnected pore space. Accordingly, effective porosity is more closely related to hydraulic conductivity than total porosity because it implies connectivity through the geologic material. Both total porosity and effective porosity are dimensionless, and are commonly expressed as a percentage. Site-specific data regarding total and effective porosity are unavailable; therefore, published data for carbonate rocks (i.e., limestone, dolomite) similar to those present at the site were reviewed to develop “Base Case” values for total and effective porosity. Domenico & Schwartz (1990)<sup>7</sup> indicate ranges from 5% to 15% and 0.1% to 5% for

<sup>7</sup> Domenico, P.A. and F. W. Schwartz, *Physical and Chemical Hydrogeology*, Wiley, New York (1990).

total and effective porosity, respectively. The approximate midpoints of these ranges (i.e., 10% for total porosity and 3% for effective porosity) were selected as “Base Case” values. The “Sensitivity Range” for effective porosity is addressed under Seepage Velocity (Section 4.1.4 of this report), and the “Sensitivity Range” for total porosity is addressed under Retardation Factor (Section 4.2.3 of this report).

#### **4.1.4 Seepage Velocity**

Dissolved species will migrate with flowing groundwater at a velocity equal to or less than the groundwater seepage velocity by the process of advection. The groundwater seepage velocity is the estimated average rate of groundwater flow through a geologic media, whereas advection is chemical movement via groundwater flow due to the groundwater hydraulic gradient. Seepage velocity ( $V_s$ ) is estimated using the following relationship (Fetter, 1993):<sup>8</sup>

$$V_s = \frac{Ki}{n_e}$$

where:

$V_s$  = Seepage Velocity [L/T];  
 $K$  = Hydraulic Conductivity [L/T];  
 $i$  = Hydraulic Gradient [L/L]; and  
 $n_e$  = Effective Porosity [-].

Using the selected “Base Case” values for hydraulic conductivity, hydraulic gradient, and effective porosity described previously in conjunction with the above-defined relationship yields an estimated groundwater seepage velocity of approximately  $4 \times 10^{-7}$  m/s, which was selected as the “Base Case” value. To assess possible variations in hydraulic gradient, hydraulic conductivity, and effective porosity, a “Sensitivity Range” of one order of magnitude lower and higher than the “Base Case” seepage velocity (i.e.,  $4 \times 10^{-8}$  m/s to  $4 \times 10^{-6}$  m/s) was selected to evaluate the sensitivity of the numerical simulations with respect to variations in groundwater seepage velocity.

#### **4.1.5 Longitudinal and Transverse Dispersivity**

Numerous attenuation mechanisms affect the fate and transport of dissolved species and tend to decrease their advective transport velocities, concentrations, and overall mass. One such attenuation mechanism is dispersion, which tends to lower dissolved concentrations, but not remove or attenuate overall contaminant mass. Dispersion occurs due to mixing as the dissolved species is transported through a geologic material. Mixing that occurs along the direction of a flow path is referred to as longitudinal dispersion, whereas mixing that occurs in directions normal to a flow path is referred to as transverse dispersion. As represented in the advection-

---

<sup>8</sup> Fetter, C.W., *Contaminant Hydrogeology*, Prentice-Hall, New Jersey (1993).

dispersion equation, dispersivity is a parameter related to the geologic media through which dissolved species are being transported. It is not dependent on the specific species being transported.

Site-specific data regarding longitudinal and transverse dispersivity are unavailable; therefore, the following empirical power law developed by Schulze-Makuch (2005)<sup>9</sup> considering dispersivity data from 109 different authors was used to provide an estimate of longitudinal dispersivity ( $\alpha_L$ ):

$$\alpha_L = c(L)^m$$

where:

$\alpha_L$  = Longitudinal Dispersivity [L];  
 $c = 0.80$  = A Parameter Characteristic for Carbonates [ $L^{1-m}$ ];  
 $m = 0.40$  = A Scaling Exponent for Carbonates [-]; and  
 $L$  = Flow Path Length [L].

Using a flow path length of approximately 60 meters (i.e., the nearest distance from the TMAs to the DMZ in a generally downgradient direction - see the figure provided as Page 1 of Appendix 8 of Volume II of the Application) and the above-defined relationship with the parameters and scaling exponents developed by Schulze-Makuch for carbonates (e.g., limestone/dolomite) yields a longitudinal dispersivity of approximately four meters, which was selected as the “Base Case” value. Transverse dispersivity is commonly about 10% of longitudinal dispersivity (Domenico & Schwartz, 1990);<sup>10</sup> therefore, a transverse dispersivity of approximately 0.4 meters was selected as the “Base Case” value. To assess possible variations in dispersivity, “Sensitivity Ranges” of one order of magnitude lower and higher than the “Base Case” longitudinal and transverse dispersivities were selected to evaluate the sensitivity of the numerical simulations with respect to variations in dispersivity.

## 4.2 Species Parameters

To model the flow and transport of dissolved species in groundwater, estimates of the following species-specific parameters are required: initial concentration, diffusion coefficient, retardation factor, and first-order decay rate. A discussion of each of these parameters for Acetone, Acrylamide, AEEA, TOHI, and AA is provided below.

---

<sup>9</sup> Schulze-Makuch, D., “Longitudinal Dispersivity Data and Implications for Scaling Behavior”, Ground Water 43(3): 443-456 (2005).

<sup>10</sup> Domenico, P.A. and F. W. Schwartz, *Physical and Chemical Hydrogeology*, Wiley, New York (1990).

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

#### 4.2.1 Initial Concentration

The initial concentration is the mass of the species dissolved in water at the source location (i.e., within the TMAs), and is expressed in dimensions of mass per unit volume, commonly milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g/L}$ ). Laboratory data provided by Heindel & Noyes for tailings product pore water for Acetone and Acrylamide, and for liquid extracted from the tailings product (i.e., 'leachate', which was extracted using modified TCLP procedures [pH=7.8]) for constituents of the flotation reagent, were used to develop "Base Case" values for initial concentration (see Appendix 3 of Volume II of the Application). Because the laboratory data for the flotation reagent expresses the sum total concentration of TOHI, AEEA, and AA, and the various components of the flotation reagent have different fate and transport properties, the initial concentrations for the individual constituents of the flotation reagent were weighted according to their relative proportion in the flotation reagent, with TOHI at 91%, AA at 7.5%, and AEEA at 1.5% of the total concentration.

Selected "Base Case" values represent 95% upper confidence levels ("95% UCLs") of the arithmetic mean of the reported concentrations,<sup>11</sup> which were calculated from the available data using accepted statistical methods. In samples where the species was not present at concentrations above the laboratory detection limit, the 95% UCL was calculated assuming a concentration equivalent to the detection limit for that sample. "Sensitivity Ranges" consistent with the ranges of concentrations reported for each individual species (i.e., lowest to highest reported concentrations) were selected to evaluate the sensitivity of the numerical simulations with respect to variations in initial concentration.

#### 4.2.2 Diffusion Coefficient

Diffusion is a transport process in which a concentration gradient causes a solute in water to move from an area where it is present at relatively high concentration toward an area where it is less concentrated. The U.S. EPA On-line Tools for Site Assessment Calculation includes a Diffusion Coefficient Estimation tool based on the method of Hayduk and Laudie, 1974,<sup>12</sup> which was used to estimate "Base Case" diffusion coefficients in water for the species of interest. As summarized in Table 2, the "Base Case" diffusion coefficients range from about  $3 \times 10^{-10}$  square meters per second ( $\text{m}^2/\text{s}$ ) for TOHI and AA to about  $1 \times 10^{-9}$   $\text{m}^2/\text{s}$  for Acetone and Acrylamide.

As represented in the advection-dispersion equation, the hydrodynamic dispersion coefficient ( $D$ ) is defined as the sum of the molecular diffusion coefficient ( $D^*$ ) and the product of the groundwater seepage velocity multiplied by the dispersivity ( $\alpha_L V_S$ ) or 'mechanical dispersion

---

<sup>11</sup> 95% UCLs of the arithmetic mean were used to select "Base Case" values intended to represent the baseline conditions, or probable values for concentrations of potential 'leachate' from the TMAs.

<sup>12</sup> Hayduk, W. and H. Laudie, "Prediction of Diffusion Coefficients for Nonelectrolytes in Dilute Aqueous Solution", Am. Inst. Chem. Eng. 20(3): 611-615 (1974).

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

coefficient'. As such, transport due to diffusion is expected to be minor relative to transport due to advection and dispersion. Furthermore, the variations in diffusion coefficient estimates are relatively minor. Therefore, "Sensitivity Range" values were not selected for diffusion coefficients.

### 4.2.3 Retardation Factor

The mechanism of adsorption tends to slow or 'retard' the advective velocity at which dissolved organic species migrate. The amount of retardation due to physical/chemical adsorption is inversely proportional to the retardation factor ( $R_f$ ), which for dissolved organic species is estimated using the following relationship (Fetter, 1993):<sup>13</sup>

$$R_f = \frac{V_s}{V_c} = 1 + \frac{\rho_b}{n} K_d$$

where:

$R_f$  = Retardation Factor [-];  
 $V_s$  = Groundwater Seepage Velocity [L/T];  
 $V_c$  = Advective Contaminant Migration Velocity [L/T];  
 $\rho_b$  = Dry Bulk Density [M/L<sup>3</sup>];  
 $n$  = Total Porosity [-];  
 $K_d$  = Distribution Coefficient [L<sup>3</sup>/M];

and:

$$K_d = K_{oc} * f_{oc}$$

where:

$K_d$  = Distribution Coefficient [L<sup>3</sup>/M];  
 $K_{oc}$  = Organic Carbon Partitioning Coefficient [L<sup>3</sup>/M]; and  
 $f_{oc}$  = Fraction of Organic Carbon [M/M].

An  $R_f$  of one indicates that the dissolved species migrates at a velocity equal to the groundwater seepage velocity, whereas an  $R_f$  greater than one indicates that the dissolved species migrates at a velocity less than the groundwater seepage velocity.

The U.S. EPA Exposure Assessment Tool PCKOCWIN<sup>TM</sup>, which is based on Meylan et al, 1992,<sup>14</sup> was used to estimate organic carbon partitioning coefficient ( $K_{oc}$ ) values for the species of interest. In addition,  $K_{oc}$  estimates developed by Heindel & Noyes based on octanol-water partitioning coefficient ( $K_{ow}$ ) values were reviewed (see Appendix 8 of Volume II of the

<sup>13</sup> Fetter, C.W., *Contaminant Hydrogeology*, Prentice-Hall, New Jersey (1993).

<sup>14</sup> Meylan, W., P. H. Howard, and R. S. Boethling, "Molecular Topology/Fragment Contribution Method for Predicting Soil Sorption Coefficients", *Environ. Sci. Technol.* 26(8): 1560-1567 (1992).

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

Application). As summarized in Table 2,  $K_{oc}$  estimates for Acetone, Acrylamide, and AEEA range from approximately 0.03 to 10.5 liters per kilogram (L/kg), while those for TOHI and AA range from approximately  $1.6 \times 10^4$  to  $2.1 \times 10^6$  L/kg.

Using the above  $K_{oc}$  estimates, the “Base Case” value for total porosity described previously, and values of approximately 2.6 kilograms per liter (kg/L) for dry bulk density and 0.002 for fraction of organic carbon (as reported by Heindel & Noyes; see Appendix 8 of Volume II of the Application) in conjunction with the above-defined relationship yields  $R_f$  values ranging from approximately 1 to 1.2 for Acetone, Acrylamide, and AEEA; approximately 920 to 10,800 for TOHI; and approximately 820 to 108,000 for AA. These  $R_f$  values indicate that adsorption is of only limited importance as an attenuation mechanism for Acetone, Acrylamide, and AEEA; however, it is of significant importance as an attenuation mechanism for TOHI and AA.

The approximate midpoints in the ranges of  $R_f$  values estimated for each individual species were selected as the “Base Case” values. To assess possible variations in retardation, “Sensitivity Ranges” consistent with the ranges of  $R_f$  values estimated for each individual species were selected to evaluate the sensitivity of the numerical simulations with respect to variations in adsorption. These ranges in estimated  $R_f$  values include those previously presented by Heindel & Noyes and Golder.

#### 4.2.4 First-Order Decay Rate

Given the physical-chemical nature of the species of interest, microbially mediated degradation (biodegradation) is considered a significant attenuation mechanism at the site. The PBT Profiler,<sup>15</sup> which is based in part on Boethling et al, 1994,<sup>16</sup> was used to estimate approximate half-lives for the species of interest. In addition, half-life estimates indicated by Golder, Heindel & Noyes, material safety data sheets, and the International Programme on Chemical Safety<sup>17</sup> were reviewed. As summarized in Table 2, half-life estimates for Acetone and Acrylamide range from approximately 1 to 15 days, while those for AEEA, TOHI, and AA range from approximately 15 to 30 days.

These half-life values represent estimates developed for dissolved species migrating with flowing groundwater while undergoing biodegradation in the presence of available electron acceptors (e.g., oxygen). Dissolved oxygen measurements recorded by Heindel & Noyes on

---

<sup>15</sup> Environmental Science Center, “Persistence, Bioaccumulation and Toxicity Profiler, <http://www.pbtprofiler.net/>, developed under contract to the U.S. EPA Office of Pollution Prevention and Toxics.

<sup>16</sup> Boethling, R.S., Howard, P.H., Meylan, W.M., Stiteler, W., Beauman, J., and Tirado, N., “Group Contribution Method for Predicting Probability and Rate of Aerobic Biodegradation”, Environmental Science and Technology 28: 459-65 (1994).

<sup>17</sup> International Programme on Chemical Safety, Environmental Health Criteria Monographs: <http://www.inchem.org/pages/ehc.html>.

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

groundwater samples indicate that oxygen is generally available in the groundwater downgradient of the TMAs (Addendum C of Appendix 9 of Volume II of the Application). The half-life estimates are not intended to represent biodegradation within the TMAs themselves because conditions within the TMAs are different from those of the surrounding groundwater. Given the length of time that the tailings product has been in place within the TMAs (over 25 years), we anticipate that biodegradation within the TMAs may be limited by a lack of available electron acceptors (e.g., oxygen) within the TMAs or other factors. As such, half-lives extrapolated from concentration data collected from borings within the TMAs are not likely to be representative of the half-lives of these constituents in groundwater outside of the TMAs.

First-order decay rates ( $\lambda$ ) were estimated using the following relationship (Fetter, 1993):<sup>18</sup>

$$\lambda = \frac{(\ln 0.5)}{-t_{\frac{1}{2}}}$$

where:

$\lambda$  = First-Order Decay Rate [1/T]; and  
 $t_{\frac{1}{2}}$  = Half-Life [T].

Using the above half-life estimates in conjunction with the above-defined relationship yields first-order decay rates ranging from approximately 0.05 to 0.7 per day for Acetone and Acrylamide, and approximately 0.02 to 0.05 per day for AEEA, TOHI, and AA. First-order decay rates estimated from the approximate midpoints in the ranges of half-lives for each individual species were selected as the “Base Case” values. To assess possible variations in first-order decay rates, “Sensitivity Ranges” consistent with the ranges of first-order decay rates estimated for each individual species were selected to evaluate the sensitivity of the numerical simulations with respect to variations in biodegradation.

## 5.0 ANALYTICAL MODELING

Preliminary analytical modeling of the transport of Acetone, Acrylamide, AEEA, TOHI, and AA was performed to assist with the development of a numerical model domain of sufficient size and spatial discretization to simulate groundwater flow and transport in the area between the boundary of the TMAs and the DMZ. The analytical modeling was completed using a solution to the advection-dispersion-biodegradation equation along the centerline of a plume as given by Domenico & Schwartz (1990):<sup>19</sup>

<sup>18</sup> Fetter, C.W., *Contaminant Hydrogeology*, Prentice-Hall, New Jersey (1993).

<sup>19</sup> Domenico, P.A. and F. W. Schwartz, *Physical and Chemical Hydrogeology*, Wiley, New York (1990).

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

$$C(x,t) = \frac{C_o}{2} \exp \left[ \frac{x}{2\alpha_L} \left( 1 - \sqrt{1 + \frac{4\lambda\alpha_L}{V_c}} \right) \right] \operatorname{erfc} \left( \frac{x - V_c t \sqrt{1 + \frac{4\lambda\alpha_L}{V_c}}}{2\sqrt{\alpha_L V_c t}} \right) \operatorname{erf} \left( \frac{Y}{2\sqrt{\alpha_T x}} \right)$$

where:

$C(x,t)$  = Concentration at a Given Time and Distance from the Source [M/L<sup>3</sup>];  
 $C_o$  = Initial Concentration [M/L<sup>3</sup>];  
 $V_c = V_s/R_f$  = Advective Contaminant Migration Velocity [L/T];  
 $\alpha_L$  = Longitudinal Dispersivity [L];  
 $\alpha_T$  = Transverse Dispersivity [L];  
 $\lambda$  = First-Order Decay Rate [1/T]; and  
 $Y$  = Source Width [L].

The “Base Case” values identified above and in Table 2 were used in conjunction with the above equation to preliminarily assess the possible scale of transport for the species of interest. To approximate steady-state conditions (i.e., stable conditions that do not change or that change insignificantly over time), a time of 10,000 days (about 27.5 years) was considered.<sup>20</sup> The source width was assumed equivalent to the approximate width of the Dolomite Quarry (about 100 meters).

The preliminary analytical modeling using “Base Case” parameter assumptions predicted downgradient transport on the order of two meters or less for Acetone, Acrylamide, and the Custamine flotation reagent. These findings are independently derived, but generally consistent with the limited analytical modeling previously completed by Golder. The results of the preliminary analytical modeling are depicted on Figures 4b, 5b, and 6d for “Base Case” parameter assumptions, and on Figures 7b, 8b, and 9d for “Sensitivity Range” parameter assumptions.

## 6.0 NUMERICAL MODELING

This section provides descriptions of the numerical model development, including the model discretization and boundary conditions, as well as a discussion of the findings of the numerical fate and transport simulations and sensitivity analysis.

---

<sup>20</sup> Please note that the analytical solution was evaluated at 10,000 days (about 27.5 years); however, the results of the analytical modeling support the conclusion that approximate steady-state conditions were generally achieved in 1,000 days or less (less than about three years), which is well shorter than the approximately 25-year time period of similar on-site tailings product storage. Based on the analytical modeling results, the numerical modeling results (Section 6.0 of this report) were also conservatively evaluated at 10,000 days (about 27.5 years) to reflect approximate steady-state conditions.

## 6.1 Model Development

As previously mentioned, a three-dimensional ‘parametric’ model was developed to simulate numerically the possible transport of the species of interest (TOHI, AA, AEEA, Acetone, and Acrylamide). As defined in Section 2.0 of this report, the term ‘parametric’ is used to denote that the model was developed to assess the possible distance of transport in groundwater considering the range of probable hydrogeologic properties indicated by the available site characterization data and a range of geochemical properties relevant to fate and transport of the key constituents (‘parameters’). The selected model parameters are outlined in Section 4.0 of this report and in Table 2.

### 6.1.1 Governing Equations

The groundwater flow model was developed using MODFLOW-2000, a version of the USGS Modular Finite Difference Model.<sup>21</sup> First published in 1983,<sup>22</sup> MODFLOW has been widely used by the USGS and other public and private parties for simulation of groundwater flow. It is a numerical computer code capable of simulation of three-dimensional groundwater flow under conditions of constant fluid density through heterogeneous and anisotropic media using a finite-difference formulation of the following partial differential equation:

$$\frac{\partial}{\partial x} \left( K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_{zz} \frac{\partial h}{\partial z} \right) + W = S_s \frac{\partial h}{\partial t}$$

where:

$K_{xx}$ ,  $K_{yy}$  and  $K_{zz}$  are values of hydraulic conductivity along the x, y, and z coordinate axes,  
which are assumed to be parallel to the major axes of hydraulic conductivity [L/T];  
 $h$  = Hydraulic Head [L];  
 $W$  = Volumetric Flux Per Unit Volume Representing Sources and/or Sinks of Water [1/T];  
 $S_s$  = Specific Storage of the Porous Material [1/L]; and  
 $t$  = Time [T].

A companion computer code, MT3D99,<sup>23</sup> was used in conjunction with MODFLOW to simulate advective solute transport of the species of interest in consideration of the possible effects of physical/chemical sorption, biochemical degradation, and variable hydrodynamic dispersion using a finite-difference formulation of the following partial differential equation:

<sup>21</sup> Harbaugh, A.W., E.R. Banta, M.C. Hill, and M.G. McDonald, 2000, “MODFLOW-2000, The U.S. Geological Survey Modular Ground-Water Model – User Guide to Modularization Concepts and the Ground-Water Flow Process,” U.S. Geological Survey Open-File Report 00-92.

<sup>22</sup> McDonald, M.G., and Harbaugh, A.W., 1984, “A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model,” U.S. Geological Survey Open-File Report 83-875.

<sup>23</sup> Zheng, C., 1990, “MT3D, A Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems,” S.S. Papadopoulos & Associates, Inc., Rockville, Maryland 20852, prepared for the USEPA, Robert S. Kerr Environmental Research Laboratory.

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

$$R_f \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + \frac{q_s}{n} C_s - \lambda \left( C + \frac{\rho_b}{n} \bar{C} \right)$$

where:

- $C$  = Concentration of Species Dissolved in Groundwater [M/L<sup>3</sup>];
- $t$  = Time [T]
- $x_i$  = Distance along the Respective Cartesian Coordinate Axis [L];
- $D_{ij}$  = Hydrodynamic Dispersion Coefficient [L<sup>2</sup>/T]
- $v_j$  = Seepage Velocity [L/T];
- $q_s$  = Volumetric Flux Per Unit Volume Representing Sources and/or Sinks Of Water [1/T];
- $C_s$  = Concentration Of The Sources Or Sinks [M/L<sup>3</sup>];
- $n$  = Total Porosity [-]
- $\rho_b$  = Bulk Density [M/L<sup>3</sup>];
- $\bar{C}$  = Concentration of Species Sorbed to the Solid Geologic Media [M/M];
- $\lambda$  = First-Order Rate Constant [1/T]; and
- $R_f$  = Retardation Factor [-].

The transport equation is linked to the flow equation via the seepage velocity term ( $v_i$ ) through the following relationship (terms as defined previously):

$$v_i = - \frac{K_{ii}}{n_e} \frac{\partial h}{\partial x_i}$$

The pre- and post-processing graphical interface shells distributed as Visual MODFLOW<sup>®</sup> by Waterloo Hydrogeologic Software<sup>24</sup> were used to facilitate data entry and review of model output.

### 6.1.2 Discretization

To assess the possible range of transport distances at a scale commensurate with the field transport of biodegradable, adsorptive solutes such as the species of interest, a high degree of spatial model discretization was required. Specifically, a comparatively higher degree of spatial model discretization was necessary where the transport solution was expected to vary considerably with distance. As such, the model grid system was tightly divided to allow for simulation of steep concentration gradients while attempting to limit ‘numerical dispersion’. Numerical dispersion is apparent dispersion that results from truncation of the partial differential equation in formulating the finite difference solution to the advection-dispersion equation.

Figures 2 and 3 depict the finite-difference grids developed for the “Base Case” and “Sensitivity Analysis” groundwater flow and transport simulations, respectively. Two levels of grid refinement were necessary for the simulations because the “Base Case” simulation required a

<sup>24</sup> Waterloo Hydrogeologic, Inc., 2005, “Visual MODFLOW User’s Manual (Version 4.1),” Ontario, Canada.

finer grid discretization than the “Sensitivity Analysis” simulation. The axes of both grids are oriented south to north (from bottom to top; the y-axis) and west to east (from left to right; the x-axis). The y-axis is oriented in the direction of groundwater flow.

For the “Base Case” simulation, a square model domain of 20 meters by 20 meters was developed with grid cells evenly spaced over 100 columns and 100 rows to create square grid cells of 0.04 square meter in size. The limited transport distances in the “Base Case” simulation required using a refined grid with a domain size that is small relative to the area of interest (i.e., the nearest distance from the TMAs to the DMZ in a downgradient direction is approximately 60 meters). For the “Sensitivity Analysis”, a square model domain of 100 meters by 100 meters was developed with grid cells evenly spaced over 100 columns and 100 rows to create square grid cells of 1.0 square meter in size.

The model domains were divided vertically into four 20-meter-thick layers, for a total depth of 80 meters. The vertical discretization was developed in consideration of the depth of the TMAs (on the order of 20 meters for the Dolomite Quarry) and the depth over which Heindel & Noyes have indicated the presence of primary water-bearing fractures.

### **6.1.3 Boundary Conditions**

The model boundary conditions were selected to approximate the apparent lateral groundwater flow field consistent with the principally northerly direction of flow as interpreted in site characterization work performed by Heindel & Noyes. The boundaries of the model domain were simulated as either specified flux (no-flow in this case) or specified head (constant head in this case). Constant head boundary conditions were applied to the top and bottom (north and south) of the model domain to establish a hydraulic gradient consistent with the arithmetic mean hydraulic gradient of approximately 0.03 m/m recorded by Heindel & Noyes in the area encompassed by the DMZ. No-flow boundary conditions were applied on the left and right sides (east and west) of the model domain to create a relatively uniform lateral flow field. Similarly, the base of the model domain represents a no-flow boundary condition.

Boundary conditions for the transport solution were selected to simulate an area containing the species of interest at specified constant concentrations (i.e., TMAs), as we conservatively neglected biochemical decay within the TMAs. The specified constant concentration boundary condition was applied at and near the upgradient constant head boundary condition in the upper 20 meters of the model domain and can be considered to represent the downgradient edge of a given TMA.

## **6.2 Model Simulations**

The above-described numerical model was used to simulate transport of the species of interest in consideration of the possible effects of physical/chemical sorption, biochemical degradation, and variable hydrodynamic dispersion. Biochemical degradation was simulated as a first-order

irreversible decay process, while physical/chemical sorption was simulated as an equilibrium-controlled linear partitioning between the dissolved phase and the geologic media. The results of simulations completed using “Base Case” parameter assumptions, as well as the results of the “Sensitivity Analysis” are discussed in the following subsections.

In addition, “Base Case” and “Sensitivity Range” simulation results are graphically portrayed on Figures 4 through 6 and Figures 7 through 9, respectively, in both plan view and in profile. Figures 4a, 5a, 6a, 6b, 6c and Figures 7a, 8a, 9a, 9b, and 9c depict the areal distribution (in plan view) of the species of interest at approximate steady-state<sup>25</sup> relative to groundwater quality standards. Using the Acetone “Base Case” simulation as an example (Figure 4a), the multi-colored area of model-simulated transport indicates declining concentrations from the specified constant input concentration (red color) to the groundwater quality standard of 0.7 mg/L (blue color). Similarly, Figure 7a shows the results of the “Sensitivity Analysis” simulation for Acetone, and Figures 5a and 8a show the results of the simulations for Acrylamide.

Please note that groundwater quality standards are not established for the individual constituents of the Custamine flotation reagent (i.e., TOHI, AA, and AEEA); rather, Vermont has established a proposed health advisory level for the flotation reagent in total (i.e., 0.126 mg/L). Because the individual constituents of Custamine have different fate and transport characteristics (e.g., TOHI and AA are much more strongly adsorbed than AEEA), the transport of each constituent was modeled separately. The multi-colored areas on Figures 6a, 6b, and 6c and Figures 9a, 9b, and 9c for TOHI, AA, and AEEA reflect model-simulated transport from the specified constant input concentrations down to values equivalent to the proportional concentrations of the component, with TOHI at 91%, AA at 7.5%, and AEEA at 1.5% of the proposed health advisory level. As such, the limits of simulated transport reflect 91%, 7.5%, and 1.5% of the proposed health advisory level, or 0.115 mg/L for TOHI, 0.00945 mg/L for AA, and 0.00189 mg/L for AEEA.

Figures 4b, 5b, 6d and Figures 7b, 8b, and 9d depict the model-predicted approximate steady-state concentration profiles downgradient along the plume centerline. For comparison, concentration profiles computed using the analytical solution are also shown (see Section 5.0 of this report). The distances along the plume centerlines (x-axes) equal zero at the downgradient limits of the constant concentration boundary conditions (i.e., the red block depicted on the previously described plan view figures), which are equivalent to points at zero meters along the y-axes of the plan view plots. Figures 4b and 7b show the profiles for Acetone, and Figures 5b and 8b show the profiles for Acrylamide.

---

<sup>25</sup> As previously noted (see footnote No. 19), the numerical solution was evaluated at 10,000 days (about 27.5 years) to reflect approximate steady-state conditions (i.e., stable conditions that do not change or that change insignificantly over time).

For comparison to the proposed health advisory level established for the flotation reagent in total, Figures 6d and 9d depict the model-simulated transport of the Custamine flotation reagent as the summation of the predicted concentrations of the individual constituents of the flotation reagent (i.e., TOHI, AA, and AEEA) at different distances downgradient of the specified concentration boundary condition.

### **6.2.1 Base Case Results**

The parameter values identified as “Base Case” values in the Table 2 were used as input parameters for the “Base Case” simulations. The results of the “Base Case” simulations indicate:

- Transport of Acetone reaching the groundwater quality standard (0.7 mg/L) approximately one meter downgradient of the specified input concentration of 1.3 mg/L (i.e., initial concentration of Acetone), as shown in plan view on Figure 4a and in profile on Figure 4b;
- Transport of Acrylamide reaching the groundwater quality standard (0.0005 mg/L) approximately 2.5 meters downgradient of the specified input concentration of 0.0026 mg/L (i.e., initial concentration of Acrylamide), as shown in plan view on Figure 5a and in profile on Figure 5b; and
- Transport of Custamine reaching the groundwater quality standard (0.126 mg/L) less than 0.5 meter downgradient of the specified input concentration of about 0.232 mg/L (i.e., approximate sum of initial concentrations of TOHI, AA, and AEEA), as indicated in plan view on Figures 6a, 6b, and 6c and in profile on Figure 6d.

A comparison of the concentration profiles predicted numerically and analytically indicates consistent predictions for the more mobile species of interest (i.e., Acetone, Acrylamide, and AEEA). More divergence between the numerical and analytical solution is apparent for TOHI and AA, which are more strongly adsorbed. Greater downgradient transport is predicted numerically reflecting numerical dispersion that limits the ability to simulate the steep concentration gradient. In short, the numerical model results conservatively over predict downgradient transport of these constituents.

### **6.2.2 Sensitivity Analysis Results**

Because the “Base Case” analysis indicated that transport of the species of interest is on the order of 0.5 to 2.5 meters, well short of the 60-meter distance from the TMAs to the DMZ, the “Sensitivity Analysis” was performed using only those parameter values expected to produce the upper end of the range of possible downgradient transport for the species of interest. These values included: the upper ends of the “Sensitivity Range” values for seepage velocity, dispersivity, and initial concentration, and the lower ends of the “Sensitivity Range” values for retardation factor and first-order decay rate (see Table 2). The results of the “Sensitivity

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

Analysis” expected to produce the upper end of the range of possible downgradient transport indicate:

- Transport of Acetone reaching the groundwater quality standard (0.7 mg/L) approximately 30 meters downgradient of the specified input concentration of 3.0 mg/L (i.e., initial concentration of Acetone), as shown in plan view on Figure 7a and in profile on Figure 7b;
- Transport of Acrylamide reaching the groundwater quality standard (0.0005 mg/L) approximately 40 meters downgradient of the specified input concentration of 0.0037 mg/L (i.e., initial concentration of Acrylamide), as shown in plan view on Figure 8a and in profile on Figure 8b; and
- Transport of Custamine reaching the groundwater quality standard (0.126 mg/L) approximately 12 meters downgradient of the specified input concentration of about 0.512 mg/L (i.e., approximate sum of initial concentrations of TOHI, AA, and AEEA), as indicated in plan view in Figures 9a, 9b, and 9c and in profile on Figure 9d.

As with the “Base Case” analyses, the concentration profiles predicted numerically and analytically are consistent for the more mobile species of interest (i.e., Acetone, Acrylamide, and AEEA), while the numerical model results over-predict downgradient transport for TOHI and AA, which are more strongly adsorbed.

## 7.0 SUMMARY OF FINDINGS

SHA completed three-dimensional numerical groundwater flow and transport modeling in support of Interim Certification Application for the TMAs at the Omya Verpol Plant in Florence, Vermont. It is our professional judgment that the overall modeling effort summarized herein provides an appropriate assessment of possible groundwater transport distances for the species of interest relative to the DMZ, and is supportable by the available site characterization data collected by others. Furthermore, it is our professional opinion that the scope of the modeling effort is consistent with the intent of the Solid Waste Management Procedures for assessment of the potential fate and transport of the chemicals present in “leachate” relative to the DMZ boundary.

The results of our modeling effort indicate that the TMAs at the Omya Verpol Plant will not result in exceedances of groundwater quality standards at the DMZ boundary at any point in time for the base condition of the model. Specifically, the results of numerical simulations completed using “Base Case” assumptions indicate approximate steady-state transport of the species of interest at concentrations above groundwater quality standards to distances on the order of 0.5 to 2.5 meters downgradient of the TMAs, well short of the 60-meter distance from the TMAs to the DMZ. These findings are supported by several years of water quality monitoring data at the site

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

that indicate the general absence of the species of interest in groundwater and surface water despite over 25 years of similar on-site tailings product storage.

Furthermore, the results of numerical simulations completed using parameter assumptions expected to produce the upper end of the range of possible downgradient movement indicate approximate steady-state transport of the species of interest to distances less than two-thirds of the distance from the TMAs to the DMZ. In other words, the upper end of the range of possible downgradient movement associated with our "Sensitivity Range" parameter values does not indicate transport of the species of interest to the DMZ boundary at concentrations above groundwater quality standards (i.e., groundwater quality standards are satisfied before reaching the DMZ boundary). Other, less conservative combinations of "Sensitivity Range" parameter values would predict even shorter transport distances.

## 8.0 LIMITATIONS

The intent of the modeling effort was to supplement field investigations of water chemistry completed at the site by Heindel & Noyes, which have demonstrated the general absence of the species of interest at concentrations above groundwater quality standards in groundwater and surface water downgradient of the existing TMAs, while providing a tool to aid in testing alternate groundwater transport scenarios. The model was developed to satisfy VTDEC modeling requirements, and is based in part on geologic, hydrogeologic, and geochemical inferences/assumptions that have not necessarily been confirmed or measured in the field for all locations and depths.

Our modeling approach was developed in consideration of the data and hydrogeologic inferences provided to us, largely in the form of a conceptual model of site conditions developed by Heindel & Noyes. Our goal was to assess possible transport of the species of interest while generally approximating groundwater flow velocities and hydraulic gradients indicated by available field data over the model area, and honoring the hydraulic parameters estimated by others at the site. The model should not be viewed as a unique solution to groundwater flow and transport at the site, but rather should be considered an approximate analog, developed based on available knowledge/interpretations of site conditions.

**TABLE 1 (REVISED)**

**Table 1**  
**EVALUATION OF NUMERICAL MODELING CONSTITUENTS**  
**Interim Certification Application Support**  
**Omya Inc., Verpol Plant TMAs**  
**Florence, Vermont**

\*\*\*REVISED IN RESPONSE TO VTDEC COMMENTS DATED APRIL 18, 2006\*\*\*

Substance Identified in Tailings Product <sup>2</sup>	Regulated?	Detected in Tailings Product Pore Water?			Detected in Tailings Product 'Leachate' (via modified TCLP)?			Detected in Groundwater?			Detected at Concentrations Greater than Groundwater Standards?	Retain for Further Review?	Comments
	Groundwater Standard <sup>3</sup> (ppm)	No. of Samples	No. of Detections	Maximum Concentration (ppm)	No. of Samples	No. of Detections	Maximum Concentration (ppm)	No. of Samples	No. of Detections	95% UCL <sup>4</sup> (ppm)			
Ortho-Phenylphenol (OPP) <sup>5</sup> (5 of 37 samples; 14%)	0.018 <sup>3a</sup>	10	2	0.907	NA (not analyzed)			112	4	0.048 <sup>5</sup>	Yes, maximum pore water and groundwater <sup>5</sup> concentrations exceed standards	No	Eliminate on the basis that OPP was detected in only 14% of the tailings product samples and its presence is related to an isolated incident rather than the typical tailings product composition.
Methyl Isothiocyanate (MITC) <sup>6</sup> (6 of 31 samples; 19%)	NE (0.018) <sup>3d</sup>	10	4	0.684	NA (not analyzed)			32	0	ND	Yes, maximum pore water concentration exceeds standards	No	Eliminate on the basis that MITC was detected in only 19% of the tailings product samples and its presence is related to an isolated incident rather than the typical tailings product composition.
Phosphoric Acid (assumed; mass balance)	NE <sup>3c</sup>	NA (no test method available)			NA (no test method available)			NA (no test method available)			NA (no test method; not regulated)	No	Eliminate on the basis of low toxicity and background. Phosphoric acid is a Generally Recognized as Safe (GRAS) food ingredient. Naturally occurring levels of phosphorus in the eastern United States range from <20 to 6,800 ppm, averaging 200 ppm. Phosphorus may be present in tailings product at a concentration of no more than 37 ppm, according to Omya's mass balance calculations.
Polyacrylamide (assumed; mass balance)	NE (1,050) <sup>3d</sup>	NA (no test method available)			NA (no test method available)			NA (no test method available)			NA (no test method; not regulated)	No	Eliminate on the basis of low toxicity. Polyacrylamide is nontoxic polymer commonly added to drinking water systems for use as a flocculant. It is also widely used in cosmetics. Polyacrylamide may be present in tailings product at a concentration of no more than 60 ppm, according to Omya's mass balance calculations.
Polyacrylates (assumed; mass balance)	NE (350) <sup>3d</sup>	NA (no test method available)			NA (no test method available)			NA (no test method available)			NA (no test method; not regulated)	No	Eliminate on the basis of low toxicity. Polyacrylates are nontoxic polymers commonly used in water treatment processing. They are also widely used in contact lenses, denture materials, and textile coatings. Polyacrylates may be present in tailings product at a concentration of no more than 4,250 ppm, according to Omya's mass balance calculations.
Stearic Acid (3 of 34 samples; 9%)	NE <sup>3c</sup>	10	0	ND	NA (not analyzed)			111	0	ND	No (not detected; not regulated)	No	Eliminate on the basis of low toxicity and no detections in pore water, 'leachate', or groundwater. Stearic acid is a Generally Recognized as Safe (GRAS) food ingredient.
Methylamine (0 of 29 samples; 0%)	NE (280) <sup>3d</sup>	7	0	ND	NA (not analyzed)			32	0	ND	No (not detected)	No	Eliminate on the basis of no detections in pore water, 'leachate', or groundwater.
Free Chlorine (0 of 20 samples; 0%)	4 <sup>3c</sup>	7	0	ND	NA (not analyzed)			29	0	ND	No (not detected)	No	Eliminate on the basis of no detections in pore water, 'leachate', or groundwater.
Barium (1 of 6 samples; 17%)	2 <sup>3a</sup>	NA (not analyzed)			NA (not analyzed)			4	4	0.05	No	No	Eliminate on the basis of no exceedances of standards and background. The maximum concentration of barium detected in the tailings product via TCLP was 108 ppb, a level within the range of naturally occurring background for Vermont bedrock.
Trihalomethanes (THMs) (4 of 24 samples; 17%)	0.08 <sup>3a</sup>	24	4	0.0146	NA (not analyzed)			90	3	0.023	No	No	Eliminate on the basis of no exceedances of standards.
Isopropanol (IPA) (8 of 32 samples; 25%)	NE (33) <sup>3d</sup>	10	7	1.53	NA (not analyzed)			96	0	ND	No	No	Eliminate on the basis of no exceedances of standards.
Toluene (7 of 42 samples; 17%)	1 <sup>3a</sup>	15	2	0.0345	NA (not analyzed)			100	15	0.009	No	No	Eliminate on the basis of no exceedances of standards.
Acrylamide (4 of 28 samples; 14%)	0.0005 <sup>3c</sup>	7	2	0.0037	NA (not analyzed)			32	0	ND	Yes, maximum pore water concentration exceeds standards	Yes	Retain on the basis that acrylamide was detected at concentrations above groundwater standards in the tailings product pore water.
Acetone (17 of 40 samples; 43%)	0.7 <sup>3a</sup>	15	13	2.95	NA (not analyzed)			96	3	0.166	Yes, maximum pore water concentration exceeds standards	Yes	Retain on the basis that acetone was detected in nearly 45% of the tailings product samples, and at concentrations above groundwater standards in the tailings product pore water.
Flotation Reagent: Tall Oil Hydroxyethyl Imidazoline (TOHI) Amine Acetate Aminoethyl-ethanolamine (AEEA) (77 of 88 samples; 88%)	0.126 <sup>3b</sup>	10	4	9.58	49	49	0.47	159	2	0.058	Yes, maximum pore water and 'leachate' concentrations exceed standards	Yes	Retain on the basis that the flotation reagent was detected in nearly 90% of the tailings product samples, and at concentrations above groundwater standards in the tailings product pore water and 'leachate'.

**Notes:**

- The information and data presented in this table were obtained from the August 15, 2005 Site Characterization Report prepared by Heindel and Noyes Consulting Hydrogeologists, Engineers, and Environmental Scientists (Heindel and Noyes) and have not been independently verified by SHA. Groundwater analytical data are from sampling completed by Heindel and Noyes from November 2000 through June 2005. Tailings product pore water analytical data are from sampling completed by Heindel and Noyes from November 2001 through April 2004. Tailings product 'leachate' analytical data are from modified TCLP analyses (pH =7.8) performed from October 2004 through January 2005.
- In addition to the substances listed in this table, Heindel and Noyes' August 15, 2005 Site Characterization Report also includes "Minerals" and "Petroleum Products" as substances identified in the tailings product. The tailings product consist primarily of minerals (over 99% of the mass), including calcium carbonate and other naturally occurring minerals. Petroleum Products are excluded from this table because analyses for volatile and semi-volatile organic compounds completed by Heindel and Noyes did not identify individual petroleum-related constituents other than Toluene, which is included in this table. Please note that the percentage of samples in which the substance was identified (e.g., for OPP - 5 of 37; 14%) considers data derived from tailings product solids, tailings product pore water, and tailings product 'leachate' analyses.
- Groundwater standards were obtained from the following sources:
  - Vermont Groundwater Enforcement Standard;
  - Vermont Proposed Health Advisory Level;
  - USEPA Drinking Water Regulations (Maximum Residual Disinfectant Level for Chlorine and Treatment Technique for Acrylamide [less than 0.05% dosed at 1 ppm]);
  - Recommended Safe Level determined by toxicologist Dr. Robert Mathews, Ph.D., D.A.B.T. of Keller and Heckman, LLP (See Heindel and Noyes' August 15, 2005 Site Characterization Report); and
  - Generally Recognized as Safe by USFDA.
- 95% upper confidence levels (UCLs) as presented in Heindel and Noyes' August 15, 2005 Site Characterization Report.
- OPP is not typically associated with the tailings product, but was present in some of the tailings product as a result of an accidental release in 2000. The OPP was remediated in 2001 as part of a State-approved monitoring and remediation program. As reported in Heindel and Noyes' August 15, 2005 Site Characterization Report, no OPP has been detected in groundwater following the remediation of the spill in 2001.
- MITC is not typically associated with the tailings product, but was present in some of the tailings product as a result of an accidental release of thione in 2003.
- NA = Not Applicable; ND = Not Detected; NE = Not Established.
- Please note that, with the exception of the Flotation Reagent, Heindel and Noyes' August 15, 2005 Site Characterization Report indicates that none of the substances included in this table have been detected in surface water samples collected by Heindel and Noyes. As reported in Heindel and Noyes' August 15, 2005 Site Characterization Report, the Flotation Reagent was detected in 1 of 20 surface water samples collected by Heindel and Noyes, but at a concentration below relevant standards.