

Modeling Study of Produced Water Release Scenarios

API Publication Number 4734
January 2005



Modeling Study of Produced Water Release Scenarios

Regulatory Analysis and Scientific Affairs Department

API Publication Number 4734
January 2005

PREPARED UNDER CONTRACT BY:

Jan M. H. Hendrickx, Department of Earth & Environmental Science
New Mexico Tech, Socorro, New Mexico

Graciela Rodriguez, R.T. Hicks Consultants, Ltd., Albuquerque, New Mexico

Randall T. Hicks, R.T. Hicks Consultants, Ltd., Albuquerque, New Mexico

Jirka Simunek, Professor and Hydrologist, Department of Environmental Sciences, University of California Riverside, Riverside, California

SPECIAL NOTES

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication, or represent that its use would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

All rights reserved. No part of this work may be reproduced, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005.

Copyright © 2005 American Petroleum Institute

FOREWORD

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

Suggested revisions are invited and should be submitted to the Director of Regulatory Analysis and Scientific Affairs, API, 1220 L Street, NW, Washington, DC 20005.

ACKNOWLEDGMENTS

API would like to acknowledge the following people for their contributions of time and expertise during this study and in the preparation of this report:

API STAFF CONTACTS

Harley Hopkins, Regulatory Analysis and Scientific Affairs Department (RASA)
Terry Twyman, Upstream

MEMBERS OF THE PRODUCTION WASTE ISSUES GROUP (PWIG) AND THE PWIG

BRINE WORK GROUP:

Evan Sedlock, ChevronTexaco Energy Technology Company; PWIG Chairman

Jeffrey Adams, BP America, Inc
Mickey Carter, ConocoPhillips Corporation
George Deeley, Shell Global Solutions (US) Inc.
Neal Goates, ConocoPhillips Corporation
Jill Kerr, Exxon Mobil Corporation
Rosemary Martinez, BP America
Greg Minnery, ChevronTexaco
Sam Small, Amarada Hess Corporation
Mike Starrett, Oxy Permian

Appreciation is extended to Carolyn Haynes of Rice Operating Company for providing funding for the field verification of the modeling.

TABLE OF CONTENTS

Table of Contents.....	i
Executive Summary.....	v
Technical Highlights	viii
1.0 Introduction	1
1.1 Project Overview.....	1
1.1.1 Research Objective	1
1.1.2 Project Organization	1
1.1.3 Scope of Modeling.....	1
1.2 Background	3
1.2.1 Fulfilling an Industry Need.....	3
1.2.2 Potential Impacts of a Release	4
1.2.3 Common Soil Restoration Programs	4
1.2.4 Restoration of Chloride in Ground Water	5
2.0 Factors Influencing the Migration of Chloride	6
2.1 Vadose Zone Factors.....	6
2.1.1 Vadose Zone Texture.....	6
2.1.2 Water Content in the Vadose Zone	6
2.1.3 Dispersion Length of Chloride in the Vadose Zone	7
2.1.4 Depth to Ground Water or Vadose Zone Thickness	7
2.2 Climate.....	8
2.3 Brine Release Factors.....	8
2.3.1 Chloride Concentration of Release	8
2.3.2 Release Volume and Total Mass	8
2.3.3 Height of Spill	8
2.4 Groundwater Characteristics.....	9
2.4.1 Ground Water Flux.....	9
2.4.2 Aquifer Thickness.....	9
2.4.3 Aquifer Ambient Chloride Concentration	9
2.5 Heterogeneity	9
2.6 Repeated Releases.....	10
3.0 Modeling Approach	11
3.1 Vadose Zone Model: HYDRUS-1D	11
3.1.1 Model Overview.....	11
3.1.2 Applicability of HYDRUS-1D for Produced Water Releases	12
3.2 Saturated Zone Model: Mixing Model and MODFLOW	12
3.3 Data Sources	16
3.3.1 Soil Data	16
3.3.2 Climate Data	16
4.0 Sensitivity Analysis of Factors Determining Brine Fate	17
4.1 Purpose.....	17
4.2 Modeling Specifics	17
4.2.1 Vadose Zone Factors.....	17
4.2.2 Aquifer Factors	19
4.2.3 Brine Release Factors.....	20
4.3 Simulation Responses.....	22
4.4 Statistical Analysis of the Responses at a Monitoring Well.....	22
4.4.1 Maximum Chloride Concentration	23
4.4.2 Arrival Time of Maximum Chloride Concentration	27
5.0 Initial Vertical Distribution of Chloride (First Year)	29
5.1 Purpose.....	29
5.2 Modeling Methodology	29
5.3 Analysis and Data Presentation.....	30

6.0	Heterogeneity	42
6.1	Purpose.....	42
6.2	Modeling Methodology and Input	42
6.3	Analysis and Data Representation	42
7.0	Vertical Chloride Distribution Over Thirty Years	46
7.1	Purpose.....	46
7.2	Modeling Methodology	46
7.3	Analysis and Data Presentation.....	46
8.0	Repeated Releases	54
8.1	Purpose	54
8.2	Modeling Methodology and Input	54
8.3	Analysis and Data Presentation	55
9.0	Soil Restoration	58
9.1	Purpose.....	58
9.2	Modeling Methodology and Input	58
9.3	Data Analysis and Presentation	58
10.0	Effects of Vegetation.....	63
10.1	Purpose.....	63
10.2	Modeling Methodology and Input.....	63
10.3	Data Analysis and Presentation.....	63
11.0	Understanding the Role of Each Factor	70
11.1	Produced Water Release Characteristics	70
11.2	Vadose Zone Characteristics	70
11.3	Climate.....	71
11.4	Vegetation.....	71
12.0	Verification of Model HYDRUS 1D for Prediction of Chloride Fate	72
12.1	Purpose	72
12.2	Approach.....	72
12.3	Description of Sites and Boundary Locations	73
12.4	HYDRUS 1D Simulations.....	73
12.4.1	Anode Beds (Sites L-21 and M-33).....	73
12.4.2	Junction Boxes (Sites EME P36-2 19S 3E and EME M-3-1A 21S 36E).....	76
12.5	Data Analysis and Presentation	76
	References.....	79
	Appendix A Results of homogenous and heterogeneous profiles	81
	Figures	
1.1	Schematic of chloride movement from brine spill through the vadose zone towards monitoring well.....	3
2.1	Soil texture triangle used by the U.S Department of Agriculture.	7
3.1	Comparison between MODFLOW and the mixing model. Perturbations in the MODFLOW curve reflect the use of actual rainfall data.....	15
4.1	Schematic of two possible brine release characteristics after a release of 100 barrels.....	21
4.2	The effect of nine brine release, vadose zone, and aquifer factors on the maximum chloride concentration in a down gradient monitoring well.....	24
4.3	Interaction effects between the factors soil, flux in aquifer, thickness of aquifer, and chloride load on the maximum chloride concentration in a down gradient monitoring well	26
4.4	The effect of nine brine release, vadose zone, and aquifer factors on the time when the maximum chloride concentration arrives in a down gradient monitoring well	28
4.5	Interaction effects between the factors climate, soil, and ground water depth on the time when the maximum chloride concentration arrives in a down gradient monitoring well	28
5.1	Sensitivity analysis of depth of maximum chloride concentration in the Weeks 1 and 2	37
5.2	Sensitivity analysis of depth of maximum chloride concentration in Weeks 3 and 4	378
5.3	Sensitivity analysis of depth of maximum chloride concentration in weeks 5 and 50	39
5.4	Distribution of chloride concentration with depth in the arid climate.....	40
5.5	Distribution of chloride concentration with depth in the humid climate	41
7.1	Vertical chloride distribution in homogeneous clay profiles in arid and humid climates	48

7.2	Vertical chloride distribution in homogeneous sand profiles in arid and humid climates	49
7.3	Vertical chloride distributions in heterogeneous profiles with 3, 10, and 20 m of accumulated clay layers in an arid climate	50
7.4	Vertical chloride distributions in heterogeneous profiles with 3, 10, and 20 m of accumulated clay layers in humid climates.....	51
8.1	Comparison of maximum well concentrations after one release and after three releases at one-year intervals in the humid and arid climates.....	56
8.2	Breakthrough curves at the well after one release and three releases at one-year and five-year intervals, respectively, through a homogeneous 30 m deep sand profile in the humid and arid climates.....	57
9.1	Chloride depth profiles in a 30 m deep sand vadose zone after a spill height of 2.5 cm with concentration 100,000 ppm with and without restoration by soil leaching during 45 days. Leaching starts on day 90 at a rate of 0.02 m/day.....	60
9.2	Chloride depth profiles in a 30 m deep clay vadose zone after a spill height of 2.5 cm with concentration 100,000 ppm with and without restoration by soil leaching during 110 days Leaching starts on day 90 at a rate of 0.02 m/day	61
9.3	Chloride concentrations in 3 m deep root zones with and without restoration by soil leaching in a sand and clay vadose zone after a spill height of 0.025 m with chloride concentration 100,000 ppm	62
10.1	Schematic of water and solute fluxes as well as chloride concentrations evaluated with HYDRUS1D and the mixing model under bare soil and vegetation	65
10.2	Vadose zone water flux and chloride concentration of the water entering into the shallow aquifer in a 30 m deep clay profile in Shreveport under bare soil and vegetation	66
10.3	Vadose zone chloride flux and chloride concentration in the well in a 30 m deep clay profile in Shreveport under bare soil and vegetation	67
12.1	Measured and simulated chloride profiles with depth under the anode beds M-33 and L-21	77
12.2	Measured and simulated chloride profiles with depth under the junction boxes EME P36-2 19S 3E and EME M-3-1A-21S 36E.....	78
Tables		
TH-1a	Distribution of the maximum chloride concentrations simulated in a down gradient monitoring well.....	viii
TH-1b	Distributions of the maximum chloride concentrations for brine concentrations of 10,000 and 100,000 ppm after spills of 100 and 10,000 barrels simulated in a down gradient monitoring well.....	ix
TH-2a	Distribution of the maximum chloride concentrations detected in a down gradient monitoring well for all 384 heterogeneous profiles simulated These profiles were 10, 20, and 30 m deep	xi
TH-2b	Distribution of the maximum chloride concentrations for brine concentration 100,000 ppm after spills of 100 and 10,000 barrels at Hobbs and Shreveport detected in a down gradient monitoring well for 384 scenarios in heterogeneous profiles These profiles were 10, 20, and 30 m deep	xi
1-1	Project Organization	2
4-1	Vadose zone, aquifer, and brine release factors determining maximum chloride concentration arriving at a monitoring well down gradient of a brine release	18
4-2	Characteristics of brine release in this study	21
4-3	Main effects of the vadose zone, aquifer, and brine release factors on the maximum chloride concentration arriving at the monitoring well C_{max} , first sensitivity analyzes	24
4-4	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} , second sensitivity analyzes	25
4-5	Statistics of maximum chloride concentrations (ppm) determined in the sensitivity analysis	27
5-1	Input Parameters for HYDRUS1D Model for Analysis of Initial Vertical Brine Distribution.....	29
5-2.1	Depth of Penetration of chloride concentration 250 ppm; Humid Climate, Depth of Ground Water Table = 3 m	31
5-2.2	Depth of penetration of chloride concentration 250 ppm; Humid Climate, Depth of Ground Water Table = 30 m.....	32

5-2.3	Depth of penetration of chloride concentration 250 ppm; Arid Climate, Depth of Ground Water Table = 3 m	33
5-2.4	Depth of penetration of chloride concentration 250 ppm; Arid Climate, Depth of Ground Water Table = 30m.....	34
5-3	Depth of Penetration of the Maximum Chloride Concentration	35
6-1	Inout Parameters for the Heterogeneous Profiles	44
6-2	Maximum Concentration at the Groundwater Table and in the Well.....	45
7-1	Factors in the Vadose Zone Considered in the Simulations.....	46
7-2	Distribution of Chloride Over Time in Homogeneous Profiles	52
7-3	Distribution of Chloride Over Time in Heterogeneous Profiles	53
8-1	Factors in the vadose zone considered in the simulations	54
9-1	Maximum chloride concentrations in a 30 m thick aquifer overlain by a 30 m thick sand vadose zone after a spill with chloride concentration 100,000 ppm.....	59
10-1	Comparison of maximum chloride concentrations and arrival times at the well under bare soil and vegetation.....	68
12-1	Characteristics of the four sites used for the verification of the HYDRUS1D model.....	74
12-2	The hydrogeological characteristics of the four sites used for the HYDRUS1D verification.....	75
A-1	Design matrix for the factors that affect chloride movement in the vadose zone and aquifer as well as two response variables in the monitoring well. Brine concentration 10,000 ppm	83
A-2	Design matrix for the factors that affect chloride movement in the vadose zone and aquifer as well as two response variables in the monitoring well. Brine concentration 100,000 ppm.....	98
A-3	Design matrix for heterogeneous profiles in Hobbs, as well as two response variables in the monitoring well	113
A-4	Design matrix for heterogeneous profiles in Shreveport, as well as two response variables in the monitoring well	119

EXECUTIVE SUMMARY

Project Goals

This document provides a scientific basis for operators, regulators and landowners to determine if assessment or remediation of produced water releases will provide a meaningful environmental benefit.

The two principal research objectives of this study are (i) the identification of produced water release scenarios that have a potential to cause ground water quality impairment in homogeneous subsurface geologic profiles, and (ii) the prediction of chloride movement through the vadose zone¹ for different release scenarios. Secondary objectives of the study included evaluation of the effect of heterogeneity on the migration of chloride through the vadose zone, the impact of repeat releases and the effect on ground water quality of surface soil restoration by revegetation and soil leaching.

This modeling study deals with sudden produced water releases of 100 to 10,000 barrels that infiltrate into the soil within a period of 1 day (sand soil) to 30 days (clay soil). Depending on the environmental conditions, the chloride molecules in the produced water may or may not reach the ground water. However, if produced water remains in the root zone, impacts to plants and soil fertility are possible.

Release Scenarios Deemed Unlikely To Cause Ground Water Quality Impairment

Numerical and analytical model simulation results suggest that large spills (100 and 10,000 barrels) will not cause unacceptable impairment of ground water quality if the depth of soil penetration is small (i.e. the release spreads over a large area) and the depth to ground water exceeds 3 meters. However, the results predict that most large produced water releases that occur over thin (< 3 meters), sandy vadose zones have the potential to cause unacceptable impairment of ground water quality. Although no simulations were performed for small releases (< 100 barrels), the results from this study can be used to infer that small releases that spread over the land are unlikely to cause unacceptable impairment to ground water quality when the depth to ground water exceeds 3 m.

Release scenarios where a high-chloride-concentration produced water collects (e.g., within an unlined bermed area or a topographic depression) above a thin vadose zone are more likely to cause ground water impairment relative to releases with contrasting characteristics (e.g.; a low-chloride-concentration-produced water and a release that spreads in a thin layer over the land surface). Other release scenario characteristics (e.g., climate and depth to ground water) have relatively less impact on the maximum chloride concentration observed in a nearby downgradient monitoring well.

The Rate of Migration and Distribution of Chloride in the Vadose Zone

In addition to evaluating scenarios that have the potential to impair ground water quality, this study examined the time required for chloride to migrate through the vadose zone into ground

¹ The vadose zone, also known as the unsaturated zone, lies between the ground surface and the water table.

water. An understanding of the temporal behavior of a chloride release is useful for timing remedial responses.

The modeling results show that chloride molecules from a produced water release will eventually migrate from the ground surface to ground water as long as there is a net downward flux to the water table. However, because the downward flux of chloride to ground water is often very small, close to zero in arid climates, the migration of chloride to ground water does not necessarily create material impairment of ground water quality. Simulated releases to a thin vadose zone in a humid climate with coarse textured soils result in the earlier arrival of the maximum concentration at an adjacent down-gradient monitoring well relative to a release with contrasting characteristics (e.g., a thick clay vadose zone, in an arid climate). Key release-scenario characteristics that have an impact on the *time* it takes for the maximum chloride concentration to be observed in the well are climate, soil type and depth to ground water.

The Impact Of Heterogeneity

Homogeneous vadose zone soil profiles are rare in nature. Therefore several scenarios with contrasting climate settings were analyzed to determine how clay layers intermixed with sand will affect chloride movement in the vadose zone and the subsequent impact on chloride concentration in ground water. Chloride concentrations simulated for a monitoring well down gradient of the release for the heterogeneous profiles decrease with increasing clay layer thickness in the vadose zone. The modeling results show that the increase in total thickness of clay layers in a profile slows down the chloride movement and results in lower concentrations in an adjacent down gradient monitoring well. Results of the heterogeneous profile simulations performed show that for vadose zones thicker than 3 m, chloride concentrations rarely exceeded 1000 mg/L at the simulated adjacent well.

The Impact of Repeat Releases

Repeat releases are an issue at some sites. Simulations were performed to determine the maximum chloride concentrations in a down gradient adjacent monitoring well as a result of three repeated releases taking place, at 1-year and 5-year time intervals, respectively. If releases are one year apart or less, the effect is a proportional increase in the chloride load. This means higher chloride concentrations in ground water than observed in a single release event. If releases occur at a time interval that is sufficient for the center of mass to reach ground water before the next release or at a time interval sufficiently large to prevent the multiple releases to merge, then repeated releases do not increase the chloride load and the maximum concentration in ground water is similar to a single release event.

The Effects of Soil Flushing

A produced water release may stunt or kill vegetation. While the agricultural industry routinely applies excess irrigation water to remove salt from the root zone, this practice is not used in some oilfields because of perceived increased threat to ground water quality. Flushing soil with water to remove chloride can be an effective alternative to soil restoration by excavation, disposal, and soil importation. Soil flushing was simulated to determine if this action would exacerbate degradation of ground water quality due to produced water releases. On the contrary, simulations show that the application of water to flush chloride below the root zone results in chloride dilution that improves the quality of ground water when compared to the no flushing alternative. Therefore, if the model predicts that a release would not impair ground water quality, then soil flushing at this site will not cause degradation as a result of the addition of water.

The Effect of Revegetation

A limited number of simulations designed to examine the affect of re-establishing a plant cover produced some preliminary results. For humid climates, scenarios that included a plant cover produce lower maximum chloride concentrations in an adjacent down-gradient monitoring well than otherwise similar scenarios without plant cover. Simulations for arid climates produce mixed results that cannot be adequately explained within the scope of the project. The small number of simulations performed for the analysis of plant cover do not allow for definitive conclusions at this time; however, re-establishment of plants after soil restoration appears to have other benefits (e.g., preventing soil erosion) that justify the practice.

The combined effect of irrigation and subsequent revegetation was not specifically examined. However one may speculate that the irrigation-induced shortening of the time for the maximum concentration to reach the nearby down-gradient monitoring well may be offset after revegetation.

TECHNICAL HIGHLIGHTS

Release Scenarios Deemed Unlikely To Cause Ground Water Quality Impairment

The sensitivity analysis performed in this study provides an overview of the likelihood of groundwater impairment for large release volumes (100 bbls and 10,000 bbls). Assuming homogeneous unsaturated zone soil profiles, the results of over 1000 modeled release scenarios reveal that 49% of single-event releases do not cause impairment of ground water above drinking water standards for chloride (250 mg/L) in a monitoring well that is adjacent to the edge of the release. In 70% of these scenarios, chloride concentrations in ground water do not exceed 1000 mg/L. Although these numbers give no information about the fate of chloride from a specific produced water release, they do indicate that a release does not necessarily cause ground water impairment. Tables TH-1 show the distribution of the maximum chloride concentrations in a well that is down gradient of a release during the course of the sensitivity study.

Table TH-1a—Distribution of the maximum chloride concentrations simulated in a down gradient monitoring well (Background chloride concentration assumed to equal zero)

Maximum Concentration (ppm)	Frequency		Cumulative Frequency	
	Number	%	Number	%
< 250	501	49	501	49
250 – 500	120	12	621	61
500 – 750	73	7	694	68
750 – 1000	25	2	719	70
> 1000	305	30	1024	100

Table TH-1b—Distributions of the maximum chloride concentrations for brine concentrations of 10,000 and 100,000 ppm after spills of 100 and 10,000 barrels simulated in a down gradient monitoring well (Background chloride concentration assumed to equal zero)

	Brine Concentration															
	10,000 (ppm)								100,000 (ppm)							
	Barrels								Barrels							
	100	10,000	100	10,000	100	10,000	100	10,000	100	10,000	100	10,000	100	10,000	100	10,000
	Frequency				Cumulative Frequency				Frequency				Cumulative Frequency			
Maximum Concentration (ppm)	#	%	#	%	#	%	#	%	#	%	#	%	#	%	#	%
< 250	187	73	161	63	187	73	161	63	87	34	66	26	87	34	66	26
250 – 500	21	8	27	11	208	81	188	73	35	14	37	14	122	48	103	40
500 – 750	15	6	20	8	223	87	208	81	20	8	17	7	142	55	120	47
750 – 1000	4	2	5	2	227	89	213	83	8	3	8	3	150	59	128	50
> 1000	29	11	43	17	256	100	256	100	106	41	128	50	256	100	256	100

A sensitivity analysis with over 2000 scenarios simulated shows that the initial depth of the produced water (spill height) and the chloride concentration of the brine has the greatest affect on ground water quality predictions. These two factors were combined into a single factor: chloride loading, or “Release Chloride Mass” (g/m^2) – a parameter that can be measured in the field or calculated with known release characteristics. The second most important factor is aquifer thickness, which basically determines the volume of ground water available for dilution of the chloride seepage (flux) from the vadose zone to the aquifer. Other factors certainly influence the predictions as well, but accurate prediction of possible ground water impairment is impossible without a reasonable knowledge of chloride loading and aquifer thickness.

Factors influencing chloride migration are introduced in Chapter 2. Sensitivity analysis of factors determining chloride fate are covered in detail in Chapter 4. A guide to understanding the role of key produced water release and chloride fate factors is presented in Chapter 11.

The Rate of Migration and Distribution of Chloride in the Vadose Zone

In addition to evaluating which scenarios have the potential to impair ground water quality, this study examined the time required for chloride to migrate through the vadose zone into ground water. The modeling results suggest that chloride molecules will migrate from the ground surface to ground water as long as there is a net downward flux to the water table. However, because the flux of chloride to ground water is often very small, especially in arid climates, the

migration of chloride to ground water does not necessarily create material impairment of ground water quality.

Model predictions of the *time* required for the maximum chloride concentration to reach an adjacent well were used to measure the sensitivity of each factor to the movement of chloride through the vadose zone. Results indicated that climate, vadose zone texture, and ground water depth exerted the most control on this prediction. Other factors were relatively unimportant in the prediction of the time of transport.

The vertical distribution of chloride in the vadose zone after a release was simulated for two representative climates: Hobbs, New Mexico (arid climate) and Shreveport, Louisiana (humid climate). The movement of chloride during the first 5 weeks after a release did not depend on climate, but rather on the particular weather conditions (e.g., rainfall events) after the hypothetical release. Review of 96 scenarios modeled showed that the center of mass (of chloride) after 5 weeks of transport was sometimes deeper in Hobbs and sometimes deeper in Shreveport, despite the fact that other input parameters were held constant. The depth of penetration depended strongly on weather conditions and, more importantly, on the soil texture.

The modeling shows that chloride migration during the first 5 weeks after a release accounts for 70% of the chloride migration observed after 50 weeks. On average, the center of mass is predicted to move about 1 m in the arid climate and 3 m in the humid climate. The average penetration depth for the center of mass for clay, clay loam, sandy loam and sand are about 0.2, 0.3, 2.0, and 5.0 m respectively.

For many scenarios, chloride migration from the ground surface to a 30-m deep aquifer requires decades and, in the arid climate, sometimes centuries. The migration of chloride over time in 22 different scenarios was examined. As expected, the maximum predicted concentration of chloride decreases with the depth of penetration: the center of mass attenuates with vertical transport. In a humid climate the observed attenuation is faster than in the arid climate. The climatic conditions do not influence the amount of attenuation, only the time frame necessary for the attenuation to take place.

Arrival time of the maximum chloride concentration is discussed in detail in Chapter 4, section 4.4.2. The initial and long-term distribution of chloride is covered in Chapters 5 and 7, respectively.

The Impact Of Heterogeneity

Homogeneous vadose zone soil profiles are rare in nature. Therefore, 384 selected heterogeneous scenarios were simulated to evaluate the importance of clay layers. Modeling confirmed what many would consider intuitive: increasing the total thickness of clay layers decrease the maximum chloride concentration at the adjacent down-gradient monitoring well and increases the time for the maximum chloride concentration to be observed. Tables TH-2a – b provide the distribution of maximum chloride concentrations for all the heterogeneous simulations conducted during the course of the study. Table TH-2a shows that 53% of the cases did not result in chloride concentrations above 250 ppm, and that the chloride concentration in ground water exceeded 1,000 ppm in 13 cases, or only 3% of all simulations. These results are better than those in Tables TH-1a – b because there are no 3 m deep profiles included in the heterogeneous profiles, and clay layers were present in each profile. (The 3 m profiles were assumed to be vulnerable in real world situations regardless of the presence of clay layers.) Because heterogeneous conditions are more common in nature than homogeneous conditions,

the statistics associated with heterogeneous conditions may be more representative of conditions commonly observed in the field. Details of the heterogeneous profile simulations are presented in Chapter 6. Appendix A presents all results of the simulations for the homogeneous and heterogeneous profiles.

Table TH-2a—Distribution of the maximum chloride concentrations detected in a down gradient monitoring well for all 384 heterogeneous profiles simulated
These profiles were 10, 20, and 30 m deep

Maximum Concentration (ppm)	Frequency		Cumulative Frequency	
	Number	%	Number	%
< 250	202	53	202	53
250 – 500	104	27	306	80
500 – 750	46	12	352	92
750 – 1000	19	5	371	97
> 1000	13	3	384	100

Table TH-2b—Distribution of the maximum chloride concentrations for brine concentration 100,000 ppm after spills of 100 and 10,000 barrels at Hobbs and Shreveport detected in a down gradient monitoring well for 384 scenarios in heterogeneous profiles.
These profiles were 10, 20, and 30 m deep

	Hobbs, brine 100,000 ppm								Shreveport, brine 100,000 ppm							
	Barrels								Barrels							
	100		10,000		100		10,000		100		10,000		100		10,000	
	Frequency				Cumulative Frequency				Frequency				Cumulative Frequency			
Maximum Concentration (ppm)	#	%	#	%	#	%	#	%	#	%	#	%	#	%	#	%
< 250	67	70	41	43	67	70	41	43	55	57	39	41	55	57	39	41
250 – 500	15	16	33	34	82	85	74	77	24	25	32	33	79	82	71	74
500 – 750	8	8	13	14	90	94	87	91	11	11	14	15	90	94	85	89
750 – 1000	3	3	5	5	93	97	92	96	4	4	7	7	94	98	92	96
> 1000	3	3	4	4	96	100	96	100	2	2	4	4	96	100	96	100

The Impact of Repeat Releases

Repeat releases are an issue at some sites. In this study, repeat releases were simulated using 5 different vadose zone profiles and different depths to ground water. If releases are 1 year apart or less, the effect is a proportional increase in the chloride load. This means higher chloride concentrations in ground water than observed in a single release event. If releases occur at a time interval that is sufficient for the center of mass to reach ground water prior to the next release or at a time interval sufficiently large to prevent the multiple releases to merge, then repeated releases do not increase the chloride load and the maximum concentration in ground water is similar to a single release event. Chapter 8 presents the results of the repeat release simulations.

The Effects of Soil Flushing

Soil flushing can be an effective alternative to soil restoration by excavation, disposal, and soil importation. Natural soil leaching occurs in the humid climate and a soil flushing program is typically used in lower permeability soils. In the arid climate, previous simulations demonstrated that the center of mass remained near the ground surface for decades. Therefore, soil leaching was simulated for the arid climate only. Although only 8 scenarios were modeled, soil restoration by leaching actually improved the ground water quality in 7 of the 8 cases. For the remaining scenario, predicted ground water quality was 295 ppm chloride with a soil leaching program and 291 ppm under the no-action alternative. Modeling of this topic is presented in Chapter 9.

The Effect of Revegetation

Some arid climate experts believe that recharge of ground water does not occur in flat areas where vegetation is present, maintaining that the plants quickly use any precipitation that would cause downward movement of soil water. The effect of vegetation was simulated in this study by assuming that warm and cold weather grass would re-vegetate a spill area in a humid climate after chloride in soil decreased to about 500 ppm. In the arid climate, the evergreen Four Wing Salt Bush was used as the volunteer species under these same conditions. Vegetation reduced the chloride flux to ground water in the humid climate. In the arid climate, model simulations predicted a lower chloride concentration in ground water in 10 of 17 sand-profile scenarios. For the seven arid climate scenarios where modeling predicted a higher chloride concentration in ground water, the increases were less than 30%. More work is required to fully understand these results. The examination of the effects of revegetation is presented in Chapter 10.

Model Verification

The model HYDRUS used in this study was verified for predicting chloride movement in the vadose zone by comparing site-specific modeling results to a limited number of well-characterized exploration and production field sites. Chapter 12 summarizes the field observations and model verification.

1. 0 Introduction

1.1 Project Overview

1.1.1 Research Objective

The American Petroleum Institute (API) retained *R.T. Hicks Consultants, Ltd. (Hicks Consultants)* to numerically model a range of representative produced water release scenarios. The project's objectives were (1) identification of release scenarios that have a potential to cause unacceptable ground water quality impairment, and (2) prediction of chloride movement through the vadose zone for the different release scenarios. Chloride was selected for the modeling exercise because it is the most common anion in produced water. Further, chloride can cause damage to the productive capacity of soil, and its concentration in ground water often defines the remedy required for an affected aquifer.

Due to the complexity inherent in nature, any model used to simulate potential outcomes of different produced water release scenarios is limited. Nonetheless, with careful attention to relevant details, a proper model can provide an acceptable forecast of chloride ion behavior after a produced water release. The numerical model HYDRUS-1D was used to simulate the transport of chloride from the land surface through the vadose zone to ground water. The predictions from HYDRUS-1D were input into a simple ground water mixing model to calculate the degree of ground water quality impairment. The findings in this report can provide the basis for a series of tools that can assist a producer, regulator, or landowner in determining if a particular release requires subsurface characterization and/or ground water remediation.

1.1.2 Project Organization

Table 1-1 shows how the project was separated into four primary tasks, tasks 1 – 4; and five supplemental tasks, tasks 1a – 3a and tasks 5 and 6.

Task 1, a sensitivity analysis, identified environmental and release factors (e.g., climate, release volume, etc.) that were most important in affecting the distribution of chloride in the vadose zone and the probability that a release would cause ground water quality impairment. Tasks 2 and 3 determined the depth of chloride infiltration and the vertical distribution of chloride over time as a function of climate. Task 4 explored the impact of the repeated releases as a function of the climate and the elapsed time between the releases. Tasks 1a, 2a, and 3a consider how vadose zone heterogeneity affects model predictions. Task 5 explored soil leaching as a technique to restore the soil impaired by produced water without compromising ground water quality. Task 6 explored the effect of vegetation on produced water movement since many spill sites become vegetated after some time.

1.1.3 Scope of Modeling

A series of simulation experiments were conducted to evaluate how different produced water release and environmental characteristics (model inputs or factors) affect the fate of chloride in the subsurface (model outputs or responses). Model inputs include the hydrological and geological characteristics of the vadose zone and of the aquifer, climate, and characteristics of the release. A total of 11 factors were identified:

1. Texture of the vadose zone (e.g. sand, clay, etc.),

2. Depth to ground water,
3. Natural water content in the vadose zone,
4. Dispersion length of chloride in the vadose zone,
5. Climate,
6. Chloride concentration of the produced water release,
7. Volume of the produced water release,
8. Initial depth of produced water on the land surface (e.g., ponded within a berm or dispersed over a large area),
9. Ground water flux of the aquifer,
10. Background chloride content in the aquifer, and
11. Saturated thickness of the aquifer.

Model outputs from HYDRUS-1D are:

- The maximum chloride concentration entering the aquifer from the vadose zone, and
- The arrival time of the maximum chloride concentration at the aquifer.

Model outputs from the groundwater mixing model are:

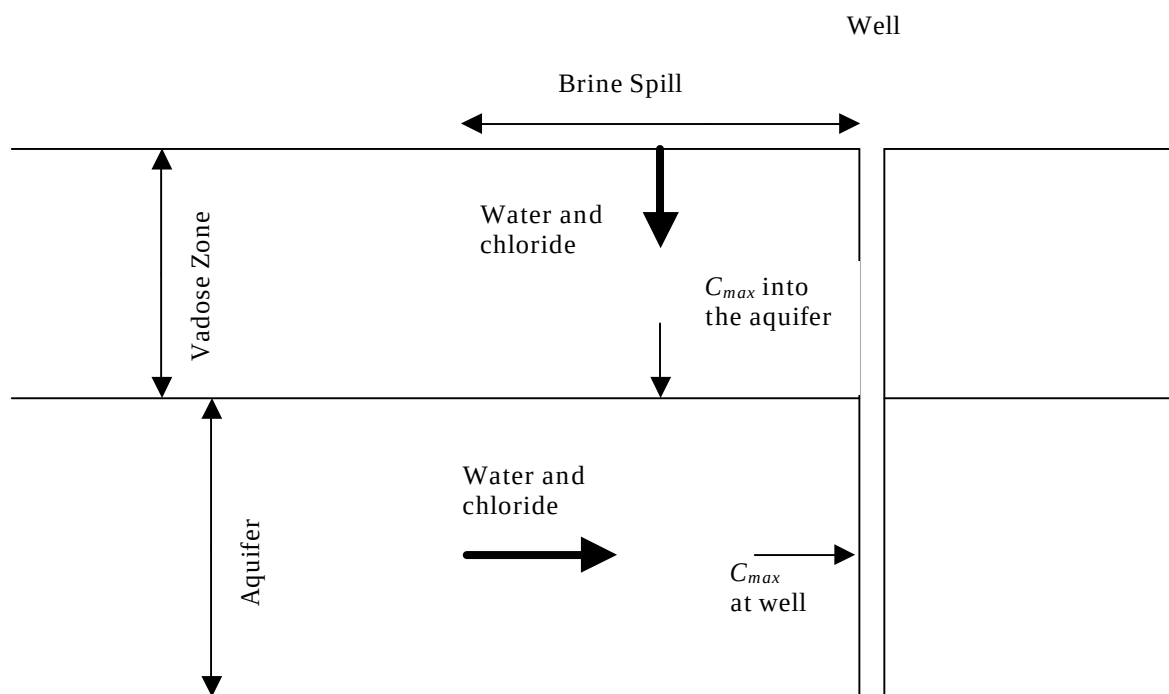
- The maximum chloride concentration measured at a monitoring well at the down gradient edge of the surface produced water release, and
- The arrival time of the maximum chloride concentration at a monitoring well at the down gradient edge of the surface produced water release.

Table 1-1—Project Organization

Task	Homogeneous Profiles	Task	Heterogeneous Profiles
1	Sensitivity analysis	1a	Sensitivity analysis
2	Initial depth of impact		
3	Vertical redistribution over time	3a	Vertical redistribution over time
4	Repeated releases	4a	Repeated releases
5	Soil restoration by leaching		
6	Effect of vegetation		

Figure 1.1 depicts the input parameters and model outputs.

Figure 1.1—Schematic of chloride movement from brine spill through the vadose zone towards monitoring well



1.2 Background

1.2.1 Fulfilling an Industry Need

Ground water is a major source of water for municipalities and is used for agriculture, mining, and manufacturing. Regulatory agencies charged with protection of ground water place the burden of mitigating the effects of accidental releases or engineered discharges on industry as the discharger. To demonstrate whether a release will cause unacceptable impairment, these agencies usually rely on guidance documents or relatively conservative assumptions to assess the effects of a release on ground water quality. However, they do not have the work force to perform independent tests of assumptions or conclusions in spill reports or permit documents. Few guidance documents exist presently and a technically robust guidance document that addresses produced water releases does not exist. In the absence of such a document, surface landowners and regulators often use very conservative assumptions in the review of release incidents.

This document describes chloride movement in the vadose zone and potential ground water quality impairment from produced water releases. Single releases of 10 barrels or less typically do not result in soil or groundwater impacts that require anything more than a minimal response action. Larger releases of produced water (such as the 100-bbl releases studied herein) can cause damage to the productive capacity of soil. A cost-effective method of soil restoration

for larger produced water releases is in-place chemical amendment and soil flushing (Carty et al., 1977). However, the regulatory sensitivity regarding protection of ground water has caused limitation of this technique because of its requirement of significant water application. Carty et al., (1977) offers little guidance relating to protection of ground water quality. This report provides information on potential effect on ground water quality caused by soil flushing.

1.2.2 Potential Impacts of a Release

Loss of Soil Productive Capacity

Productive capacity is the ability of the soil to support vegetation such as range land grass, irrigated crops or turf. Two types of soil damage can occur because of a produced water release. The first is a loss of soil permeability due to the high sodium concentrations in the produced water, and related to the first is the immediate death or severe stress of vegetation. Sodium ions in produced water replace natural calcium ions in clay minerals, causing swelling of the clay and a loss of soil permeability complicating soil restoration because it causes retention of chloride and sodium in the root zone. The loss of soil permeability will also cause a long-term deterioration of the original soil productivity.

Ground Water Impairment

The secondary drinking water standards for TDS and chloride are 500 mg/L and 250 mg/L, respectively. A produced water release can degrade ground water quality by elevating total dissolved solids (TDS) and chloride concentrations above these standards. Elevated ground water TDS and chloride concentrations higher than 5,000 mg/l and 2,500 mg/l respectively may render ground water unfit for domestic, livestock, or agricultural use. Runyan and Bader (1995) state that salinities [TDS] measuring between 5000 – 6999 mg/L are marginal quality for beef cattle, sheep, swine, and horses and should not be used for pregnant or lactating animals. Salinities above 5000 mg/L are not suitable for poultry

1.2.3 Common Soil Restoration Programs

Commonly accepted alternatives for soil restoration include: (1) passive or natural remediation, (2) *in-situ* chemical amendment remediation, and (3) mechanical remediation (Carty et al., 1997, API Publication 4663, *Remediation of Salt-Affected Soils at Oil and Gas Production Facilities*). Below is a brief description of each alternative.

1. Passive Remediation

Passive remediation uses little human intervention to restore soil. Instead, it relies on natural processes such as precipitation and chemical diffusion to dilute and mitigate the effects of a produced water release.

2. In-Situ Chemical Amendment Remediation

The agricultural industry has used this technique extensively to restore the productive capacity of soils. The approach uses chemical amendments, such as gypsum, calcium nitrate, calcite, acidified water, and surfactants, to improve soil drainage damaged by excess sodium in the soil. In addition to these chemicals, water is added to flush the built-up salts beyond the root zone and mulch (e.g. hay) is added to improve soil permeability.

3. Mechanical Restoration

This technique involves the permanent removal of soil that has been contaminated and its replacement with clean soil. This technique is often the most expensive remediation alternative because large machinery is necessary to remove and replace contaminated soils. This method has a high success rate when the soils are completely removed, but the addition of clean soil poses some risks for erosion and the introduction of non-native plants.

1.2.4 Restoration of Chloride in Ground Water

High chloride concentrations in ground water caused by produced water releases are typically addressed in one of three ways: natural attenuation, pumping and disposal/use, or a pump-and-treat system.

1. Natural Attenuation

Chloride attenuation consists of dilution and dispersion in the aquifer. This technique can require years or decades to meet EPA Secondary Drinking Water Standards and is widely used where high chloride concentrations in ground water pose little risk to human health or the environment.

2. Pumping and Disposal/Use

Landowners, regulators or other stakeholders may desire a more active remedy to halt the movement and spread of high TDS and chloride at some locations. In oilfields with injection wells, disposal water can be cost effectively pumped and disposed of using systems already in place. However, unlike natural attenuation or a pump-and-treat systems (described below), this method permanently removes water from the aquifer, depleting the resource. Therefore, some operators employ water from affected aquifers for dust suppression, chilling fluids, and other uses.

3. Pump-and-treat Techniques

These techniques provide containment of high TDS and chloride ground water, and preserve water resources. Unlike hydrocarbons, microorganisms in ground water do not metabolize TDS and chloride. Therefore, ground water restoration requires often expensive mechanical or chemical treatment systems (such as reverse osmosis). The cost of pump-and-treat methodology is often 10-100 times more expensive than natural attenuation or pumping and disposal/use.

2.0 FACTORS INFLUENCING THE MIGRATION OF CHLORIDE

Chloride migration is controlled by a combination of factors related to the vadose zone, the aquifer, and the produced water release. As discussed earlier, 11 factors controlling chloride migration were analyzed. This chapter discusses how these factors affect the movement of the chloride through the vadose zone and in the aquifer.

2.1 Vadose Zone Factors

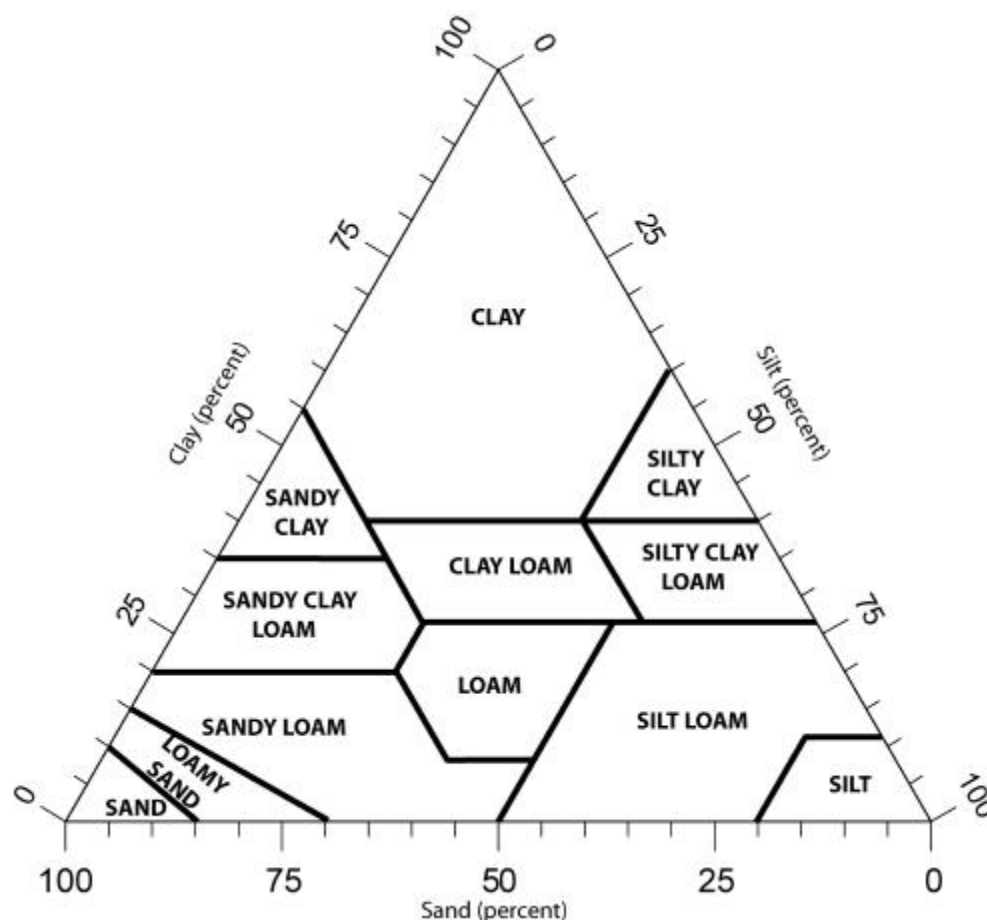
2.1.1 Vadose Zone Texture

The proportion of sand, silt, and clay in a soil or sediment defines its texture (see Figure 2.1). Texture affects the flow of water and the transport of dissolved chloride in two ways. First, the texture determines the nature of the interconnected open pores of the soil or sediment. Clean gravel generally exhibits large, well-connected pore spaces while silty-clay has smaller pores with poorer connectivity but a higher porosity. As a result, the saturated hydraulic conductivity of gravel is higher than the saturated hydraulic conductivity of silty-clay. In the unsaturated zone, however, the ability of a soil or sediment to transmit chloride depends on how much of the available pore space is filled with water. In a nearly dry soil or sediment, capillary forces hold the water (and chloride) in place, preventing down ward (or upward) movement. As the moisture content of a soil or sediment increases, more pores become interconnected with water and the soil water pressure becomes less negative, increasing the ability of the unit to transmit water and chloride. In other words, the unsaturated hydraulic conductivity of a soil or sediment increases with increasing moisture content. In the vadose zone, fine-grained layers containing silt and clay generally have relatively higher moisture content than adjacent gravel. The higher moisture content translates into higher unsaturated hydraulic conductivity. Therefore, a silty clay 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.

2.1.2 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 strongly 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 a brine may migrate much faster in a wet soil profile, the natural water in the soil also dilutes the produced water and provides some mitigation of its effects on ground water quality.

Figure 2.1—Soil texture triangle used by the U.S Department of Agriculture.

2.1.3 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 on professional judgment and published values (from laboratory or field experiments) to arrive at the dispersion length for a particular site.

2.1.4 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 produced water release more effectively than a thin vadose zone.

2.2 Climate

Precipitation and evaporation affect the water content of the vadose zone (prior to 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 drought periods, the infiltration is not uniform and occurs only immediately after large precipitation events that result in vadose zones with relatively low water contents.

Daily precipitation and evaporation data are inputs to the HYDRUS-1D model. Therefore, it can effectively simulate the effect of the two climate extremes, humid and arid, discussed above.

2.3 Brine Release Factors

2.3.1 Chloride Concentration of Release

Chloride concentration in oilfield produced water can be 100,000 ppm, or much lower if the producing formation is diluted with fresher water over geologic time. One of the easiest input parameters to measure in the field is the chloride concentration of the produced water. The effect of chloride concentration is also straightforward: the higher the chloride concentration, the greater the environmental threat.

2.3.2 Release Volume and Total 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. The total mass of chloride can generally be estimated by a field investigation.

2.3.3 Height of Spill

Produced water releases occur within bermed areas when storage tanks fail or to the natural terrain due to transmission line leaks and other transportation accidents. Releases may pond in a berm or natural depression or can be dispersed over a large area. If the release is contained in 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 produced water infiltration into the soil is a function of the hydraulic head or ponding depth. As the ponding depth increases, so does the hydraulic head, (pressure, at the soil/produced water spill interface). Understanding the depth of ponding and the total amount of infiltration guides the characterization efforts.

2.4 Groundwater Characteristics

The potential for ground water quality impairment depends to some extent on the aquifer characteristics such as ground water flux, aquifer thickness, and ambient chloride concentration.

2.4.1 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 3 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 $\text{m}^3/(\text{m}^2 \cdot \text{day}) = \text{m/day}$). The lower the ground water flux, the higher the probability that a release will cause unacceptable ground water quality impairment.

2.4.2 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 dilution. 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.

2.4.3 Aquifer Ambient Chloride Concentration

Ambient chloride concentrations of ground water will influence whether or not a produced water release causes unacceptable ground water quality impairment. If ground water has a low chloride concentration, even a considerable amount of produced water may not cause chloride concentrations to exceed the U.S. 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 produced water 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.

2.5 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 conductivity.

One of the most common simplifying assumptions employed by regulators and guidance manuals is the assumption of homogeneity. However, a clay lens 1 m thick found 3 m below a produced water 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. Heterogeneity is not one of the 11 factors specifically considered in the initial research, but its effect on these 11 factors is considered in Chapters 6, 7, and 10.

2.6 Repeated Releases

Repeat releases are an issue at some sites. Several releases in the same location may result in a higher threat to ground water quality than a single event. Repeated releases can cause:

1. More chloride mass to enter the subsurface,
2. Higher water content in the vadose zone, and
3. Increased ambient chloride concentration in the underlying aquifer.

3.0 MODELING APPROACH

The modeling of produced water migration from the soil surface through the vadose zone into a shallow aquifer towards a monitoring well would require a sophisticated 3-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 3-dimensional models capable of such simulations are still being developed.

This study used an approach based on 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 aquifer. It is assumed 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 input into the model for the aquifer. In this study, two models were used 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, a validated excel spreadsheet mixing model was used to generate results more cost effectively.

3.1 Vadose Zone Model: HYDRUS-1D

3.1.1 Model Overview

HYDRUS-1D (Simunek et. al, 1998) is used to simulate 1-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 Ground Water Modeling Center (IGWMC), Golden, Colorado. A Microsoft Windows™-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.

HYDRUS-1D was used for the vadose zone simulations of this research project because of the importance of understanding 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^{-1} and $\text{mg cm}^{-2} \text{ day}^{-1}$ respectively. These outputs are used as inputs into the simple mixing model.

3.1.2 Applicability of HYDRUS-1D for Produced Water Releases

Surface or near surface releases of produced water 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, HYDRUS-1D was selected 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. The researchers' familiarity with the model.

Dr. Jirka Šimunek of this 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.

3.2 Saturated Zone Model: Mixing Model and MODFLOW

As stated, the objective of this part of this study is to evaluate the impact of produced water releases on ground water quality as measured in a well adjacent to and down gradient of the produced water 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 to determine the time-varying chloride concentration in the well.

Therefore, a simple spreadsheet ground water mixing model was implemented to determine the chloride concentration in the well. This mixing model uses the output of the HYDRUS-1D model as input. The aquifer volume and the mixing compartment underneath the spill must be defined 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 or the length of screen in a nearby observation well (generally 3 m). The width, W , of the mixing compartment is taken to equal unity to simplify the calculations.

Considered next is the relation between the water flux seeping out of the vadose zone, 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 release, C_{out} . The latter concentration will be monitored in the down gradient well.

The following reasonable assumptions were made to determine C_{out} :

1. Ground water flow is in steady state. The discharge entering into the mixing compartment from the vadose zone, q_vDW , plus the horizontal discharge in the aquifer entering the mixing compartment at its up-gradient side, $q_{in}HW$, are equal to the discharge leaving the mixing compartment, $q_{out}HW$.
2. Changes in thickness of the saturated aquifer are small compared to the total thickness of the aquifer H (i.e., water table fluctuations are small).
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). The results of the mixing model can be used as an excellent indicator of the mean chloride concentration in a supply well penetrating the aquifer underlying the produced water 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

$$V = D \times H \times W \times n \quad (3-1)$$

The water balance of the mixing compartment is equal to:

$$q_{in} \times H \times W + q_v \times D \times W = q_{out} \times H \times W \quad (3-2)$$

One can eliminate variable W from Eqs. [3-1] and [3-2] by putting $W = 1$ m.

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

$$[(q_{in} \times C_{in} \times H + q_v \times C_v \times D) - (q_{in} \times H + q_v \times D) \times C_{out}] dt = [D \times H \times n] dC \quad (3-3)$$

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

Rearranging Eq. [3-3], one obtains the ordinary differential equation:

$$\frac{dC}{dt} = \frac{q_{in} \times C_{in} \times H + q_v \times C_v \times D - (q_{in} \times H + q_v \times D) \times C_{out}}{H \times D \times n} \quad (3-4)$$

As soon as chloride from the produced water 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 compartment, C_{out} , becomes:

$$C = C_{out} \quad \text{and} \quad dC = dC_{out} \quad (3-5)$$

Therefore, one can convert Eq. [3-4] in a forward finite difference expression:

$$\frac{C_{out}^{i+1} - C_{out}^i}{t^{i+1} - t^i} = \frac{q_{in}^i \times C_{in}^i \times H + q_v^i \times C_v^i \times D - (q_{in}^i \times H + q_v^i \times D) \times C_{out}^i}{H \times D \times n} \quad (3-6)$$

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

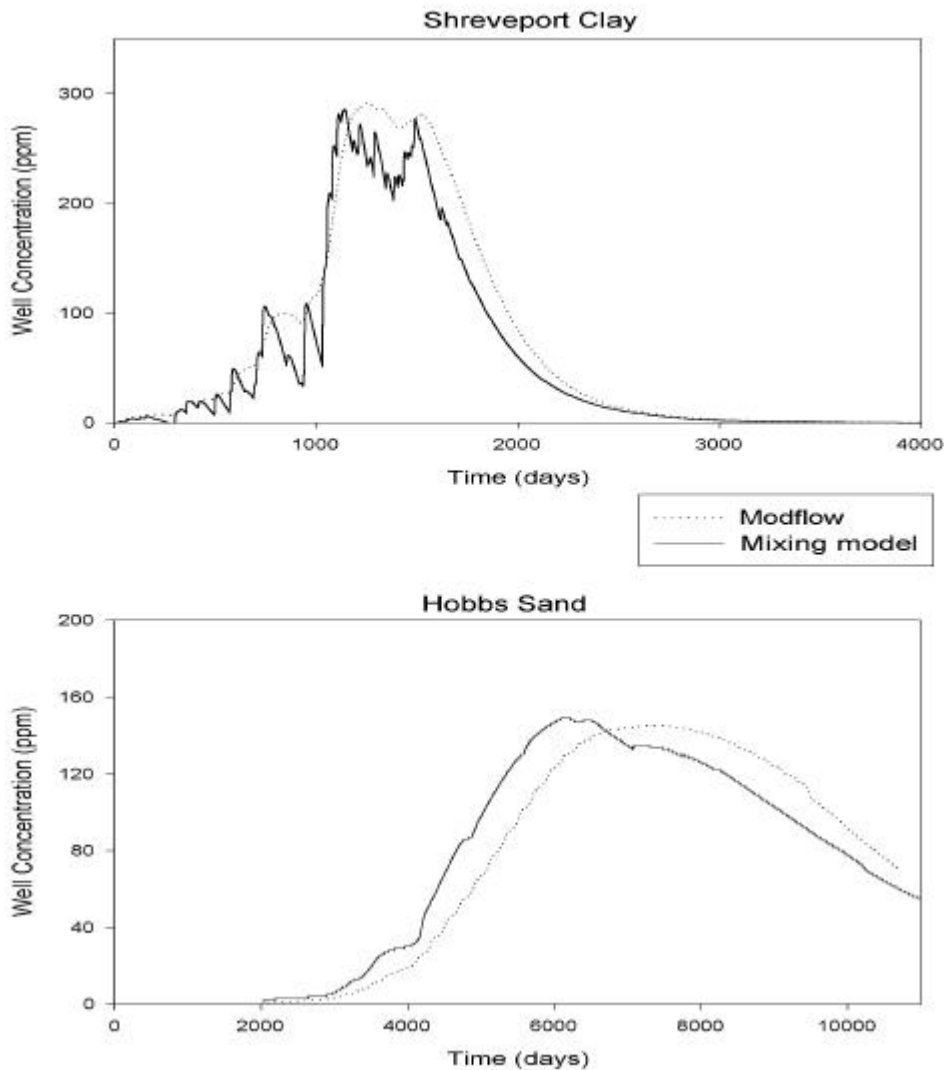
$$C_{out}^{i+1} = C_{out}^i + \frac{[q_{in}^i \times C_{in}^i \times H + q_v^i \times C_v^i \times D - (q_{in}^i \times H + q_v^i \times D) \times C_{out}^i] \times [t^{i+1} - t^i]}{H \times D \times n} \quad (3-7)$$

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 , the mixing model of Eq. [3-7] has been put into a spreadsheet. 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 , the effect of these 4 factors of an unconfined aquifer have been evaluated.

Figure 3.1 presents 2 comparisons between the chloride concentrations in the well located down gradient of the entry point of the release obtained with the mixing model Eq. [3-7] and those obtained with the model MODFLOW. The two comparisons deal with 2 complete different sets of environmental and release factors. In Shreveport, Louisiana 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, New Mexico 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 for each model. This part of the study was conducted using the less expensive mixing model Eq. [3-7]. This approach using HYDRUS-1D in combination with MODFLOW and Eq. [3-7] 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 0 – (+/-) 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.

Figure 3.1—Comparison between MODFLOW and the mixing model. Perturbations in the MODFLOW curve reflect the use of actual rainfall data.



An upward flux is sometimes found in the sand 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 brine to stay in the vadose zone and protects the ground water from impairment. In hydrogeological situations where capillary rise is common, brine movement towards ground water is sporadic. However, a big storm can suddenly push all of the brine into a shallow aquifer.

A strong dynamic interaction exists among all 11 factors, outlined in section 1.1.3, when water leaving the vadose zone, q_v , 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 and then to the atmosphere is common. The only manner to correctly simulate the interaction

between these factors under these conditions is by employing a 2- or 3-dimensional model, such as HYDRUS-2D. However, the main objective of this study is to examine the effect of surface spills of produced water on ground water quality, thus the mixing model Eq. [3-7] for ground water table depths of 3 m was used. The effect of capillary rise in diminishing the leaching of chloride to the ground water, and concentrating chloride in the root zone was not examined. The equation was used only for downward fluxes and was made inactive when the vadose zone flux, q_v , goes upward. It was 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 ground water tables.

3.3 Data Sources

3.3.1 Soil Data

The HYDRUS-1D's catalog of soil hydraulic property values was used to define hydraulic characteristics of the vadose zone (Carsel and Parish, 1988). The catalog defines hydraulic properties for parameters in the van Genuchten (1980) analytical functions.

Data from the Soil Survey of Caddo Parrish, LA, and Lea County, NM, were used as well as data collected from state and federal government agencies to construct heterogeneous soil profiles. State and federal government agencies included the US Geological Survey (USGS), National Resource Conservation Service (NRCS), and NM Oil Conservation Division (NMOCD). Like the homogeneous profiles, hydraulic properties for each soil horizon or geologic unit were estimated from the soil hydraulic property values of HYDRUS-1D.

3.3.2 Climate Data

Climate data were purchased for Shreveport, LA and Lea County, NM from the National Climatic Data Center (NCDC, www.ncdc.noaa.gov). The data consisted of historical daily temperature and precipitation measurements collected at specific weather stations identified by a NCDC Coop identification number. Data for Lea County and Shreveport were collected at the Pearl, NM weather station (Coop # 296659) and the Shreveport Regional Airport, LA (Coop # 168440), respectively.

Potential evapotranspiration (PET) was calculated from daily temperature observations using the method of Samani and Pessarakli (1986).

When a HYDRUS-1D simulation was performed for a longer time period than the period of record for a weather station, the climate data was repeated for as many years as was necessary.

4.0 SENSITIVITY ANALYSIS OF FACTORS DETERMINING BRINE FATE

4.1 Purpose

After a produced water 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 produced water 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 11 factors have the greatest effect on prediction of maximum chloride concentration in the well down gradient of the release.

4.2 Modeling Specifics

Simulation work was optimized 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) provided ways 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 the simulation models. The outputs of the simulations are the responses. The responses that were considered 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} .

A 2^k factorial design was chosen that requires the selection of 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. Two values were chosen 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 4-1) resulted in 2^{11} or 2,048 different produced water release scenarios.

4.2.1 Vadose Zone Factors

Climate

Two contrasting climates of Lea County, New Mexico, and Shreveport, Louisiana were selected 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 in. and 59 in., respectively, while annual precipitation and potential evapotranspiration for Shreveport is 46 in. and 67 in., respectively. Lea County and Shreveport also differ when 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.

Table 4-1—Vadose zone, aquifer, and brine release factors determining maximum chloride concentration arriving at a monitoring well down gradient of a brine release

#	Description	Abbreviation	Maximum Chloride Concentration	
			Decrease	Increase
1	Climate	clim	Arid	Humid
2	Soil Texture	soil	Clay	Sand
3	Initial Water Content	wcin	Wet	Dry
4	Chloride Dispersion Length	disp	2.0 m	0.1 m
5	Ground Water Depth	gwl	30 m	3 m
6	Ground Water Flux	qaq	0.05 m/day	0.001 m/day
7	Ambient Aquifer Cl Concentration	cin	0 ppm	100 ppm
8	Aquifer Thickness	thick	30 m	3 m
9	Release Volume	vol	100 bbls	10,000 bbls
10	Release Height	depth	0.025 m	.60 m
11	Release Chloride Concentration	clcon	10,000 ppm	100,000 ppm
10*11	Release Chloride Mass	clmass	250 g/m ²	60,000 g/m ²

Vadose Zone Texture

Sand and clay were selected 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.

Water Content in Vadose Zone

Higher initial water content in the vadose zone results in slower brine movement because the initial moisture must be displaced before the brine can move downward through the vadose zone. HYDRUS-1D was used to predict initial water contents for both vadose zone textures in both Lea County and Shreveport. These predictions were used as initial conditions in the sensitivity analysis.

Computer simulations were run for 100 years or until dynamic equilibrium was achieved between soil water content and climatic conditions for both the wet and dry initial conditions. To create *wet* conditions, simulations were run without any vegetation (low evapotranspiration); vegetation (high evapotranspiration) was included to create *dry* conditions. Evergreen plants capable of transpiring soil water all year round with a 3 m (~10 ft) deep root zone were assumed in the simulations. Transpiration of soil water created a drier soil profile than simulations without vegetation.

Dispersion Length of Chloride in Vadose Zone

A minimum and maximum chloride dispersion lengths of 0.10 m (0.33 ft) and 2.0 m (6.6 ft) was selected, respectively. The larger dispersion length will produce greater mixing of brine 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. Dispersion lengths were selected from values reported in the literature (Gelhar, 1993).

Depth to Ground Water

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

4.2.2 Aquifer Factors

Ground Water Flux

Groundwater flux represents the rate of groundwater movement and affects the ability of an aquifer to dilute chloride and other constituents of a produced water release. A large groundwater flux produces greater dilution.

The selection of minimum and maximum groundwater fluxes was based on literature values for the Ogallala aquifer, Southern Lea County, New Mexico (Native and Smith, 1987). Minimum and maximum values used were 0.10 cm/day (0.0033 ft/day) and 5.0 cm/day (0.16 ft/day), respectively. The maximum flux used is lower than some of the ground water fluxes reported in the literature (e.g. 40 cm/day by Zhang et al., 1998), thus, reducing the dilution in the mixing zone in the simulations.

Aquifer Ambient Chloride Concentration

Ambient chloride concentrations selected for groundwater were 0 ppm and 100 ppm. One hundred parts per million or less is typical for groundwater 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, 0.0 ppm was selected to create a greater difference between minimum and maximum chloride concentrations of groundwater.

Aquifer Thickness

The thicker the aquifer, the more opportunity for mixing (dilution), and the lower the predicted chloride concentration in the aquifer. Two aquifer thicknesses were selected, 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 m 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 for the sake of conservatism, 30 m was selected 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).

4.2.3 Brine Release Factors

Release Volume

Minimum and maximum release volumes of 100 bbl (16 m³) and 10,000 bbl (1,600 m³), respectively, were selected for this analysis. These release volumes are representative of large and very large releases based on the experience of oil and gas industry personnel.

The 1-dimensional HYDRUS-1D model uses only spill height as an input variable. The spill volume was introduced into the mixing model using the spill diameter. For example, a 100 barrel release resulting in a produced water release of 0.025 m height with circular shape will have a diameter of 29 m while a release of 0.6 m height will have a diameter of only 6 m (Figure 4.1). Table 4-2 summarizes the 4 produced water release areas evaluated with the mixing model. These 4 release areas are combinations of the 2 spill heights (0.025 and 0.6 m) and 2 release volumes (large: 100 bbls and very large: 10,000 bbls).

All spill areas are represented as circles, and then, the mixing model is used to evaluate mixing along the diameter of each circular spill (see Table 4-2). 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

Chloride concentrations of 10,000 and 100,000 ppm were selected as the minimum and maximum concentrations for the produced water release input parameter in consultation with API. These concentrations are representative of most produced water releases.

The mixing model does not consider density differences between the density of the brine arriving at the aquifer and the density of the water in the aquifer. These differences (even if small) may cause brine to sink in an aquifer (LeBlanc et al., 1991; Zhang et al., 1998) and would influence the distribution of brine 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 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 produced water release on an aquifer.

Height of Spill

Minimum and maximum values of 0.025 m (1 in.) and 0.6 m (2 ft), respectively, were used as the spill height of produced water on the land surface, based on observations of oil and gas industry personnel. A 0.6 m (2 ft) height represents a discharge of 1600 m³ (10,000-bbls) of produced water to a 2670 m² (0.7 acre) bermed area or large depression. Releases to flat or gently sloped areas are likely to result in initial heights of 0.025 m (1 in.) or less.

Figure 4.1—Schematic of two possible brine release characteristics after a release of 100 barrels.

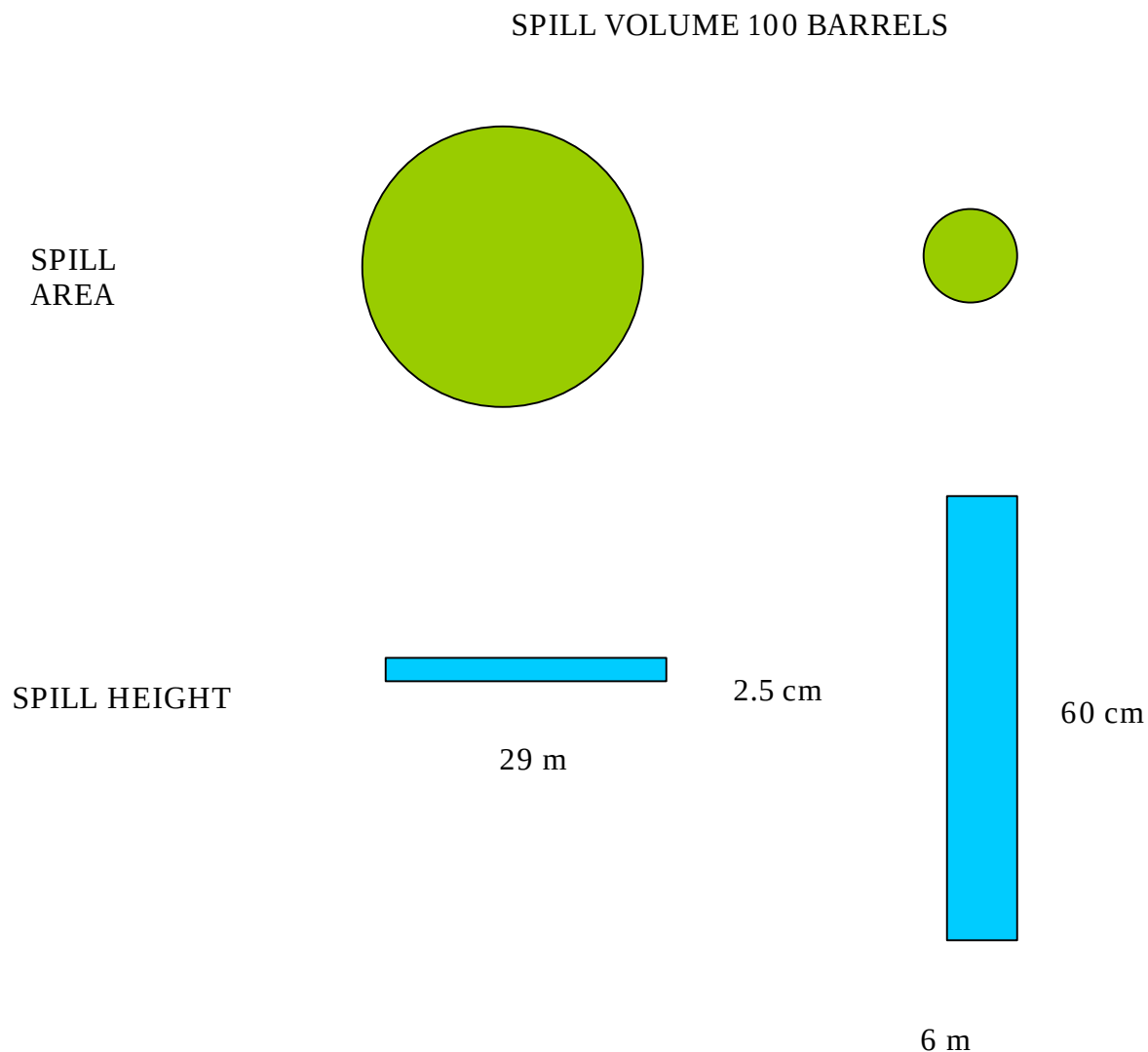


Table 4-2—Characteristics of brine releases in this study

Volume		Depth		Area		Diameter
Barrels	m ³	m	m ²	acres	m	
100	16	0.025	640	0.16	29	
		0.6	26.67	0.007	6	
10000	1600	0.025	64000	16	285	
		0.6	2666.67	0.7	58	

Chloride Mass

Table 4-1 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 4-1 shows, a produced water 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 g/m² (the Release Chloride Mass). This factor is discussed in more detail in later sections of this report.

4.3 Simulation Responses

The simulations with the HYDRUS-1D code and the mixing model yield large amounts of information about the water flow and the transport of chloride through the vadose zone and the underlying aquifer. As mentioned above, two critical response variables were selected 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, the maximum chloride concentration, C_{max} , is used to identify those factors listed in Table 4-1 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 conditions that result in significant attenuation of brine. For example, for those simulations where C_{max} is much less than the original chloride concentration of the produced water, environmental factors cause significant brine 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 provides important information 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.

4.4 Statistical Analysis of the Responses at a Monitoring Well

Following the statistical approach by Law & Kelton (2000) for simulation modeling and analysis, the impact of each factor presented in Table 4-1 on the migration of chloride through the vadose zone and aquifer was determined. This was accomplished 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.

4.4.1 Maximum Chloride Concentration

Table 4-3 presents the sensitivity of C_{max} to each of the 11 factors considered in this study (Table 4-1). The factors are sorted according to their impact on C_{max} in Table 4-3. The most important factors are the Height of Brine (produced water) Release and the Release Chloride Concentration. Changing the Height of Brine Release from 0.025 – 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 setup of the simulation experiment. The relative effects of each factor were added in Table 4-3. The factors Height of Brine 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 Brine Release. The predicted difference in C_{max} for the two climates indices, however, was only 28% of predicted difference for the Height of Brine Release. As Table 4-3 shows, Initial Water Content of Soil exerts the smallest influence on the prediction of C_{max} .

The two most important factors, Height of Brine Release and the Release Chloride Concentration, determine the Mass of Chloride entering the soil surface during a release. If the Height of Brine 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 monitoring well, the sensitivity analysis was repeated using Mass of Chloride instead of Height of Brine Release and Release Chloride Concentration. The Initial Water Content of Soil was eliminated in the second sensitivity analysis since this factor has very little effect on C_{max} .

The results of the second analysis are presented in Table 4-4 and in Figure 4.2. The mean chloride concentration of all 256 scenarios with Mass of Chloride 250 g/m² is 89 ppm and that of all 256 scenarios with Mass of Chloride 60,000 g/m² is 8,446 ppm (See Figure 4-2). The difference between these two values is 8,357 ppm, which is the predicted sensitivity of the maximum chloride concentration for an increase of Mass of Chloride from 250 to 60,000 g/m² when holding all other factors fixed.

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, the relative impacts of each factor was determined by dividing each affect by the influence of the Mass of Chloride (Table 4-4). The most important factors Mass of Chloride and Thickness of Aquifer have relative effects of 1.00 and 0.67, respectively. The factors Soil, Aquifer Flux, and Dispersion Length have relative effects of 0.43, 0.42, and 0.32, respectively. The factors Climate, Ground Water Depth, and Volume of Brine Release have much less impact with relative effects of 0.25, 0.22, and 0.20. Ambient Chloride Concentration (Relative effect 0.01) has virtually no effect.

Table 4-3—Main effects of the vadose zone, aquifer, and brine release factors on the maximum chloride concentration arriving at the monitoring well C_{max} , first sensitivity analyzes

Factor	Effect on C_{max}	
	ppm	Relative Effect
Height of Brine Release	4340	1
Release Chloride Concentration	4017	0.93
Thickness of Aquifer	3237	0.75
Soil	2070	0.48
Aquifer Flux	1994	0.46
Dispersion Length	1545	0.36
Climate	1184	0.27
Ground Water Depth	1081	0.25
Volume of Brine Release	932	0.21
Ambient Cl Concentration	76	0.02
Initial Water Content of Soil	25	0.01

Figure 4.2—The effect of nine brine release, vadose zone, and aquifer factors on the maximum chloride concentration in a down gradient monitoring well

