# AP - <u>50</u>

# STAGE 1 & 2 REPORTS

# DATE: Jan. 30, 2004

### R. T. HICKS CONSULTANTS, LTD.

901 Rio Grande Blvd NW 🛦 Suite F-142 🛦 Albuquerque, NM 87104 🛦 505.266.5004 🛦 Fax: 505.266-0745

January 29, 2004

Mr. Wayne Price New Mexico Oil Conservation Division 1220 South St. Francis Drive Santa Fe, New Mexico 87505

RE: Zachary Hinton EOL Final Report

Dear Mr. Price

On behalf of Rice Operating Company, we are pleased to submit the final Corrective Action Plan for the above-referenced site. We are pleased to report that the chloride concentration in samples from the on-site monitoring well has returned to background levels. We conclude that the residual chloride in the vadose zone poses no threat to human health or the environment. We recommend filling the excavation with soil capable of sustaining vegetation and plugging the monitoring well.

Please contact us with any comments or questions regarding our recommended closure protocol for this site.

Sincerely,

R.T. Hicks Consultants, Ltd.

Randall Hicks Principal



R.T. HICKS CONSULTANTS, LTD.

### Zachary Hinton EOL Junction Box

January 30, 2004

901 RIO GRANDE BLVD. NW, SUITE F-142, ALBUQUERQUE, NM

### 1.0 PURPOSE AND BACKGROUND

The Zachary Hinton EOL Junction Box is located about 2.5 miles southeast of the intersection of State Routes 18 and 8/176, near Eunice, New Mexico. Plate 1 of the NMOCD-approved work plan (Appendix A) shows the location of the site relative to Eunice. The work plan identified the following tasks:

- 1. Collection and Evaluation of Data for Simulation Modeling
- 2. Evaluate Migration of Chloride Flux from the Vadose Zone to Ground Water
- 3. Design Remedy and Submit Report

The goal of our work is to identify the surface and subsurface remedy for the site that creates the greatest environmental benefit while causing the least environmental damage.

The disclosure report prepared by Rice Operating Company (ROC) in January 21, 2003 (Appendix B) summarizes the initial activities at the site. The soil boring and backhoe excavation data show relatively consistent concentrations of chloride from 11 feet below ground surface (2000 ppm chloride) to 50 feet below ground surface (6410 ppm chloride). The consistency of these chloride



concentrations suggests that a release from the junction box may have created saturated conditions in the vadose zone. Hydrocarbons, often associated with releases from produced water pipelines, were not present in concentrations that warrant further inquiry (see ROC Disclosure Report.)

Figure 1 presents ground water quality data from the monitoring well that is located within 20 feet of the former Zachary Hinton EOL junction

CORRECTIVE ACTION PLAN - Zachary Ninton EOL Junction Box January 29, 2004

*Figure 1. Ground water quality data near Zachary Hinton EOL junction box.* 

box (Table 1). Chloride concentrations were about 1000 mg/L in early 2002, soon after replacement of the junction box. Throughout 2003, chloride concentrations remained stable (less than 500 mg/L).

As stated in the work plan, R.T. Hicks Consultants, Ltd. used HYDRUS-1D to simulate chloride fate and transport to ground water and to develop a surface remedy for the site. This report presents the results of our study and proposes a final remedy for the site to permit closure of the regulatory file.

### 2.0 APPROACH

We used the numerical model HYDRUS-1D to simulate the transport of chloride from the surface through the vadose zone to ground water. We used the predicted flux of chloride to ground water from HYDRUS-1D as input into a simple ground water mixing-model to evaluate the impact on ground water quality. As Appendix C describes, this modeling effort requires 11 input parameters. Appendix C also describes the modeling approach used in this effort.

In our previous work with HYDRUS-1D, we found that some input parameters had little effect on the prediction of chloride concentration in ground water while other factors had a profound effect. The Sensitivity Analysis presented in Appendix C describes the relative importance of each of the eleven input parameters. Two of these eleven factors (release volume and height of the spill) are not relevant in our simulations, since we evaluated the movement of the chloride load already in the soil profile. Site specific data exist for the most important input factors (e.g. chloride load, depth of ground water, soil texture, etc.).

## 3.0 DATA EMPLOYED FOR THE ZACHARY HINTON SITE

For some input parameters we employed regional data or values based upon professional judgment (see Table 2). For most of the input data to our simulations, we relyed upon site data collected by Rice Operating Company. Our field inspection of the site and our evaluation of the data allow us to conclude that the site data used in our simulations reflect the conditions at the site.

Plate 2 shows the soil profile texture and thickness of the vadose zone at the site (input parameters # 1 and #2 of Table 2). We input the soil texture into HYDRUS-1D and allowed the model's library to generate the hydraulic properties. We then used these hydraulic properties in simulations of these scenarios.

Based upon our experience, we employed a dispersion length of 100 cm (input #3). The selected dispersion length is 7% of the total length of the HYDRUS-1D model (55 feet). Many researchers suggest that a dispersion length that is 7-10% of the total model length provides reasonable results for simulation experiments.

We used the soil moisture content (input # 4) presented in Table 2 from HYDRUS-1D simulations. Because we did not have site-specific soil moisture data, we assumed a "dry" soil profile then used the climate data to add moisture to the profile via precipitation over 100 years. We found that initial soil moisture in the profile changed over this 100-year period, responding to the climatic conditions. Therefore, we ran the simulations under both "wet" and "dry" conditions as determined by the 100-year simulation experiment. As Table 2 shows, we elected to employ the "wet" conditions in our simulations because leakage from the junction box over the past years has created "wet" conditions within the profile.

Plate 2 shows the measured soil chloride concentration per unit weight of soil. We converted these values to concentrations per liter of soil water (input #5) by using the equations in Appendix D. The length of the release (input #6) was measured in the field.

The daily climate data available from the Pearl weather station near the Hobbs Airport served as input for all climate indices required by HYDRUS-1D (input #7). We simulated 10 years after the release with

CORRECTIVE ACTION PLAN - Zachary Hinton EOL Junction Box January 29, 2004

### R.T. HICKS CONSULTANTS, LTD.

average precipitation 36 cm/year.

For the input parameter #8, background ground water chloride concentration, we used 100 mg/L based upon data from the City of Eunice. We used data for the Ogallala Aquifer as described in Nicholsen and Clebsch, (1961) as input to the mixing model ( input #9, ground water flux; input#10, aquifer thickness).

We also used data from the BD Zachary Hinton Jct monitor well to verify the predictions of the HYDRUS-1D model and the mixing model.

### 4.0 SET-UP OF SIMULATIONS

### **SCENARIO 1: NO ACTION**

The no action alternative evaluates the potential of the chloride mass in the vadose zone to materially impair ground water quality at the site in the absence of any action by Rice Operating Company and in the absence of any natural restoration (e.g. re-establishing vegetation). As described in Appendix C, the distribution of the mass of chloride in the vadose zone (input #5) is the most important input parameter for prediction of chloride concentrations in ground water. For this and all simulations, we assumed the chloride concentrations shown in Plate 1 existed in the profile at time zero. At time zero, we also assume that man-made leakage of produced water has ceased and the chloride concentration in the monitoring well is equal to background (100 mg/L). While the first and second assumptions are acceptable, the assumption that the chloride concentration in the monitoring well is equal to background is false. We make this last assumption as a matter of convenience to simplify our model and we explain the effect of this simplification in our discussion of the results of the simulations.

The chloride concentration of soil water  $Cl^{soil water}$  (mg/liter) depends on the gravimetric chloride content of moist soil Clg<sup>moist soil</sup> (mg/kg of moist soil), the bulk density of the soil Dsoil<sup>dry</sup> (kg/m<sup>3</sup>), and the volumetric water content of the soil èv (m<sup>3</sup>/m<sup>3</sup>) input #4 . To convert the chloride concentration in the soil to chloride concentration in soil water ( see Appendix D), we used a soil density of 1,858 kg/cubic meter and the soil moisture content in Table 2.

We entered the chloride concentration of soil water in the soil profile in HYDRUS and ran the simulation for 10 years with total precipitation and evaporation from the soil. Vegetation was assumed to not be present to enhance water transfer from soil to the atmosphere. We calibrated the results from the model with the chloride data from a monitoring well located 20 feet downgradient from the center of the spill.

#### **SCENARIO 2: REDUCE INFILTRATION**

To minimize the potential for any leaching of residual chloride from the vadose zone, we assumed a surface remedy that would reduce infiltration of precipitation. To simulate such a remedy, we simply reduced the precipitation by assuming that heavy rains (that cause the majority of

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the infiltration) run off after 1.5 cm fell. This simulation predicts the effect of (a) sloping the site to cause runoff of the larger precipitation events and/or (b) placement of a graded compacted layer at the surface to minimize infiltration, facilitate runoff and prevent ponding of precipitation. All other input parameters are the same as Scenario 1.

### **SCENARIO 3: VEGETATION**

This scenario consists of placing 30 cm of silt loam and reseeding with pasture. The transpiration is zero during the winter months but soil evaporation takes place. During the growing season, evapotranspiration is greatest. All other input parameters are the same as Scenario 1.

### SCENARIO 4: A SILT CLAY BELOW THE TOP SOIL

In this scenario we placed 60 cm of a silt clay below the top soil under the same conditions of Scenario 3. Placing the clay below the top soil minimizes infiltration into the deeper profile and provides a place for the infiltration of winter precipitation to reside until the plants take it up in the following spring and summer. All other input parameters are the same as Scenario 1.

# 5.0 SIMULATION RESULTS AND DISCUSSION

Figure 2 shows the response of Scenario 1 in a monitoring well located 20 feet from the center of the spill at the release site. The simulation shows chloride concentration increasing to a maximum of 1,652 ppm in year 1.7. As stated in the previous section, in this and other simulations. when man-made leakage ceased, the chloride concentrations in the vadose zone are equal to that represented in Plate 1. To simplify our modeling experiment, we



assumed that the chloride concentration in the monitoring well at time zero in Figure 2 is equal to background (100 mg/L). Therefore, the initial increase in chloride concentration from background (100 mg/L) to a maximum (1,652 in this simulation) is the model's response to the downward movement of the initial distribution of chloride in the profile. Because the well was installed after replacement of the junction box and cessation of periodic leakage, we cannot know the chloride concentration at the monitoring well during past man-made leakage events. We hypothesize, however, that chloride concentration in ground water would be 1,652 mg/L or more during the time that the juction box periodically released produced water. Chloride concentrations in the monitoring well might remain at or above the 1,652 mg/L during the years of periodic discharges from the former junction box, as chloride migrated from the ground surface to ground water via saturated flow. After replacement of the junction box, water additions to the soil profile cease and the soil profile would drain. During the drainage of the soil profile, chloride concentrations in the monitoring well would decrease as saturated flow ceased and slower, unsaturated flow conditions occurred in the profile.

Figure 3 modifies the HYDRUS-1D output to better represent the conditions described above. In this Figure, time X represents background conditions, before any leakage from the junction box. As periodic leakage occurs, chloride concentration in ground water rises and chloride is

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Figure 2. Chloride concentration in the monitoring well for the no action scenario. (Scenario 1)

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distributed throughout the unsaturated zone, as shown in Plate 1. We believe that the maximum chloride concentration in ground water in Figure 3 (1,652 mg/L) is approximately what we would have observed during the period of leakage from the junction box if the monitoring well had been installed. After repair of the junction box (here noted as approximately time zero), chloride



concentrations decline as discussed above and as shown in Figure 3. About five years after repair of the junction box under the No Action Scenario, ground water chloride approaches background concentrations.



Figure 4 shows the results of our simulations of Scenario 2 with the same modified time line as in Figure 3. Reducing infiltration of precipitation creates a maximum concentration 1,048 mg/ L marked approximately as year 0 to show when junction box repair occured. Reducing infiltration slows the drainage of vadose zone water relative to the no action scenario. Therefore, water and chloride



enter the ground water more slowly in this scenario as compared to the no action scenario. In other words, the chloride flux (mass/time) into ground water is lower in Scenario 2 than in scenario 1. The ground water flux and aquifer thickness, however, remain the same in both scenarios. The lower chloride flux into ground water results in a lower maximum concentration observed in the monitoring well. This lower flux also results in a longer time of predicted non-compliance at the monitoring well.

Figure 4. Modification of HYDRUS-1D simulation results to show a more realistic time scale for chloride concentration in the monitoring well for the scenario reducing the infiltration. (Scenario 2)

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About six years after repair of the junction box, the majority of the chloride has drained from the vadose zone and concentrations in the well declines to the standard of 250 mg/L. We did not simulate the

length of time necessary for ground water to reach background conditions under this scenario.

Figure 5 shows the results of the Scenario 3, which assumes further reduction of infiltration due to evapotranspiration as a result of plant cover. The maximum chloride concentration in the well is 693 mg/L at



approximately zero time on the modified scale. As discussed previously, the time of maximum chloride concentration is the time when the junction box is repaired. The chloride concentration declines to the standard of 250 mg/L in year 2.11. However, we predict an increase in ground water chloride concentrations to 323 ppm in year 6.5 followed by a decrease to the standard by year 7.5. This increase at year 6.5 is probably due to increased infiltration associated with the El Niño weather pattern. Because most the chloride has drained from the profile by year 6.5, we conclude that any additional increase in ground water chloride concentration (perhaps at year 14) would not exceed the ground water standard of 250 mg/L.

The concentrations in the root zone in Scenario 3 are quite high as result of capillary rise that accumulates the salts at the top of the profile. Concentrations of 4,000 ppm will prevent the grass of developing unless chloride moves deeper into the subsurface due to a soil flushing program or natural rainfall.

Figure 6 shows the result of Scenario 4 with the modified time scale. The maximum concentration in the well is 604 ppm in year 0. It declines to 250 ppm in year 1.75. The concentrations in the root zone are about 1300 ppm, suitable for vegetation. By year 8, background conditions exist in the monitoring well.

Figure 1 shows the chloride concentration in the monitoring well at the Zachary Hinton site. This well was installed after replacement of the

CORRECTIVE ACTION PLAN - Zachary Hinton EOL Junction Box January 29, 2004

Figure 5. Modification of HYDRUS-1D simulation results to illustrate a more realistic time scale, chloride concentration in the well for the vegetation scenario. (Scenario 3)

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produced water pipeline junction that we believe caused the release of chloride to the subsurface. The data show chloride concentraton declining from 1,000 mg/L to 500



mg/L over a two-month period. The concentration then declines to about 400 mg/L after one year. Obviously, these data do not correlate with the model predictions of Scenario 1, no action. Instead, the field data are more similar to the predictions of Scenario 3, where infiltration into the vadose zone is relatively low due to evapotranspiration associated with vegetation.

The similarity between Figures 1 and 5 should not be surprising if one visits the site. Vegetation does exist around the area of the suspected release (Figure 7). We believe the current flux of chloride from the vadose zone to ground water is approximately the same as that simulated in Scenario 3. We can also conclude from Figure 7 that the chloride concentration in the root zone is low enough to support vegetation. The no action scenario, which does not provide for evapotranspiration or

any reduced infiltration, obviously overestimates the impact of the chloride load to ground water quality.



Figure 6. Modification of HYDRUS-1D simulation results showing a more realistic time scale of chloride concentration in the well for the scenario with vegetation and a silt clay layer below the topsoil. (Scenario 4).

*Figure 7.* Vegetation near the release site.

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### 6.0 GROUND WATER QUALITY AND FLOW

Although the quality of the City of Eunice water supply wells is about 100 mg/L chloride (see Nicholson and Clebsch, 1961), a more detailed investigation of the area near the Zachary Hinton EOL site shows higher background levels. Plate 2 shows the locations of wells with past and present water quality data and Table 3 presents the results for chloride.

The chloride concentration in the City of Eunice wells and the Peters West well are below Water Quality Control Comission standards for ground water. Wells within or near Monument Draw, however, generally exceed the standards. The difference between the water quality west of Monument Draw and the water quality within and near the Draw has been evident since the 1950s when Nicholson and Clebsch sampled the water of the area (Table 3).

Today, as in the 1950s, ground water flows from the west toward Monument Draw. Ground water then flows south within the draw as shown in Plate 3 from Nicholson and Clebsch (1961). Up gradient from the Zachary Hinton EOL site, chloride concentrations in the Active Windmill of Section 36 (see Plate 2) is 460 ppm. The chloride in this active windmill is consistent with the chloride concentrations observed in wells 22.37.1.440 and 22.37.24.133b ( average of 422 and 675 ppm respectively) in the 1950s. The Peters East well, which lies within Monument Draw, exhibits a chloride concentration of 438 ppm while the chloride concentration in the Zachary Hinton EOL monitoring well is 354 ppm. This measuable difference in chemistry between the Zachary Hinton Site and the Peters East well could be due to the effect of higher quality ground water flowing into the Monument Draw area from the west (e.g. 200 ppm chloride in the Peters West well), or the difference may be due to normal variance associated with sampling and analysis.

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## 7.0 CONCLUSION AND RECOMMENDED ACTION

The HYDRUS-1D simulations for the Zachary Hinton site provide reasonably good, albeit conservative, predictions of chloride concentrations in ground water for the various scenarios. Currently, about two years after the repair of the pipeline and cessation of water leakage, chloride concentrations in the ground water monitoring well are 354 ppm, background correlations. The field data correlate well with early time predictions of Scenario 3, reduced flux due to vegetation. We conclude Scenario 3 predicts higher chloride concentrations than observed.

We conclude that the background chloride concentration in ground water at the Zachary Hinton EOL site is about 350 ppm. We base this conclusion on historical and recent water quality analyses from the area. Natural restoration has mitigated the transient impact of past leakage from the site. Data from the Peters East well suggest that past leakage from the Zachary Hinton EOL Junction box have not caused measurable degradation of ground water quality.

We recommend restoring the ground surface in the excavation using soil that will permit re-vegetation. Because the water quality at the site has returned to background conditions, we recommend plugging and abandonment of the existing monitoring well and closure of the regulatory file for this site, pending documentation of appropriate surface reclamation.



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County	Iry Hinton EOL, Lea	Calculation of Chloride Load, Zach	F-142 Albuguerque, NM 87104
	company	RICE Operating (	R.T. Hicks Consultants, Ltd. 901 Rio Grande Blvd. NW, Suite.
ited Chloride Load	Calcula	Aquifer = Sandy Clay 60-63 ft	Total Depth of MW
		Aquifer = Gray Sand 56-50 ft	60
1858 5	500		Aquifer 56
1858 5	6410		50
1858 5	5000		
1858 5	5300	Various Colored Sands	40
1858 5	8160	19-56 feet	
1858 5	3270		30
1858 5	1750		
1856 5	3000		20
1858 5	2450	13-19 feet Sandy Clay	
1858 5	2000	3-13 feet Caliche and Sand	Q
1858 5	1500		
		0-3 feet Sandy Top Soil	
in Jensiny of nple kg/cubic Thicknes meter Column	Concentration San mg/kg	Lithologic Description	Depth ground surface
lik Daneity of	Measured Soil Chloride		
	Ik Density of Thickne meter Column Thickne Thi	Measured Soil Chloride Chloride Sample kg/cubic     Bulk Density of Sample kg/cubic       Chloride Concentration     Sample kg/cubic       Thickne mg/kg     ISSB       1500     1858       2450     1858       2000     1858       2300     1858       2450     1858       3000     1858       3270     1858       6410     1858       5000     1858       6410     1858       500     1858	Massured Sol Cloincide Concentration     Massured Sol Sample Kigcubic     Massured Sol Thickne mg/kg       0.3 leet Sandy Top Soli     Sample Kigcubic     Thickne mg/kg       0.3 leet Sandy Top Soli     1500     1858       3-13 feet Caliche and Sand     2000     1858       3-13 feet Caliche and Sand     2000     1858       9     13-19 feet Sandy Clay     2150       13-19 feet Sandy Clay     2150     1858       Various Colored Sands     3000     1858       13-19 feet Sandy Clay     500     1858       13-19 feet Sandy Clay     500     1858       Aurieus Colored Sands     3270     1858       Various Colored Sands     500     1858       Aniver Sand See0 ft     500     1858       Aquifer = Sandy Clay 6test in Aquifer = Sandy Clay 6test in     500     1858



### APPENDIX A

### R.T. HICKS CONSULTANTS, LTD.

Suite 266

219 Central Avenue NW

Albuquerque, NM 87112

505.266.5004

Fax: 505.246-1818

July 2, 2003

Mr. Wayne Price New Mexico Oil Conservation Division 1220 South St. Francis Drive Santa Fe, New Mexico 87505

RE: Zachary Hinton EOL Junction Box, Section 12, 22S, 37E Unit O

Dear Mr. Price

Rice Operating Company retained R.T. Hicks Consultants, Ltd. to address potential environmental concerns at the above referenced site. This submission proposes a scope of work that we believe will best mitigate any threat to human health and the environment and lead to closure of the regulatory file for this site.

### Background

The Zachary Hinton EOL Junction Box is located about 2.5 miles southeast of the intersection of State Routes 18 and 8/176, near Eunice, New Mexico. Plate 1 shows the location of the site.

Rice Operating Company (ROC) prepared a disclosure report dated January 21, 2003 that summarizes activities to date. This report is part of the annual submission to NMOCD, due in April of each year. For your convenience, we have attached a copy of this ROC report and a copy of recent ground water data from the adjacent monitoring well. The soil boring and backhoe excavation data show relatively consistent concentrations of chloride from 11 feet below ground surface (5200 ppm chloride) to 50 feet below ground surface (6410 ppm chloride). The consistency of these concentrations suggests that a release from the junction box may have created saturated conditions in the vadose zone.

ROC installed a monitoring well adjacent to the junction box. Four quarters of ground water data show chloride concentrations in ground water are currently between 400 and 500 mg/L. The most recent analysis of total dissolved solids (11/6/02) from this well shows a result of 1290 mg/L. Because these values exceed the New Mexico Water Quality Commission Standards, we propose the work outlined below.

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### 1. Evaluate Migration of Chloride Flux from the Vadose Zone to Ground Water

We propose to employ HYDRUS1D and a simple ground water mixing model to evaluate the potential of residual chloride mass in the vadose zone to materially impair ground water quality at the site. We will employ predictions of the migration of chloride ion from the vadose zone to ground water in our selection of an appropriate remedy for the land surface and underlying vadose zone. This simulation is the "no action" alternative, which predicts chloride flux to ground water in the absence of any action by ROC.

We might provide simulations of two "no action" scenarios. For both simulations, we will employ the input parameters to HYDRUS and the mixing model outlined in Table 1. In the first simulation, we will assume that vegetation is not present over the release site (no evapotranspiration) and a minimum aquifer thickness of 10 feet. This will simulate restriction of any released chloride to a portion of the underlying aquifer. If this first simulation does not return results that are consistent with the existing ground water monitoring data, we will increase the aquifer thickness in the mixing model to the maximum value allowed by data (a bout 35 feet). At other sites, we have found that chloride can be distributed throughout the thickness of the aquifer. Employing the entire thickness of the aquifer in the mixing model calculations may be appropriate for the Zachary Hinton site.

Input Parameter	Source
Vadose Zone Thickness	Attached well log
Vadose Zone Texture	Attached well log
Dispersion Length	Professional judgment
Soil Moisture	Nearby Field Measurements
Vadose Zone Chloride Load	ROC Data from Disclosure Report
Length of release perpendicular to ground	Field Measurements
water flow	
Climate	Pearl, NM station (Hobbs)
Background Chloride in Ground Water	Samples from nearby wells
Ground Water Flux	Calculated from regional hydraulic
	data
Aquifer Thickness	Nicholson and Clebsch (1960) and
	SEO data

*Table 1: Input Parameters for Simulation Modeling* 

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### 2. Collection and Evaluation of Data for Simulation Modeling

The HYDRUS1D and mixing model simulation requires input of 10 parameters. As Table 1 shows, we must collect site specific data for several of these parameters, some data are available from previous ROC work at the site, and other data are available from public sources. Our previous work with the American Petroleum Institute showed that soil moisture values did not strongly influence the ability of the model to predict chloride migration from the vadose zone to ground water. We plan to use soil moisture data from nearby sites for model input.

We propose a field program to collect important site-specific data for model input. First we will measure the depth to ground water at five nearby windmills and the adjacent monitoring well to determine the hydraulic gradient (Plate 1). We have examined these abandoned and active windmills; we can measure these water levels. To establish background chloride concentrations in ground water, we propose to sample the active windmill located in Section 13 (Plate 1) and, if possible, two additional up gradient wells in Sections 2 and 11 (identified as "Field Check Required" on Plate 1).

### 3. Design Remedy and Submit Report

ROC has completed the repair of the pipeline junction at the Zachary Hinton EOL. We do not anticipate additional releases of produced water at this site. Our modeling of the "no action alternative" (Task 1) may show that the residual chloride mass in the vadose zone poses a threat to ground water quality. If such a threat does exist, we will use the HYDRUS-1D model predictions to develop a remedy for the vadose zone. If necessary, we will simulate:

- 1. excavation, disposal and replacement of clean soil to remove the chloride mass,
- 2. installation of a low permeability barrier to minimize natural infiltration,
- 3. surface grading and seeding to eliminate any ponding of precipitation and promote evapotranspiration, thereby minimizing natural infiltration, and
- 4. a combination of the above potential remedies.

We will select the vadose zone remedy that offers the greatest environmental benefit while causing the least environmental damage.

We will use the ground water mixing model or a suitable alternative to assist in the design of a ground water remedy. It is possible, however, that the background chloride concentrations in ground water measured in the nearby windmills are equal to or higher than the chloride concentration in the adjacent monitoring well. Such data would strongly suggest that the Zachary Hinton EOL Junction Box has not caused any material impairment of ground water quality. If we find no evidence of impairment of water quality due to past activities at Zachary Hinton EOL Junction Box, we will not prepare a ground water remedy. If data suggest that the Zachary Hinton EOL Junction Box has contributed chloride to ground water and caused ground water impairment, we will examine the following alternatives:

- 1. Natural restoration due to dilution and dispersion,
- 2. Pump and dispose to remove the chloride mass in the saturated zone,
- 3. Pump and treat to remove the chloride mass in the saturated zone,
- 4. Because of the location of the site, institutional controls negotiated with the landowner may provide an effective remedy. Such controls may be restriction of water use to livestock until natural restoration returns the water quality to state standards, a provision for alternative supply well design, or a provision for well head treatment to mitigate any damage to the water resource.

We plan to commence data collection for the HYDRUS1D simulations described above in mid July. Your approval to move forward with this workplan will facilitate our access to nearby windmills and speed the implementation of a surface remedy.

Sincerely, R.T. Hicks Consultants, Ltd.

Kanddel T. Ha

Randall T. Hicks Principal



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### **APPENDIX B**

### RICE OPERATING COMPANY JUNCTION BOX DISCLOSURE FORM

				BOX LOC/	ATION					
SWD SYSTEM	JUNCTION	UNIT	SECTION	TOWNSHIP	RANGE	COUNTY	BOX DI	MENSIONS	- FEET	
	Zachary		10	226	275		Length	Width	Depth	
60	Hinton EOL	<u> </u>	12	223	370	Lea	Box Ha	s Not Been	Built Yet	
LAND TYPE: E	3LM	STATE	FEE LA	NDOWNER	Tom	i Kennan	OTHER_	,		
Depth to Grou	ndwater	56	feet	NMOCD	SITE ASSE	SSMENT F	RANKING SC		10	
Date Started	2/6/	2001	Date Cor	mpleted	ot complet	<u>e</u> OCD \	Witness		No	
Soil Excavated	0	cubic ya	rds Exc	cavation Ler	ngth0	Width	0	Depth	0	feet
Soil Disposed	0	cubic ya	rds Off	fsite Facility_	n	/a	Location_		n/a	
FINAL ANAL	TICAL F	RESULT	S: Sampl	e Date	n/a		Sample De	pth	n/a	

Procure 5-point composite sample of bottom and 4-point composite sample of sidewalls. TPH, BTEX and Chloride laboratory test results completed by using an approved lab and testing procedures pursuant to NMOCD guidelines.

Sample	Benzene	Toluene	Ethyl Benzene	Total Xylenes	GRO	DRO	Chlorides
Location	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Vad	ose Zone Sam	ples Will Be Inc	luded With Fina	I Closure Repo	ort	-

### General Description of Remedial Action: Site was delineated vertically and laterally

#### CHLORIDE FIELD TESTS

with a backhoe. Chloride impact was consistent vertically, while TPH was minimal at the location.	
The site was bored on 2/28/02 and chloride was found to impact groundwater. A cased monitor	L
well was installed and the groundwater has been sampled and analyzed quarterly (see annual	
groundwater report for results). ROC has contracted a hydrologic consultant to assist ROC in	
developing a remediation plan for the vadose zone at groundwater-impacted sites with the	
ultimate objective being final closure.	

LOCATION	DEPTH (ft)	ppm
Vertical	5	2500
	7	1400
	9	1800
	11	5200
	13	5000
	15	5400
Soil Bore	35	8160
	45	5000
	50	6410
	55	500

### I HEREBY CERTIFY THAT THE INFORMATION ABOVE IS TRUE AND COMPLETE TO THE BEST OF MY KNOWLEDGE AND BELIEF.

DATE	1/21/2003		Kristin Farris	
SIGNATURE		TITLE	Project Scientist	

### APPENDIX C

### 1.0 FACTORS INFLUENCING THE MIGRATION OF CHLORIDE FROM A RELEASE

Chloride ion migration is controlled by a combination of factors related to the vadose zone, the aquifer and the characteristics of a release. Eleven factors control chloride ion migration. Here we discuss how these factors affect the movement of the chloride ion through the vadose zone and in the aquifer.

### 1. Vadose Zone Texture

The proportion of sand, silt, and clay in a soil or sediment defines vadose zone texture. Texture affects the flow of water and the transport of dissolved chloride. In the vadose zone, fine-grained layers containing silt and clay, which generally have relatively high moisture content, can often transmit water more quickly than drier coarse-grained units containing sand and gravel. A vadose zone composed of layers of fine-grained and coarse-grained units will often transmit water more slowly than a homogeneous, fine-grained profile. In the unsaturated zone, open fractures do not transmit water.

### 2. Water Content in the Vadose Zone

The soil moisture content is the volumetric fraction of water in a soil or sediment. Climate and soil texture influence soil moisture contents. Wetter, more humid environments result in higher moisture contents. Fine grained and heterogeneous soils retain water better than coarse-grained, more homogeneous soils. Therefore, the more heterogeneous and finer grained the material, the greater the water content.

The water content of a soil or sediment affects its ability to transmit fluids because the hydraulic conductivity increases with increasing water content. The hydraulic conductivity of a sandy soil with water content of 20% can be 1,000 times greater than the same soil in an arid climate where water content is only 5%. Although chloride ion from a release may migrate much faster in a wet soil profile, the natural water in the soil also dilutes the chloride concentration and provides some mitigation of its effects on ground water quality.

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#### 3. Dispersion Length of Chloride in the Vadose Zone

The dispersion length describes the amount of mixing a solute such as chloride will undergo in the vadose zone. Dispersion causes dilution of solute concentrations through mixing with ambient vadose water or ground water in a longitudinal direction parallel to water flow as well as in a transverse direction perpendicular to water flow. Systems with larger dispersion lengths produce greater mixing. Soil and aquifer heterogeneity tend to increase dispersion.

The dispersion length is very difficult to measure in the field. Researchers and field personnel rely upon professional judgement and published values (from laboratory or field experiments) to arrive at the dispersion length for a particular site. In general, researchers employ a dispersion length that is 7-10% of the total model length. When modeling a ten meter thick vadose zone, one may set the dispersion length at 10% of ten meters (100 cm).

#### 4. Depth to Ground Water or Vadose Zone Thickness

The vadose zone is the region between the land surface and ground water table, and its thickness is defined by the depth to the ground water table. The vadose zone (also referred to as the unsaturated zone) includes the capillary fringe (pore space completely filled with water, under negative soil water pressure) and the overlying soil and sediment where the pore space is partially filled with water. Because ground water table depth rises and falls due to seasonal fluctuations in precipitation, ground water pumping withdrawals, and other factors, the thickness of the vadose zone is not constant. Like soil texture, the thickness of the vadose zone affects the time required for a release at the ground surface to reach the water table. The thicker the vadose zone, generally, the longer the travel time from ground surface to the water table. A relatively thick vadose zone also has more open pore space to temporarily store released fluid. A thick vadose zone can attenuate the effects of a chloride ion release more effectively than a thin vadose zone.

### 5. Climate

Precipitation and evaporation affect the water content of the vadose zone (before a release) and exert control over the migration of chloride after a release. In a humid climate regular and generous precipitation over the annual cycle can create relatively uniform infiltration patterns and a predictable soil water profile. In arid climates, where rainfall occurs in short-duration thunderstorms punctuated by long periods of drought, the infiltration is not uniform and occurs only immediately after large precipitation events. Arid climates exhibit vadose zones with relatively low water contents.

In humid climates with relatively uniform infiltration patterns, one could employ monthly climate data for simulation modeling. In arid climates, daily precipitation and evaporation data are necessary.

### 6. Chloride Concentration of Release

Chloride concentration in oil field brine water can be 100,000 ppm, or much lower if the producing formation contains fresh water due to infiltration of precipitation over geologic time. One of the easiest input parameters to measure in the oil and gas fields is the chloride concentration of the produced water. The chloride concentration in other types of released fluids can also be measured. The effect of chloride concentration in a released substance is straightforward: the higher the chloride concentration, the greater the environmental threat.

### 7. Release Volume and Chloride Mass

The volume of the release multiplied by the chloride concentration of the release yields the total mass of chloride released to the environment. The total mass released is a very important input parameter because it determines for a specific site the risk for ground water impairment. In the absence of reliable data on the volume of a release, the total mass of chloride can generally be estimated by a field investigation.

### 8. Height of Spill

Chloride ion releases occur in bermed areas when produced water storage tanks fail or within the natural terrain due to transmission line leaks and other transportation accidents. Releases may pond in a berm, pit, or natural depression, or can be dispersed over a large area. If the release is contained within a berm, the spill height is equal to or less than the height of the berm. In an open field, the spill height may vary. For a given site the amount of chloride ion infiltration into the soil is a function of the hydrau-

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lic head or ponding depth. As the ponding depth increases, so does the hydraulic head, (pressure, at the soil/chloride ion spill interface). Understanding the depth of ponding and the total amount of infiltration per unit area guides the characterization efforts. A large amount of infiltration may require deep drilling for site characterization while a small release may require sampling with a hand shovel.

#### 9. Ground Water Flux

Ground water moves through an aquifer in response to its capacity for transmitting water, or, hydraulic conductivity (m/day), and the driving force caused by a sloping water table (hydraulic gradient). The hydraulic conductivity of aquifers can be measured in the field, and can be found in publications that often provide estimates of this parameter. The hydraulic gradient can be measured in the field by determining the depth to water at three wells of known surface elevation. Multiplication of the hydraulic conductivity by the hydraulic gradient yields the ground water flux, which is the volume of water flowing through a unit area of aquifer over a specified time period (expressed in  $m^3/(m^2 * day) =$ m/day). The lower the ground water flux, the higher the probability that a release will cause unacceptable ground water quality impairment.

#### 10. Aquifer Thickness

A thick aquifer contains more water than a thin aquifer. A given amount of chloride that enters from the vadose zone in a thick aquifer will result in a lower chloride concentration than the same amount entering a thin aquifer since aquifers that contain more water can be more effective at diluting contaminates. A thick aquifer that exhibits a large ground water flux may be able to absorb chloride from a large surface release without any severe impact to water quality.

### 11. Aquifer Ambient Chloride Concentration

Ambient chloride concentrations of ground water will influence whether or not a release causes unacceptable ground water quality impairment. If ground water has a low chloride concentration, even a considerable release may not cause chloride concentrations to exceed the US EPA Secondary Standard of 250 ppm or preclude the use of the water for agricultural needs. A high chloride concentration in ground water increases the risk that a chlo-

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ride ion release will render the groundwater unfit for use. Simple field measurements from nearby well water or published data can supply an accurate estimate of the ambient chloride concentration in an aquifer.

### **1.1 HETEROGENEITY**

Heterogeneity, most often caused by the layering of different sediment or soil types within a vadose zone, is more common in nature than not. Heterogeneity affects the distribution of chloride and other solutes through its strong influence on dispersion and hydraulic permeability.

One of the most common simplifying assumptions employed by regulators and guidance manuals is the assumption of homogeneity. However, a clay lens one meter thick found 3 meters below a release in a sandy soil will have a profound effect on the migration of chloride through the vadose zone. Heterogeneity can increase the attenuation of a release and help mitigate the effects on ground water quality.

### 1.2 RELEASE VOLUME, SPILL HEIGHT, AND CHLORIDE CONCENTRATION OF THE RELEASE

We have found that knowledge of the volume of a release is less important than understanding (1) the chloride load per unit area and (2) the geometry of the release with respect to ground water flow. Because release volume is seldom known with accuracy, we have combined chloride concentration in the release and spill height into a single parameter: chloride load/ unit area. We then used the release volume and spill height to calculate the size of a circular release. As described below, we used the diameter of the release as the length of a release parallel to ground water flow. If an oblong release geometry is oriented parallel to ground water flow, more chloride will enter the aquifer along a specific flow line, yeilding a higher chloride concentration in the down gradient well. If the long axis of the oval release is perpendicular to ground water flow, the impact to a well will be less. By re-arranging and combining these factors, we reduced the total number of factors from 11 to 10.

### 2.0 MODELING APPROACH

The modeling of chloride ion migration from the soil surface through the vadose zone into a shallow aquifer towards a monitoring well would require a sophisticated three-dimensional model, which takes into account the full coupling between unsaturated flow in the vadose zone and saturated flow in the aquifer. Such an approach is outside the scope of this study since generally acceptable three-dimensional models capable of such simulations are still being developed. Moreover, the computer time necessary to conduct such simulations would have been prohibitive for regulators and oil field personnel.

We used an approach based upon the assumption that flow through the vadose zone is mainly downward. This assumption is reasonable for humid climates where precipitation exceeds evapotranspiration most of the year. It is also reasonable in arid climates when the ground water table is so deep that no upward flow due to capillary rise can be maintained. Under these conditions, it is possible to de-couple the modeling of water flow and chloride transport in the vadose zone from the modeling of water flow and chloride transport in the aguifer. We assume that flow in the vadose zone is one-dimensional downward and flow in the aquifer is one-dimensional horizontal. This assumption allows us to first simulate water flow and chloride transport through the vadose zone using the model HYDRUS-1D. The output from HYDRUS-1D is the downward water flow seeping out of the vadose zone and the downward chloride flux over time. These outputs are used as inputs into the model for the aquifer. In this study, we used two models for the aquifer: MODFLOW and a simple groundwater mixing model. MODFLOW is a standard code for modeling water flow and solute transport through aquifers (Domenico & Schwartz, 1998). Since it takes quite some time to setup a simulation in MODFLOW, we used a validated excel spreadsheet mixing model to generate results more cost effectively.

### 2.1 VADOSE ZONE MODEL: HYDRUS-1D

#### 2.1.1 Model Overview

HYDRUS-1D (Simunek et. al, 1998) is used to simulate one-dimensional transport of water, heat, and solute movement in variably saturated porous media. The HYDRUS- 1D model was developed by the George E. Brown Jr., Salinity Laboratory, USDA, ARS, Riverside, California and is distributed by the International

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Ground Water Modeling Center (IGWMC), Golden, Colorado. A Microsoft Windows<sup>™</sup> based Graphics User Interface (GUI) supports HYDRUS-1D.

The HYDRUS-1D model numerically solves the Richards' equation for water flow and Fickian-based advection-dispersion equations for heat and solute transport. The HYDRUS-1D flow equation includes a sink term (a term used to specify water leaving the system) to account for transpiration by plants. The solute transport equation considers advective, dispersive transport in the liquid phase, diffusion in the gaseous phase, nonlinear and non-equilibrium sorption, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and first-order degradation. The heat transport equation describes conduction as well as convection.

HYDRUS-1D can handle large numbers of soil layers, and uses the van Genuchten-Mualem, Brooks-Corey, Kosugi lognormal, and Durner dual porosity models to describe soil hydraulic properties. When values of soil hydraulic properties are unavailable, HYDRUS-1D can estimate them from a small catalog of values based on major textural classes (e.g., sand, sandy loam, etc.) or neural network based predictions.

The HYDRUS-1D code can simulate a wide range of boundary conditions. These are constant and time-variable pressure heads and fluxes, free drainage, seepage face, and an atmospheric boundary condition. An atmospheric boundary condition can be used to either generate run-off when the precipitation rate exceeds the infiltration capacity of the soil, or store excess water on the land surface allowing the water to infiltrate when precipitation stops. Time-variable conditions can be entered hourly, daily, or any general time interval.

We used HYDRUS-1D for the vadose zone simulations of this research project because we are interested in the vertical transport of water and chloride through the vadose zone. The outputs from HYDRUS-1D are the daily water flow and chloride flux from the vadose zone over the time period of the simulation expressed as cm day<sup>-1</sup> and mg cm<sup>-2</sup> day<sup>-1</sup> respectively. These outputs are used as inputs into the simple mixing model.

#### 2.1.2 Applicability of HYDRUS-1D for Chloride ion Releases

Surface or near surface releases of chloride ion migrate through the vadose zone under variably saturated conditions as a function of release volume, topography, and climatic conditions (i.e., precipitation and evapotranspiration). Although other vadose zone models exist that satisfy this criterion, we selected HYDRUS-1D over other models for the following three reasons:

- 1. It can simulate water and solute transport through heterogeneous porous media: horizons and sediments of varying geology;
- 2. It can incorporate daily climatic data; and
- 3. We are familiar with the model.

Dr. Jirka Šimùnek of our team developed the HYDRUS-1D model with his colleagues Dr. van Genuchten and Dr. Sejna; Dr. Jan Hendrickx, another team member, has used the HYDRUS-1D model for many years for evaluation of groundwater recharge and salt movement through the vadose zone.

### 2.2 SATURATED ZONE MODEL: MIXING MODEL AND MODFLOW

As stated, the objective of this part of this study is to evaluate the impact of choride releases on ground water quality as measured in a well adjacent to and down gradient of the release. The chloride flux leaving the vadose zone, the horizontal flux in the unconfined aquifer, the original chloride concentration in the ground water, and the thickness of the unconfined aquifer also affect the chloride concentration of the aquifer. Since the water flux seeping from the vadose zone and its chloride concentration vary with time, no simple analytical solutions are available for determination of the time-varying chloride concentration in the well.

Therefore, we implemented a simple spreadsheet ground water mixing model for the determination of the chloride concentration in the well. This mixing model uses the output of the HYDRUS-1D model as input. We have to define the aquifer volume, (the mixing compartment underneath the spill) as a first step in the ground water mixing modeling process. Assuming a circular spill area and a unidirectional horizontal flux in the aquifer, the highest impact will occur where the ground water has the longest exposure to the incoming chloride from the vadose zone. This takes place along the diameter of the circular spill. Therefore, the length of the mixing compartment is made equal to the diameter of the spill area, *D*. The depth of the mixing compartment is the thickness of the aquifer, *H*. The width, *W*, of the mixing compartment is taken equal to unity (one) to simplify the calculations.

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Now we will develop the relation between the water flux seeping out of the vadose  $q_v$ , the chloride concentration in the vadose zone flux,  $C_v$ , the horizontal flux in the aquifer underneath the release entering the compartment,  $q_{in}$ , the original chloride concentration in the aquifer,  $C_{in}$ , the horizontal flux in the aquifer underneath the release leaving the compartment,  $q_{out}$ , and the chloride concentration of the aquifer flux leaving the area underneath the chloride ion release,  $C_{out}$ . The latter concentration is the one that will be monitored in the down gradient well. We make the following reasonable assumptions to determine  $C_{out}$ :

1. Ground water flow is in steady state. The discharge entering into the mixing compartment from the vadose zone,  $q_v HDHW$ , plus the horizontal discharge in the aquifer entering the mixing compartment at its up-gradient side,  $q_{in}HHHW$ , are equal to the discharge leaving the mixing compartment,  $q_{out}HHHW$ .

2. Changes in thickness of the saturated aquifer are small compared to the total thickness of the aquifer H.

3. The thickness of the aquifer, *H*, and its porosity, *n*, are constant.

4. Mixing of the chloride entering the mixing compartment is complete and immediate. This assumption appears invalid from data published in the recent literature (LeBlanc et al., 1991; Zhang et al., 1998). We can use the results of the mixing model as an excellent indicator of the mean chloride concentration in a supply well penetrating the aquifer underlying the release, but not as an indicator of the chloride distribution in the aquifer.

The volume of the mixing compartment, *V*, will be constant under these assumptions, and is equal to:

$$V = D \times H \times W \times n \tag{2-1}$$

The water balance of the mixing compartment is equal to:

$$q_{in} \times H \times W + q_{v} \times D \times W = q_{out} \times H \times W$$
(2-2)

We can eliminate variable *W* from Eqs. [2-1] and [2-2] by putting W= 1 m.

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The chloride balance of this mixing compartment during any time period dt is:

$$\left[\left(q_{ln} \times C_{ln} \times H + q_{r} \times C_{r} \times D\right) - \left(q_{ln} \times H + q_{r} \times D\right) \times C_{out}\right] dt = \left[D \times H \times n\right] dC$$
(2-3)

where dC is the change of chloride concentration occurring during time period dt.

Rearranging Eq. [2-3] we obtain the ordinary differential equation:

$$\frac{dC}{dt} = \frac{q_{in} \times C_{in} \times H + q_v \times C_v \times D - (q_{in} \times H \times q_v \times D) \times C_{out}}{H \times D \times n}$$

(2-4)

As soon as chloride from the release enters the ground water, the volume average concentration in the mixing compartment is  $C_{out}$  after complete mixing has occurred. Thus the chloride concentration of the water leaving the department,  $C_{out}$ , becomes:

$$C = C_{out}$$
 and  $dC = dC_{out}$  (2-5)

Therefore, we can convert Eq. [2-4] in a forward finite difference expression:

$$\frac{C_{out}^{i+1} - C_{out}^{i}}{t^{i+1} - t^{i}} = \frac{q_{in}^{i} \times C_{in}^{i} \times H + q_{v}^{i} \times C_{v}^{i} \times D - (q_{in}^{i} \times H + q_{v}^{i} \times D) \times C_{out}^{i}}{H \times D \times n}$$
(2-6)

which yields an explicit expression for  $C_{out}^{i+1}$ ,

$$C_{out}^{i+1} = C_{out}^{i} + \frac{\left[q_{in}^{i} \times C_{in}^{i} \times H + q_{v}^{i} \times C_{v}^{i} \times D - \left(q_{in}^{i} \times H + q_{v}^{i} \times D\right) \times C_{out}^{i}\right] \times \left[t^{i+1} - t^{i}\right]}{H \times D \times n}$$
(2-7)

Using the output from HYDRUS-1D: the chloride concentration,  $C_{v}^{i}$ , of the water,  $q_{v}^{i}$ , entering the ground water table on day,  $t^{i}$ , we have put into a spreadsheet the mixing model of Eq.

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for  $C_{max}$  to reach a well:

- · Vadose Zone Texture and Climate,
- · Climate and Depth to Ground Water, and
- Vadose Zone Texture and Depth to Ground Water.

The lower right section of Figure 3-5 shows that the depth to ground water has little effect on the arrival time of  $C_{max}$  if the texture of the vadose zone is sand. In a clay profile, however, the time of arrival is very different: nearly 80,000 days (219 years). This same relationship is expressed with the interaction between Climate and Depth to Ground Water (plotted in the upper right portion of Figure 3-5). In a humid climate, the texture of the vadose zone has little impact on the arrival time of  $C_{max}$ . However, in the arid Lea County, a release to a clay profile will require over 200 years longer for  $C_{max}$  to reach a well than the same release to a sandy vadose zone would.





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[2-7]. By changing the values for spill diameter, D, ground water flux,  $q_{in}$ , original chloride concentration in the aquifer,  $C_{in}$ , and the aquifer thickness, H, we have evaluated the effect of these four factors of an unconfined aquifer.

Figure 2-1 Comparison between MODFLOW and the Mixing Model



Figure 2-1 presents two comparisons between the chloride concentrations in the well located down gradient of the entry point of the release obtained with the mixing model Eq. [2-7] and those obtained with the model MODFLOW. The two comparisons deal with two complete different sets of environmental and release factors. In Shreveport the vadose zone texture is clay, the dispersion length 0.1 m, release chloride concentration 10,000 ppm, spill height 0.6 m, and aquifer flux 0.05 m/ day. In Hobbs, vadose zone texture is sand, dispersion length 2.0 m, release chloride concentration 100,000 ppm, spill height 0.025 m, and aquifer flux 0.004 m/day. The maximum chloride concentrations predicted by the two models is quite similar, although the time of arrival to the maximum concentration is different between the two models. We have conducted

HYÖRÖS 10 APPENDIZA Somonider 12, 2003 this part of the study using the less expensive mixing model Eq. [2-7]. (Our approach using HYDRUS-1D in combination with MODFLOW and Eq. [2-7] is valid for situations where the vadose zone seepage flux,  $q_v$ , is downward. A downward flux in the vadose zone is always found in the profiles with a deep ground water table depth. However, in the profiles with a ground water table depth between  $\mathbf{0} - (+/-)\mathbf{10}$  m an upward flux from ground water table towards the soil surface does occur as a result of capillary rise. The magnitude of the upward capillary flux depends on soil type and climate.

A large amount of precipitation enables the downward vadose zone flux to dominate the chloride transport in both the sandy and clayey soil in the humid climate of Shreveport. Occasionally in the clayey soil an upward flux is encountered during short periods without rain.

An upward flux is sometimes found in the sanyd soil but is prevalent in the clay soil in the arid climate of Hobbs. For example, when the ground water table depth is 3 m, the average upward flux in a clay profile would be 0.04 cm/day or 13.5 cm/ year; this upward capillary flux causes the chloride and soil water from the release to stay in the vadose zone and protects the ground water from impairment. In hydrogeological situations where capillary rise is common, vadose zone water movement towards ground water is sporadic. However, a big storm can push chloride ion into a shallow aquifer very quickly.

There is a strong dynamic interaction between all eleven factors, outlined in section 1.1., when water leaving the vadose zone,  $q_{i}$ , changes direction frequently in response to precipitation events (downward movement) and evapotranspiration (upward movement). In dry climates with shallow ground water (less than 3 m), upward movement of ground water into the vadose zone thnce to the atmosphere is common. The only manner to correctly simulate the interaction between these factors is by employing a two- or three-dimensional model, such as HYDRUS-2D. However, since the main objective of this study is ground water impairment and the effect of capillary rise in diminishing the leaching of chloride to the ground water, and is not the chloride ion concentration in the root zone, we used the mixing model Eq. [2-7] for ground water table depths of 3 m. We used the equation only for downward fluxes and made it inactive when the vadose zone flux  $q_{i}$ , goes upward. It was

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initiated again with the next occurrence of a downward flux,  $q_v$ , taking the  $C_{out}$  value of the previous occurrence of a downward  $q_v$ . In this manner a conservative estimate is obtained of the chloride concentration in the monitoring well assuming perfect mixing for shallow groundwater tables.

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### 3.0 SENSITIVITY ANALYSIS OF FACTORS DETERMINING CHLORIDE ION FATE

### 3.1 PURPOSE

After a brine release, the concentration of chloride in the vadose zone decreases with time and distance traveled through the vadose zone towards ground water because of dilution with ambient soil water. Further dilution occurs in the aquifer after the chloride reaches the ground water. The maximum chloride concentration occurring at a well down gradient from the release will depend on all the factors that affect chloride transport through the vadose zone and shallow aquifer. Understanding these factors is critical for the design and implementation of a site characterization program after a chloride ion release. The degree of ground water quality impairment determines to a large extent the need for a ground water remedy. The purpose of this sensitivity study is to evaluate which of the eleven factors have the greatest effect on prediction of maximum chloride concentration in the well down gradient of the release.

### 3.2 MODELING SPECIFICS

We needed to optimize our simulation efforts in order to obtain the maximum amount of information from the modeling. Statistics of experimental designs (e.g. Law & Kelton, 2000; Snedecor & Cochran, 1967; Steel & Torrie, 1980) allow us to decide which combination of factors to simulate so that the desired information can be obtained with the lowest possible number of simulations.

The factors used in experimental design statistics are the input variables to our simulation models. The outputs of our simulations are the responses. The responses that we consider in this study are the maximum chloride concentration,  $C_{max}$ , occurring in the well and the time at which the maximum chloride concentration reaches the well,  $T_{max}$ .

We have opted for a  $2^k$  factorial design that requires us to choose two levels of each factor in this study. This design results in a

total of  $2^k$  simulation runs, where *k* is the number of factors. We chose the two values for each factor so that they represent two opposite conditions such as an arid and a humid climate. The factors can be qualitative like climate or quantitative like depth to ground water. The two input values should not be too extreme or unrealistic. Additionally, the two values should not be too similar or the simulations may not adequately evaluate important aspects of the transport process under consideration. The 11 factors of this sensitivity analysis (see Table 3-1) resulted in  $2^{11}$  or 2,048 different chloride ion release scenarios.

## **Table 3-1:** Vadose zone, aquifer, andbrine release factors determiningmaximum chloride concentrationarriving at a monitoring well downgradient.

### 3.2.1 VADOSE ZONE FACTORS

#### Climate

We selected the two contrasting climates of Lea County, New Mexico, and Shreveport, Louisiana for the sensitivity analysis. Lea County is located in the arid southwest, and Shreveport is in the humid south. Lea County's annual precipitation and potential evapotranspiration is 14 inches and 59 inches, respectively, while annual precipitation and potential evapotranspiration for Shreveport is 46

		Maximum Chloride	
		Concentr	ation
Description	Abbreviation	Decrease	Increase
Climate	clim	Arid	Humid
Soil Texture	soil	Clay	Sand
Initial Water Content	wein	Wet	Dry
Chloride Dispersion Length	disp	2.0 m	0.1 m
Ground Water Depth	gwl	30 m	3 m
Ground Water Flux	qaq	0.05 m/day	0.001 m/day
Ambient Aquifer Cl	cin	0 ppm	100 ppm
Concentration			
Aquifer Thickness	thick	30 m	3 m
Release Volume	vol	100 barrels	10,000 barrels
Release Height	depth	0.025 m	.6m
Release Chloride	cleon	10,000 ppm	100,000 ppm
Concentration			
Release Chloride Mass	clmass	250 g/m <sup>2</sup>	60,000 g/m <sup>2</sup>
	Description Climate Soil Texture Initial Water Content Chloride Dispersion Length Ground Water Depth Ground Water Flux Ambient Aquifer Cl Concentration Aquifer Thickness Release Volume Release Height Release Chloride Concentration Release Chloride Mass	DescriptionAbbreviationClimateclimSoil TexturesoilInitial Water ContentwcinChloride Dispersion LengthdispGround Water DepthgwlGround Water FluxqaqAmbient Aquifer ClcinConcentrationthickRelease VolumevolRelease HeightdepthRelease ChlorideclconConcentrationclcon	DescriptionAbbreviationDecreaseClimateclimAridSoil TexturesoilClayInitial Water ContentwcinWetChloride Dispersion Lengthdisp2.0 mGround Water Depthgwl30 mGround Water Fluxqaq0.05 m/dayAmbient Aquifer Clcin0 ppmConcentration100 barrelsRelease Volumevol100 barrelsRelease Chlorideclcon10,000 ppmConcentration250 g/m²

inches and 67 inches, respectively. Lea County and Shreveport also differ in how precipitation occurs. In Lea County, the majority of precipitation occurs during the "monsoon" of July-August and much of the remainder of the year resembles drought conditions. Shreveport's precipitation falls throughout the year.

### Vadose Zone Texture

We selected sand and clay as contrasting soil textures for the sensitivity analysis. Sand and clay differ not only in grain size but also in their ability to retain and transmit water. Sand has a relatively high-saturated hydraulic conductivity and low water retention; whereas clay has a relatively low saturated hydraulic conductivity and high water retention.

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#### Water Content in Vadose Zone

We hypothesized that higher initial water content in the vadose zone would result in slower chloride ion movement because the initial moisture must be displaced before the chloride ion can move downward through the vadose zone. We used HYDRUS-1D to predict initial water contents for both vadose zone textures in both Lea County and Shreveport. We used these predictions as initial conditions in the sensitivity analysis.

We ran simulations for one hundred years or until we achieved dynamic equilibrium between soil water content and climatic conditions for both the wet and dry initial conditions. To create *wet* conditions, we ran simulations without any vegetation (low evapotranspiration); and ran simulations with vegetation (high evapotranspiration) in *dry* conditions. We used evergreen plants capable of transpiring soil water all year round with a 3 meter (~10 ft) deep root zone. Transpiration of soil water created a drier soil profile than simulations without vegetation.

### Dispersion Length of Chloride in Vadose Zone

For the sensitivity analysis, we selected minimum and maximum chloride dispersion lengths of 0.10 m (0.33 ft) and 2.0 m (6.6 ft), respectively. The larger dispersion length will produce greater mixing of chloride ion with ambient soil water in the vadose zone, and it is expected to result in a lower maximum chloride concentration in the well. Conversely, the smaller dispersion length will result in minimal mixing, e.g. minimal attenuation of the release, and larger maximum chloride concentrations. We based our selection of dispersion lengths on values reported in the literature (Gelhar, 1993).

### Depth to Ground Water

Deep ground water allows for more storage of chloride ion and more attenuation of the maximum chloride concentration during its downward migration. We selected ground water depths of 3.0 m (9.8 ft) and 30 m (98 ft) for the sensitivity analysis. These depths represent reasonable values for a shallow and deep aquifer, respectively.

### **3.2.2 AQUIFER FACTORS**

#### **Ground Water Flux**

Ground water flux represents the rate of ground water movement and effects the ability of an aquifer to dilute chloride and other constituents of a chloride ion release. A large ground water flux produces greater dilution.

orannis in hopfiging a Soutomber 12 2093 We based our selection of minimum and maximum groundwater fluxes on literature values for the Ogalalla aquifer, Southern Lea County, New Mexico (Native and Smith, 1987). We used 0.10 cm/day (0.0033 ft/day) and 5.0 cm/day (0.16 ft/day) as minimum and maximum values, respectively. The maximum flux is lower than some of the ground water fluxes reported in the literature (e.g. 40 cm/day by Zhang et al., 1998) and, thus, is a conservative estimate.

### **Aquifer Ambient Chloride Concentration**

We selected ambient chloride concentrations for ground water of o ppm and 100 ppm. One hundred parts per million or less is typical for ground water of the Ogallala aquifer (Nicholson and Clebsch, 1961) and the Carrizo-Wilcox aquifer in Caddo Parish, Louisiana (Rapp, 1992). Although 10-ppm chloride is a more characteristic minimum value for the Ogallala and Carrizo-Wilcox aquifers, we selected 0.0 ppm to create a greater difference between minimum and maximum chloride concentrations of ground water.

#### **Aquifer Thickness**

The thicker the aquifer, the more opportunity for mixing (dilution), and the lower the predicted chloride concentration will be in the aquifer. We selected two aquifer thicknesses, 3.0 m (9.8 ft) and 30 m (98 ft). Three meters are approximately equal to the length of most well screens used to monitor the chloride changes. Therefore, an aquifer thickness of 3 meters provides a good estimate of expected chloride concentrations at a monitor well in a thicker aquifer under conditions of limited vertical mixing. Many unconfined, alluvial aquifers are greater than 30 m thick, but we have selected 30 m as the maximum value. A 30 m thick saturated sandy formation with a hydraulic conductivity of at least 0.0005 m/s (140 ft/day) is classified as a good aquifer (Freeze and Cherry, 1979).

### 3.2.3 CHLORIDE ION RELEASE FACTORS

#### **Release Volume**

We used minimum and maximum release volumes of 100 bbl (16 m<sup>3</sup>) and 10,000 bbl (1,600 m<sup>3</sup>), respectively. These release volumes are representative of large and very large releases based on the experience of oil and gas industry personnel.

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### R.T. HICKS CONSULTANTS, LTD.

In the one-dimensional HYDRUS-1D model we used only spill height as an input variable. The spill volume was introduced into the mixing model using the diameter of the spill. For example, a

Figure 3-1. Schematic of Two Possible Brine Release Characteristics After a Release of 100 Barrels.

100 barrel release resulting in a chloride ion release of 0.025 m height with circular shape will have a diameter of 29 m while a release of 0.6m height will have a diameter of only 6m (Figure 3-1). Table 3-2 summarizes the four chloride ion release areas evaluated with the mixing model. These four release areas are combinations of the two spill heights (0.025 and 0.6 m) and two release volumes (large: 100 barrels and very large: 10,000 barrels).

We represented all spill areas as circles, and then, used the mixing model to evaluate mixing along the diameter of each circular spill (see Table 3-2). The diameter of each circle represents

the longest path groundwater must flow beneath each release area, and thus provides a conservative estimate of groundwater quality impairment at a well immediately down gradient of a release.

### **Chloride Concentration of Release**

We selected chloride concentrations of 10,000 and 100,000 ppm, as the minimum and maximum concentrations for the chloride ion release input parameter in consultation with experienced professionals. These concentrations are representative of most chloride ion releases. Volume Depth Diameter Area Barrels m<sup>3</sup> m  $m^2$ acres m 100 16 0.025 640 0.16 29 0.6 26.67 0.007 6 10000 16

The mixing model does not consider density differences between the density of the chloride ion arriving at the aquifer and the density of the water in the aquifer. These differences (even if small) may cause chloride ion to sink in an aquifer (LeBlanc et al., 1991; Zhang et al., 1998) and would influence the distribution of chloride ion in the aquifer. Since our approach assumes complete mixing in the aquifer, the chloride distribution is not taken into account. Water extracted from a well by bailing or pumping typically would represent a well mixed sample. The

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600	0.025	64000	16	285
	0.6	2666.67	0.7	58
-	- 14440 1444			
	1			

*Table 3-2.* Characteristics of brine releases in this study.



results of the mixing model help to identify environmental and release characteristics that cause groundwater quality impairment and provide a measure of the overall impact of a chloride ion release on an aquifer.

### **Height of Spill**

We selected 0.025 m (1 inch) and 0.6 m (2 ft) as the minimum and maximum spill heights, respectively, of brine water on the land surface, based on observations of oil and gas industry personnel. A 0.6 m (two-foot) height represents a discharge of 1600 m<sup>3</sup> (10,000-bbls) of chloride ion to a 2670 m<sup>2</sup> (0.7 acre) bermed area or large depression. Releases to flat or gently sloped areas are likely to result in initial heights of 0.025m (an inch) or less.

#### **Chloride Mass**

Table 3-1 presents a final factor, "Release Chloride Mass". This factor, which is the product of "Release Height" and "Release Chloride Concentration", is the mass of chloride released to the ground surface per unit area. As Table 3-1 shows, a chloride ion release (see Release Chloride Concentration) of 100,000 ppm chloride that ponds to a depth of 0.6 meters (see Release Height) causes a subsurface chloride input of 60,000 grams per square meter (the Release Chloride Mass).

### 3.3 SIMULATION RESPONSES

The simulations with the HYDRUS-1D code and the mixing model yield large amounts of information about the flow of water and the transport of chloride through the vadose zone and the underlying aquifer. As mentioned above, we have selected two critical response variables for the sensitivity analysis: (i) the maximum chloride concentration in a down gradient monitoring well,  $C_{max}$ , and (ii) the time of arrival of the maximum chloride concentration at the monitoring well,  $T_{max}$ .

#### **Maximum Chloride Concentration**

The maximum chloride concentration defines the center of mass of a release as it migrates through the vadose zone into the aquifer and reaches a well. For this reason, we used the maximum chloride concentration,  $C_{max}$ , to identify those factors listed in Table 3-1 that have a significant influence on chloride migration through the vadose zone and the aquifer as the release moves toward the well. Evaluation of  $C_{max}$  can also identify the environmental con-

HYDRES TO APPENDING TABUSHINGT (T. 2014) ditions that result in significant attenuation of chloride ion. For example, for those simulations where  $C_{max}$  is much less than the original chloride concentration of released chloride ion, environmental factors cause significant chloride ion attenuation. Additionally, an evaluation of  $C_{max}$  can be used to identify release scenarios that pose little or no threat to groundwater quality. For instance, simulations that predict a  $C_{max}$  less than the EPA Secondary Water Quality Standard of 250-ppm chloride will not cause water quality impairment. On the other hand, when predictions of  $C_{max}$  are greater than 250-ppm, ground water quality may be threatened by the release. Thus, the maximum chloride concentration in the well informs us about the risk for ground water impairment and its severity.

### Time of Arrival of Maximum Concentration at the Well

Time of arrival of maximum concentration,  $T_{max}$ , is the time required for the chloride center of mass to reach the well. It dictates the urgency to implement a field investigation and possible remedy. A relatively rapid response is required if simulations suggest a chloride concentration of 250 ppm or more at a well within a few years. However, when input factors combine to predict that decades or centuries are required for a well to show ground water impairment, an immediate ground water investigation may be of little value.

### 3.4 STATISTICAL ANALYSIS OF THE RESPONSES AT MONITORING WELL

**Table 3-3.** Main effects of the vadosezone, aquifer, and brinerelease factorson the maximum chloride concentration

Following the statistical approach by Law & Kelton (2000) for simulation modeling and analysis, we determined the impact of each factor presented in Table 3-1 on the migration of chloride ion through the vadose zone and aquifer. We did this by inspecting the effect of each factor on the maximum chloride concentration in a down gradient well,  $C_{max}$ , and the arrival time of this concentration,  $T_{max}$ , at the well.

Factor	Effe	ct on Cmax
	ppm	<b>Relative Effect</b>
Height of Brine Release	4,340	1
Release Chloride Concentration	4,017	0.93
Thickness of Aquifer	3,237	0.75
Soil	2,070	0.48
Aquifer Flux	1,994	0.46
Dispersion Length	1,545	0.36
Climate	1,184	0.27
Ground Water Depth	1,081	0.25
Volume of Brine Release	932	0.21
Ambient Cl Concentration	76	0.02
Initial Water Content of Soil	25	0.01

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### 3.4.1 MAXIMUM CHLORIDE CONCENTRATION

Table 3-3 presents the sensitivity of  $C_{max}$  to each of the 11 factors considered in this study (Table 3-1). The factors are sorted according to their impact on  $C_{max}$  in Table 3-3. The most important factors are the Height of Chloride ion Release and the Release Chloride Concentration. Changing the Height of Chloride ion Release from 0.025 to 0.6 m while holding all other factors fixed results in an average increase of maximum chloride concentration of 4,340 ppm. Changing the Release Chloride Concentration from 10,000 to 100,000 ppm results in an average increase of 4,017 ppm in maximum chloride concentration in the well. The absolute concentration values depend on the set up of the simulation experiment. We have added the relative effects of each factor in Table 3-3. The factors Height of Chloride ion Release and Release Chloride Concentration have relative effects of 1.00 and 0.93 respectively, much higher than of any other factor. The predicted difference in  $C_{max}$  due to the difference in Release Chloride Concentration is 93% of predicted difference for the Height of Chloride ion Release. The predicted difference in  $C_{\scriptscriptstyle max}$  for the two climate's indices, however, was only 27% of predicted difference for the Height of Chloride ion Release. As Table 3-3 shows, Initial Water Content of Soil exerts the smallest influence on the prediction of  $C_{max}$ .

The two most important factors, Height of Chloride ion Release and the Release Chloride Concentration, determine the Mass of Chloride entering the soil surface during a release. If the Height of Chloride ion Release or the Release Chloride Concentration increases, the Mass of Chloride increases and consequently, the maximum chloride concentration increases. Because the Mass of Chloride appears to be the key factor in determining the maximum chloride concentration arriving at a down gradient moni-

toring well, we repeated the sensitivity analysis using Mass of Chloride instead of Height of Chloride ion Release and Release Chloride Concentration. We eliminated the Initial Water Content of Soil in the second sensitivity analysis since this factor has very little impact on  $C_{max}$ .

The results of the second analysis are presented in Table 3-4 and in Figure 3-2. The mean chloride concentration of all 256 scenarios with

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**Figure 3-2** The effect of nine brine release, vadose zone, and aquifer factors



Mass of Chloride 250 g/m<sup>2</sup> is 89 ppm and that of all 256 scenarios with Mass of Chloride 60,000 g/m<sup>2</sup> is 8,446 ppm (See Figure 3-2). The difference between these two values is 8,357 ppm, which is the predicted sensitivity of the maximum chloride concentration for an increase of factors fixed.

**Table 3-4.** Main effects and important interactions of the vadose zone, aquifer, and brine release factors on the maximum chloride concentration arriving at the monitoring well  $C_{max}$  and the time of arrival of the maximum concentration  $T_{max}$ .

The Thickness of Aquifer also has a large impact with a sensitivity of 5,632 ppm for a change from 3 to 30 m. All other factors are less important. For comparison, we have determined the relative impacts of each factor by dividing each affect by the influence of the Mass of Chloride (Table 3-4). The most important factors Mass of Chloride and Thickness of

Factor	Effe	ect on C <sub>max</sub>	Effe	ect on T <sub>max</sub>
	ppm	Relative Effect	Years	Relative Effect
Main Effects				
Chloride Mass	8357	1	52	0.46
Aquifer Thickness	5632	0.67	5	0.04
Soil	3560	0.43	106	0.93
Aquifer Flux	3525	0.42	7	0.06
Dispersion Length	2699	0.32	11	0.06
Climate	2099	0.25	114	1
Ground Water Depth	1826	0.22	104	0.91
Volume of Brine Release	1631	0.2	0	0
Ambient Cl Concentration	82	0.01	44	0.39
Interaction Effects				
Chloride Mass x Aquifer Thickness	5573	0.67		
Chloride Mass x Soil	3519	0.42		
Chloride Mass x Aquifer Flux	3509	0.42		
Aquifer Thickness x Aquifer Flux	2529	0.3		
Aquifer Thickness x Soil	2509	0.3		
Soil x Aquifer Flux	1223	0.15		
Soil x Climate			98	0.86
Climate x Depth Ground Water			95	0.83
Soil x Depth Ground Water			90	0.79

Aquifer with relative affects of 1.00 and 0.67, respectively. The factors Soil, Aquifer Flux, and Dispersion Length have relative affects of 0.43, 0.42, and 0.32, respectively. The factors Climate, Ground Water Depth, and Volume of Chloride ion Release have much less impact with relative affects of 0.25, 0.22, and 0.20. Ambient Chloride Concentration (Relative effect 0.01) has virtually no effect.

We know that the predicted maximum and minimum values of  $C_{max}$  for a factor of interest can depend on the values of other factors. Where this is the case, the two factors are said to interact. An Analysis of Variance revealed that six interactions affect the **traceim**um chloride concentration. These are the interactions be-

- · Chloride Mass and Thickness of Aquifer,
- · Chloride Mass and Vadose zone texture,
- · Chloride Mass and Aquifer Flux,

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- Thickness of Aquifer and Aquifer Flux,
- · Thickness of Aquifer and Vadose zone texture, and
- · Vadose Zone Texture and Aquifer Flux.

Table 3-4 shows the relative importance of each interaction and the interactions are presented in Figure 3-3. As shown in Figure 3-3, if Mass of Chloride increases from 250 to 60,000 g/m<sup>2</sup> above an aquifer with a thickness of 3 m, the maximum chloride concentration at the well increases from 118 to 14,501 ppm. The same increase of Mass of Chloride occurring above an aquifer with a thickness of 30 m causes only a modest chloride increase

from 60 to 2,757 ppm. In a sandy vadose zone,  $C_{max}$ increases from 110 to 11,985 ppm in response to the different chloride loads to the ground surface. However, different chloride ion releases to a clay result in smaller differences, 68 to 4,906 ppm, but fall within the range of responses in a sandy zone.

The implication of the results of our sensitivity analysis is that determination of Mass of Chloride per unit surface area and

Thickness of Aquifer is critical for the evaluation of ground water impairment. Knowledge of Vadose Zone Texture Conditions, Aquifer Flux, Dispersion length, Climate, Ground Water Depth, and Volume of Chloride ion Release can provide useful additional information, while ambient Chloride Concentration and Initial Water Content of Soil provide little relevant information.

The results of the sensitivity analysis cannot be used to directly evaluate field sites because they are based on the average change of maximum chloride concentration. For each factor, the maximum chloride concentration exhibits a wide range of values as is shown in Table 3-5.

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Figure 3-3. Interaction effects between the factors soil, flux in aquifer, thickness of aquifer, and chloride load on the maximum chloride concentration in a downgradient monitoring well.



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Main Effect	Level	Mean	Minimum	Maximum
Mass of Chloride	250 g/m2	89	0	303
	60,000 g/m2	8,446	0	46,633
Thickness of Aquifer	30 m	1,429	0	15,354
	3 m	7,195	0	46,633
Soil	Clay	2,487	0	37,233
	Sand	6,047	2	46,633
Aquifer Flux	0.05 m/day	2,505	0	29,779
	0.001 m/day	6,030	0	46,633
Climate	Arid	3,218	0	44,372
	Humid	5,317	0	46,633
Ground Water Depth	30 m	3,354	0	40,758
	3 m	5,181	0	46,633
Volume of Brine Release	100 barrels	3,452	0	41,603
	10,000 barrels	5,083	0	46,633
Dispersion Length	2.0 m	2,918	0	25,653
	0.1 m	5,617	0	46,633
Ambient Cl Concentration	o ppm	4,226	0	46,593
	100 ppm	4,308	0	46,633

*Table 3-5.* Statistics of maximum chloride concentrations (ppm) determined in the sensitivity analysis.

### 3.4.2 ARRIVAL TIME OF MAXIMUM CHLORIDE CONCENTRATION

We present the effects of the factors on the arrival time of the maximum chloride concentration at the well in Table 3-4. The arrival time strongly depends on climate (relative effect of 1.0 in Table 3-4), vadose zone texture, and depth of ground water. In the arid climate of Lea County, New Mexico, a chloride ion release will require an additional 114 years (40,515 days) for the maximum concentration to arrive at a well than a similar release in the humid climate of Shreveport, Louisiana. The vadose

Figure 3-4 The effect of nine brine release, vadose zone, and aquifer factors on the time when the maximum chloride concentration arrives in a downgradient monitoring well.

zone texture and ground water table effects are of the same order of magnitude (106 and 104 years respectively). Other factors are less important. Figure 3-4 graphically displays this same information. Our Analysis of Variance identified three important interactions that effect the length of time required



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### APPENDIX D

### Chloride Content in the Vadose Zone

The purpose of this appendix is to explain different ways to quantify the amount of chloride present in the vadose zone. First, we present a number of concepts dealing with quantifying water and chloride contents. Next, we present our approach to calculate the chloride load.

### Definitions

Gravimetric water content  $2_g$ 

$$\theta_g = \frac{W_{water}}{W_{dry\ soil}} \tag{1}$$

where  $W_{water}$  is the weight of water (kg) and  $W_{soil}$  is the weight of the dry soil (kg).

*Volumetric water content*  $2_v$ 

$$\theta_{v} = \frac{V_{water}}{V_{soil}}$$
[2]

where  $V_{water}$  is the volume of water (m<sup>3</sup>) and  $V_{soil}$  is the volume of the soil (m<sup>3</sup>). The relationship between  $2_g$  and  $2_v$  is

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$$\theta_{v} = \frac{\rho_{soil}^{ary}}{\rho_{water}} \theta_{g}$$
[3]

where  $\Delta_{soil}^{dry}$  is the bulk density of the dry soil (kg/m<sup>3</sup>) and  $\Delta_{water}$  is the density of water (in this appendix taken as 1000 kg/m<sup>3</sup>). We also recognize the bulk density of moist soil  $\Delta_{soil}^{moist}$ . The bulk densities can be found using the following expressions.

$$\rho_{soil}^{moist} = \frac{W_{moist\ soil}}{V_{soil}} = \frac{W_{dry\ soil} + W_{water}}{v_{soil}}$$
[4]

$$\rho_{soit}^{dry} = \frac{W_{dry\ soil}}{V_{soit}}$$
[5]

Gravimetric chloride content in moist soil Clg<sup>moist soil</sup>

$$Cl_g^{moist \ soil} = \frac{W_{Chloride}}{W_{moist \ soil}}$$
[6]

where  $W_{chloride}$  is the weight of chloride (kg) and  $W_{moist soil}$  is the weight of the moist soil (kg). Since the chloride content is often so small compared with the amount of soil, it is a custom to express chloride content in mg and soil in kg. The dimensions of  $Cl_g^{moist soil}$  are then mg/kg or ppm.

Since the water content of a soil will vary, we prefer to express the chloride content as a weight fraction of the dry soil.

Gravimetric chloride content in dry soil Clg<sup>dry soil</sup>

$$Cl_g^{dry\ soil} = \frac{W_{Chloride}}{W_{dry\ soil}}$$
[7]

where  $W_{chloride}$  is the weight of chloride (kg) and  $W_{dry soil}$  is the weight of the dry soil (kg).

*Volumetric chloride content in the soil* Cl<sub>v</sub>, (mg/m<sup>3</sup>)

$$Cl_{v} = \frac{W_{Chloride}}{V_{soil}}$$
[8]

The relationship between  $Cl_v^{dry \ soil}$  and  $Cl_g^{moist \ soil}$  is

$$Cl_{v}^{dry \, soil} = \frac{Cl_{g}^{moist \, soil} \, W_{dry \, soil} \, (1+\theta_{g})}{V_{soil}} = Cl_{g}^{moist \, soil} \, \rho_{b}^{dry \, soil} \, (1+\theta_{g})$$
[9]

#### Calculation of chloride load and chloride concentration

### Step 1. Gather data.

The minimum set of data we need for the calculation of the chloride load are the gravimetric chloride content in moist soil  $Cl_g^{moist soil}$ , the gravimetric soil water content

 $\mathcal{Z}_{g}$ , and the bulk density of the dry soil  $\Delta_{soil}^{dry}$ . The gravimetric chloride content and the gravimetric water content can be measured from core samples; the bulk density of dry soil will often be estimated.

Example:  $Cl_g^{moist \ soil} = 6,000 \text{ ppm}; 2_g = 0.08; \Delta_{soil}^{dry} = 1500 \text{ kg/m}^3.$ 

Step 2. Express water content on a volumetric basis.

Since computer models for water flow and chloride transport are constructed on a volumetric basis, we need to express the measured gravimetric chloride and water contents on a volumetric basis. We can do this using Eq. [3] for the water content.

Example:  $2_v = 0.08 \times 1500/1000 = 0.12$ 

Step 3. Calculate chloride load for one-meter depth.

Chloride load in one  $m^3$  which equals a volume of soil with thickness 1 m and area 1  $m^2$  is 9,720,000 mg/m<sup>3</sup> or 9.720 kg/m<sup>3</sup>.

Example:  $Cl_v = 6,000 \text{ (mg/kg)} * 1,500 \text{ (kg/m}^3) * (1 + 0.08) = 9,720,000 \text{ (mg/m}^3)$ 

Step 4. Calculate chloride load for entire vadose zone.

For a homogeneous vadose zone with thickness D, the total chloride load is the sum of the chloride loads of all depths.

Example: Depth of vadose zone 10 m. Total chloride load is  $9.720 \times 10 = 97.2 \text{ kg/m}^2$ .

For a heterogeneous vadose zone first calculate for each layer the chloride load following Steps [1-4] and sum over entire vadose zone.

### R. T. HICKS CONSULTANTS, LTD.

901 Rio Grande Blvd NW 🛦 Suite F-142 🛦 Albuquerque, NM 87104 🛦 505.266.5004 🛦 Fax: 505.266-0745

December 8, 2004

Mr. Wayne Price New Mexico Oil Conservation Division 1220 South St. Francis Drive Santa Fe, New Mexico 87505

RE: M-5 Redwood Tanks, Section 5 T20S R37E Unit M

Dear Wayne:

In your December 3, 2004 email to Rice Operating Company (attached) you asked for the following submissions:

- 1. Photos of the site before, during and after excavation.
- 2. Photos of the liner and backfill.
- 3. A plat showing location of all monitor wells and a chloride/TDS chronologic summary table for these wells.
- 4. A copy of the NMOCD approved work plan (July 02, 2003) that R.T. Hicks is working under.
- 5. A copy of the Hicks January 30, 2004 final corrective action plan.

I attach a CD that contains all of the requested information.

In the CD folder named "site photos" you will find digital images of the site after excavation of the box associated with the Zachary Hinton End of Line (EOL) site. This site was excavated in 2001, when the Junction Box Plan was being written by ROC and under review by NMOCD. At this time, ROC was not creating a photographic record of their efforts. Therefore, no images exist that show the site before excavation.

Because the site remains open pending NMOCD approval of the Corrective Action Plan, there is no liner and backfill at this time. The Corrective Action Plan does not call for a liner at this site:

Because the site is so small, we elected to show the location of the monitoring well relative to the former EOL box with Figure 7 of the Corrective Action Plan. Figure 7 of the CAP is reproduced herein.



May 16, 2007 Page 2

Note the red monitor well protection box with the concrete pad in the left center of the image – that is the monitoring well discussed in the CAP. The former EOL box excavation is in the center of the photograph. No other monitoring wells exist at this site. The monitoring well lies to the south-southeast of the former EOL, directly down gradient of ground water flow. The image on the CD titled "Northwest ZH 12.8.04" shows that the site remains relatively unchanged since Figure 7 of our CAP. The Corrective Action Plan, as submitted to NMOCD via email on 1/30/2004 (from Katie Lee of R.T. Hicks Consultants to Wayne Price), is on the CD in the zip-file folder titled "ZH\_CAP".

In the CAP, Figure 1 provides the graphical display of the chemical data for the monitoring well to the end of 2003. Table 1 of the CAP presents these same data in tabular format.

We included the July 2, 2003 workplan in the CAP as Appendix A. NMOCD approval of the workplan is attached to this letter.

We are using the Zachary Hinton CAP as a template for other sites where slow leakage of produced water over time has created potential impacts to ground water. Examples of such sites are Vacuum G-35 and the various sites associated with the Hobbs Salt Water Disposal System abandonment. We urge you to carefully review the Zachary Hinton CAP and provide us with the guidance that will allow us to improve future submissions. One improvement already implemented by Hicks Consultants is submission of the deliverables (on CD) via US Mail to NMOCD as well as via E-mail. In advance, thanks for your input.

Sincerely, R.T. Hicks Consultants, Ltd.

Randall Hicks Principal May 16, 2007 Page 3

### December 3 Request for Information from NMOCD

```
From: "Price, Wayne" <WPrice@state.nm.us>
To: "Price, Wayne" <WPrice@state.nm.us>; "'Carolyn Doran Haynes (E-mail)'"
<riceswd@leaco.net>; "'Kristin Farris Pope (E-mail)'" <enviro@leaco.net>
Sent: Friday, December 03, 2004 4:35 PM
Subject: RE: Zachary Hinton EOL BD SWD System
                                                             See.
> Added Case OCD Case Number 1R0426-36
>
>> ----Original Message-----
>> From: Price, Wayne
>> Sent: Friday, December 03, 2004 4:33 PM
>> To: Carolyn Doran Haynes (E-mail); Kristin Farris Pope (E-mail)
>> Subject: Zachary Hinton EOL BD SWD System
                                                                  -20
>>
>> Dear Ms. Haynes:
>>
>> The New Mexico Oil Conservation Division (OCD) is in receipt of the
>> Rice Operating Company (ROC) March 04, 2004 letter requesting closure
>> of the above subject site. OCD whas a copy of the Disclosure report
>> which was submitted as part of the
>> ROC BD Junction Box Generic closure project approved by OCD on July 22,
>> 2003.
                                              >>
>> In order for OCD to properly evaluate this closure please provide
>> the
>> following:
>>
>> 1. Photos of the site before, during and after excavation. 2. Photos
>> of the liner and backfill. 3. A plat showing location of all monitor
>> wells and a chloride/TDS chronologic summary table for these wells.
>> 3. A copy of the NMOCD approved work plan (July 02, 2003) that R.T.
>> Hicks is working under.
>> 4. A copy of the Hicks January 30, 2004 final corrective action plan.
>>
>> Please provide ASAP so OCD can respond to your request. The Case
>> Number for this site will be 1R0426-36. Please include this case
>> number on all documnet's pertaing to this site.
>>
>> Sincerely:
                       N.
>>
>> Wayne Price
>> New Mexico Oil Conservation Division
>> 1220 S. Saint Francis Drive
>> Santa Fe, NM 87505
>> 505-476-3487
>> fax: 505-476-3462
>> E-mail: WPRICE@state.nm.us
```

May 16, 2007 Page 4

NMOCD Approval E-mail string

-----Original Message----From: Price, Wayne [mailto:WPrice@state.nm.us]
Sent: Thursday, August 21, 2003 3:53 PM
To: 'Randall Hicks'; Price, Wayne
Cc: Carolyn Doran Haynes (E-mail)
Subject: RE: Zachary Hinton

APPROVED!

Please be advised that NMOCD approval of this plan does not relieve Rice Operating Company of liability should their operations fail to adequately investigate and remediate contamination that pose a threat to ground water, surface water, human health or the environment. In addition, NMOCD approval does not relieve Rice Operating Company of responsibility for compliance with any OCD, federal, state, or local laws and/or regulations.

[Price, Wayne] -----Original Message-----From: Randall Hicks [mailto:R@rthicksconsult.com] Sent: Thursday, August 21, 2003 3:45 PM To: 'Price, Wayne' Subject: FW: Zachary Hinton

-----Original Message----- **From:** Randall Hicks [mailto:R@rthicksconsult.com] **Sent:** Thursday, July 31, 2003 9:37 AM **To:** 'WPRICE@state.nm.us' **Cc:** 'enviro@leaco.net'; 'riceswd' **Subject:** FW: Zachary Hinton

Wayne

Glad I ranginto you today. Here is the workplan that we originally sent to you on July 3.

I am pleased to hear that you are ready to approve the Champion remedy for chloride – please finish your review of Champion then tear into this workplan next week. We plan on submitting two more in short order and you might want to review all three simultaneously. All of the workplans follow the same format – so a simultaneous review may be time efficient.

Thanks for pointing us to the data for the Chevron site west of Eunice – we will need these data to spot a monitor well location for one of the workplans coming your way.

Randy







					sandy	red & silty					
Table 1. Rice Operating Co. Monitor Well Data Sheet	(gal) All parameter concentrations are in mg/L.	TOTAL	XYLENES	<0.006	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
		ЕТНҮL	BENZENE	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
			TOLUENE	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
			BENZENE	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
			TDS	2403	1470	1450	1290	1160	1140	1350	1170
			CL-	1000	478	514	408	354	354	408	346
			TIME	1236	1000	1050	1015	1345	1530	1200	1330
		SAMPLE	DATE	030502	051502	081302	110602	030603	060503	082203	112003
		VOLUME	BAILED	 5.30	4.00	5.00	5.25	5.00	5.00	4.90	5.00
		WELL	VOLUME	1.800	1.620	1.700	1.682	1.670	1.692	1.600	1.600
-12 (Zachary Hinton) S, 37E	(ff)	TOTAL	DEPTH	67.00	66.08	66.7	66.65	66.54	66.58	66.40	66.45
		WATER	LEVEL	56.10	55.98	56.10	56.14	56.07	56.00	56.00	56.00
BD Jct. C 0, 12, 22			# MM	-	-	-	-	-	-	-	٢

\* Depth to water is measured from the top of the casing Casing is <u>3.458 ft</u>

Parameter	Values	Source of Data		
1. Depth to Ground Water	56	Site Data		
(feet)				
2. Vadose Zone Texture (see	Attached well log	Site Data		
Plate 1)				
3. Dispersion Length (meters)	1	Professional Judgment		
4. Water Content $\theta_{g}$ (%)	High $\theta_{g}$	Estimated from hydrus		
	Layer 1 : 10%	simulations		
	Layer 2:30%			
	Layer 3 : 25%			
5. Vadose Zone Chloride	Attached well log	ROC data from Disclosure		
Distribution (gr/kg)		Report		
6. Length of release	20	Field measurements		
perpendicular to ground water				
flow (feet)				
7. Cimate Index	Pearl, NM station	NOAA data		
	(Hobbs)			
8. Background Ground Water	100	Samples from nearby wells		
Chloride (mg/L)				
9. Ground Water Flux	1.4	Calculated from regional		
(cm/day)		hydrological data		
10. Aquifer Thickness (feet)	35	Nicholson and Clebsh (1960)		
		and SEO data		

Table 2.Input parameters for the simulations

Table 3. Cl	hloride data
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Location	Date	Chloide (ppm)	Source of Data
22.37.1.440	10/14/1953	525	Nicholson and Clebsch, 1961
22.37.1.440	9/8/1958	320	Nicholson and Clebsch, 1961
22.37.24.133b	10/14/1953	675	Nicholson and Clebsch, 1961
22.37.24.133b	4/22/1955	770	Nicholson and Clebsch, 1961
22.37.24.133b	9/5/1958	580	Nicholson and Clebsch, 1961
Peters East	11/7/03	438	ROC Analysis
Peters West	11/7/2003	200	ROC Analysis
Section 36 Active Windmill	3-Dec	460	ROC Analysis
ZH EOL MW-1	11/20/2003	346	ROC Analysis