

PHONE (575) 397-6388 • FAX (575) 397-0397 • 1324 W. MARLAND • P.O. BOX 805 • HOBBS, NM 88241-0805 E-MAIL: cbrunson@bbcinternational.com

#### **DELINEATION WORKPLAN**

# OXY – BRAVO DOME LEG 5 (Leak Date: 2/15/17)

**RP # 4RP-12** 

This delineation workplan and remediation proposal addresses the releases associated with RP # 4RP-12.

The following information includes:

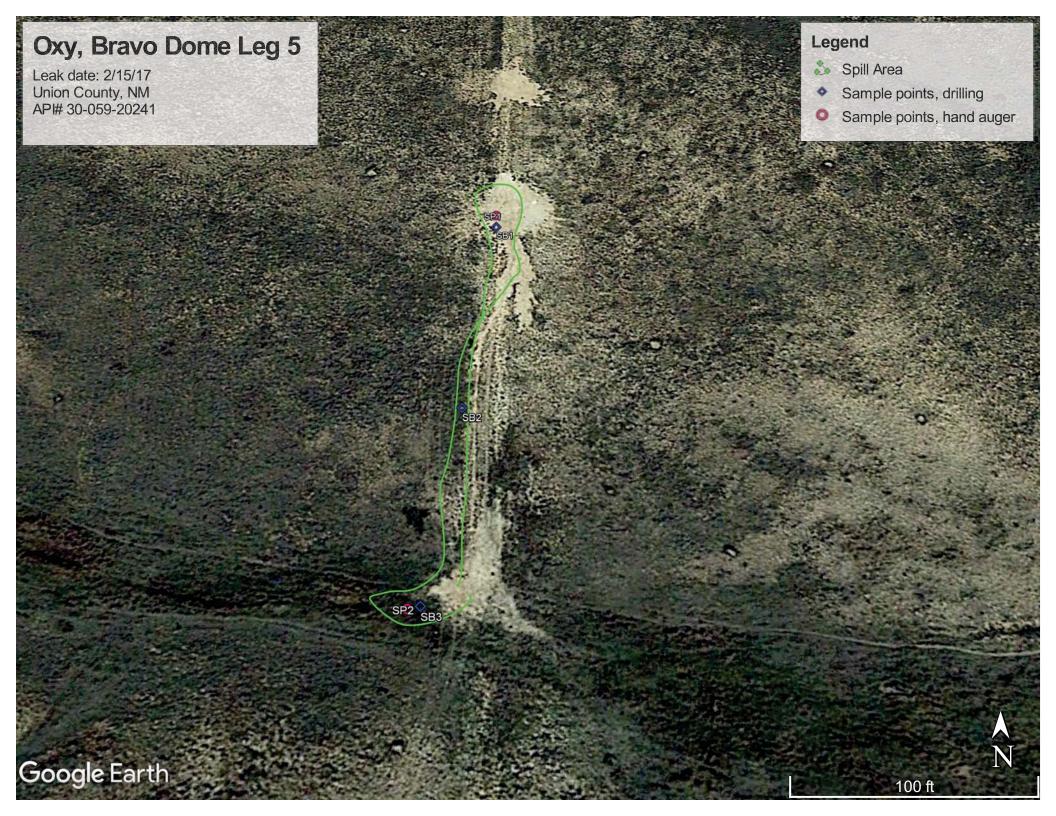
- 1. Scaled digital site map with spill area demarcated and leak point identified along with sample point locations and areas of remediation at appropriate depths.
- 2. GPS information for sample points and sample methodology
- 3. Depth to groundwater information (i.e., pdf of OSE search results and/or copy of Chevron groundwater trend map).
- 4. Laboratory analysis results summary table and original laboratory analysis reports
- 5. A copy of the initial C-141
- 6. Potentially other pertinent information as necessary for site specific purposes.

Based on the information included in this package and the NMOCD guidelines, the following remediation is proposed:

OXY will excavate the spill area as depicted on the following site diagram. The entire leak area (pink shade on diagram) will be excavated to a depth of 1 foot.

The entire site will then be backfilled with clean soil and revegetated (if warranted) to the standards of the appropriate regulatory agency or private surface owner.

All excavated materials will be disposed of at an NMOCD-approved disposal facility.



# Oxy, Bravo Dome Leg 5

Sample points, hand auger SP1, N 35.82552 W-103.30847 SP2, N 35.82488 W-103.30859

Sample points, drilling SB1, N 35.82549 W-103.30847 SB2, N 35.82517 W-103.30852 SB3, N 35.82488 W-103.30857



# New Mexico Office of the State Engineer

# Water Column/Average Depth to Water

(A CLW##### in the POD suffix indicates the POD has been replaced & no longer serves a water right file.)

(R=POD has been replaced, O=orphaned,

(quarters are 1=NW 2=NE 3=SW 4=SE)

C=the file is closed)

(quarters are smallest to largest) (NAD83 UTM in meters)

(In feet)

		POD Sub-		QQ	^									Vater
POD Number	Code		County		_	Sec	Tws	Rng	X	Y	DistanceDep	thWellDep		
L 02679 POD2	R	L	LE		2	22	18S	35E	645876	3622973*	0	187	65	122
<u>L 05810</u>		L	LE	2	3	22	18S	35E	645479	3622564*	569	145	95	50
<u>L 02677</u>		L	LE	3	4	15	18S	35E	645863	3623780*	807	194	54	140
<u>L 02678</u>		L	LE	3	4	22	18S	35E	645890	3622166*	807	200	58	142
<u>L 02678</u>	R	L	LE	3	4	22	18S	35E	645890	3622166*	807	200	58	142
L 02678 POD2	R	L	LE	3	4	22	18S	35E	645890	3622166*	807	185	58	127
L 02678 POD3		L	LE	3	4	22	18S	35E	645890	3622166*	807	190	154	36
<u>L 03866</u>		L	LE	3	3	22	18S	35E	645082	3622155*	1139	127	65	62
L 04399		L	LE	3	3	22	18S	35E	645082	3622155*	1139	90	75	15
<u>L 03963</u>		L	LE	1	2	27	18S	35E	645896	3621762*	1211	127	70	57
<u>L 02520</u>		L	LE	4	1	23	18S	35E	647088	3622989*	1212	134	78	56
<u>L 03772</u>		L	LE	2	2	21	18S	35E	644659	3623361*	1277	130	60	70
L 02679		L	LE	4	4	21	18S	35E	644680	3622151*	1451	200	68	132
L 02679	R	L	LE	4	4	21	18S	35E	644680	3622151*	1451	200	68	132
<u>L 09373</u>		L	LE	1	1	26	18S	35E	646704	3621773*	1457	120	60	60
<u>L 02675</u>		L	LE	3	2	15	18S	35E	645850	3624587*	1614	197	47	150
<u>L 02680</u>		L	LE	1	2	21	18S	35E	644257	3623357*	1663	190	59	131
L 09588		L	LE	4 3	4	16	18S	35E	644349	3623659*	1674	155	84	71
										Averag	ge Depth to Wat	er:	70 fee	et
											Minimum De	pth:	47 fee	et

Record Count: 18

UTMNAD83 Radius Search (in meters):

**Easting (X):** 645876 **Northing (Y):** 3622973 **Radius:** 1700

\*UTM location was derived from PLSS - see Help

The data is furnished by the NMOSE/ISC and is accepted by the recipient with the expressed understanding that the OSE/ISC make no warranties, expressed or implied, concerning the accuracy, completeness, reliability, usability, or suitability for any particular purpose of the data.

4/21/17 11:46 AM

WATER COLUMN/ AVERAGE DEPTH TO WATER

154 feet

Maximum Depth:

#### Laboratory Analytical Results Summary Bravo Dome Leg 5

		Sample	ТТ1 @ Тор	TT1 @ 6'	TT1 @ 12'	TT1 @ 17'
Analyte	Method	Date	3/27/17	3/27/17	3/27/17	3/27/17
			mg/Kg	mg/Kg	mg/Kg	mg/Kg
Chloride	SM4500CI-B		12000	3360	6800	8930

		Sample	TT2 @ 4'	TT2 @ 10'	TT2 @ 17'
Analyte	Method	Date	3/27/17	3/27/17	3/27/17
			mg/Kg	mg/Kg	mg/Kg
Chloride	SM4500CI-B		2160	2880	1410

#### Laboratory Analytical Results Summary Bravo Dome Leg #5

		Sample	SB1 @ SURFACE	SB1 @ 5'	SB1 @ 10'	SB1 @ 15'	SB1 @ 17'	SB1 @ 20'	SB1 @ 23'	SB1 @ 28'
Analyte	Method	Date	6/6/17	6/6/17	6/6/17	6/6/17	6/6/17	6/6/17	6/6/17	6/6/17
			mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
Chloride	SM4500CI-B		4560	240	4160	784	352	1280	160	208

		Sample	SB2 @ SURFACE	SB2 @ 5'	SB2 @ 10'
Analyte	Method	Date	6/6/17	6/6/17	6/6/17
			mg/Kg	mg/Kg	mg/Kg
Chloride	SM4500CI-B		3840	64	96

		Sample	SB3 @ SURFACE	SB3 @ 5'	SB3 @ 10'	SB3 @ 15'	SB3 @ 17'	SB3 @ 22'
Analyte	Method	Date	6/6/17	6/6/17	6/6/17	6/6/17	6/6/17	6/6/17
			mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
Chloride	SM4500CI-B		4080	2200	1660	304	32	32



April 06, 2017

Cliff Brunson

BBC International, Inc.

P.O. Box 805

Hobbs, NM 88241

RE: LEG 5

Enclosed are the results of analyses for samples received by the laboratory on 03/31/17 9:45.

Cardinal Laboratories is accredited through Texas NELAP under certificate number T104704398-16-8. Accreditation applies to drinking water, non-potable water and solid and chemical materials. All accredited analytes are denoted by an asterisk (\*). For a complete list of accredited analytes and matrices visit the TCEQ website at <a href="https://www.tceq.texas.gov/field/ga/lab">www.tceq.texas.gov/field/ga/lab</a> accred certif.html.

Cardinal Laboratories is accreditated through the State of Colorado Department of Public Health and Environment for:

Method EPA 552.2 Haloacetic Acids (HAA-5)
Method EPA 524.2 Total Trihalomethanes (TTHM)
Method EPA 524.4 Regulated VOCs (V1, V2, V3)

Accreditation applies to public drinking water matrices.

Celey D. Keene

This report meets NELAP requirements and is made up of a cover page, analytical results, and a copy of the original chain-of-custody. If you have any questions concerning this report, please feel free to contact me.

Sincerely,

Celey D. Keene

Lab Director/Quality Manager

Tamara Oldaker

Sample Received By:



#### Analytical Results For:

BBC International, Inc.

Cliff Brunson P.O. Box 805 Hobbs NM, 88241

Fax To: (575) 397-0397

Received: 03/31/2017 Sampling Date: 03/27/2017

Reported: 04/06/2017 Sampling Type: Soil
Project Name: LEG 5 Sampling Condition: Cool & Intact

Project Location: BRAVO DOME ,NM

NONE GIVEN

#### Sample ID: TT1 TOP (H700854-01)

Project Number:

Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	12000	16.0	04/05/2017	ND	432	108	400	3.64	
Sample ID: TT1 6' (H70	0854-02)								
Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	3360	16.0	04/05/2017	ND	432	108	400	3.64	
Sample ID: TT1 12' (H7 Chloride, SM4500Cl-B	00854-03) mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	6800	16.0	04/05/2017	ND	432	108	400	3.64	
Sample ID: TT1 17' (H7	00854-04)								
Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
	Result	Reporting Limit	Allalyzeu	riculou blank	55	70 110001017	True Turde Qu	5	Quac.

#### Cardinal Laboratories \*=Accredited Analyte

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BBC International, Inc.

Cliff Brunson P.O. Box 805 Hobbs NM, 88241

Fax To: (575) 397-0397

Received: 03/31/2017 Sampling Date: 03/27/2017

Reported: 04/06/2017 Sampling Type: Soil

Project Name: LEG 5 Sampling Condition: Cool & Intact
Project Number: NONE GIVEN Sample Received By: Tamara Oldaker

Project Location: BRAVO DOME ,NM

Sample ID: TT2 4' (H700854-05)

Chloride, SM4500Cl-B mg/kg Analyzed By: AC

Analyte Result Reporting Limit Analyzed Method Blank BS % Recovery True Value QC RPD Qualifier

**Chloride** 2160 16.0 04/05/2017 ND 432 108 400 3.64

Sample ID: TT2 10' (H700854-06)

Chloride, SM4500Cl-B Analyzed By: AC mg/kg Reporting Limit Analyzed Method Blank BS True Value QC RPD Qualifier Analyte Result % Recovery Chloride 2880 16.0 04/05/2017 432 400 3.64 ND 108

Sample ID: TT2 17' (H700854-07)

Chloride, SM4500Cl-B mg/kg Analyzed By: AC Analyte Result Reporting Limit Analyzed Method Blank BS % Recovery True Value QC RPD Qualifier Chloride 1410 04/05/2017 ND 400 16.0 432 108 3.64

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Celeg D. Freene



#### **Notes and Definitions**

ND Analyte NOT DETECTED at or above the reporting limit

RPD Relative Percent Difference

\*\* Samples not received at proper temperature of 6°C or below.

\*\*\* Insufficient time to reach temperature.

- Chloride by SM4500Cl-B does not require samples be received at or below 6°C

Samples reported on an as received basis (wet) unless otherwise noted on report

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# ARDINAL LABORATORIES 101 East Marland, Hobbs, NM 88240

# CHAIN-OF-CUSTODY AND ANALYSIS REQUEST

(505) 393-2326 FAX (505) 393-2476 ANALYSIS REQUEST BILL TO Company Name: BBC International, Inc. P.O. #: Project Manager: Cliff Brunson Address: P.O. Box 805 Company: State: NM Zip: 88241 Attn: city: Hobbs Fax #: 575-397-0397 Phone #: 575-397-6388 Address: City: Project Owner: Project #: Leg 5 State: Zip: Project Name: Project Location: BRAVO Dome, NM Phone #: Fax #: Sampler Name: PRESERV. SAMPLING MATRIX Llorid FOR LAB USE ONLY (G)RAB OR (C)OMP GROUNDWATER ACID/BASE ICE / COOL Sample I.D. Lab I.D. SLUDGE OTHER: SOIL DATE TIME H 700854 3/27/17 9:304 10:00 A 10:30A 10-48A 11 11 11:004 11:304 H 12:000 13 11

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Service, an no event shall condition or	to the state of th	have of whather every claim is have	d upon any of the above stated re-	asons or otherwise.				
affiliates or successors arising out of or related to the performance of	services hereunder by Cardinal, regard	ed Bu:	a appear and	Phone Result:	☐ Yes	□ No	Add'l Phone #:	
Relinquished By:	Date:2/31/17 Receive	ва Бу /		Fax Result:	☐ Yes	□ No	Add'l Fax #:	
4. 3	Time: 8.000m Je	mifer Gel	Key	REMARKS:				
Relinquished By:	Date: 3-3/-17 Receiv							
Jennifer Colkey	Time: 45	mara Vl	dotAR					
Delivered By: (Circle One)		Cool Intact	CHECKED BY:					
Sampler - UPS - Bus - Other:	-18.9°	Yes Yes No No	TO.418					

<sup>†</sup> Cardinal cannot accept verbal changes. Please fax written changes to 505-393-2476



June 13, 2017

Cliff Brunson

BBC International, Inc.

P.O. Box 805

Hobbs, NM 88241

RE: BRAVO DOME LEG #5

Enclosed are the results of analyses for samples received by the laboratory on 06/07/17 16:40.

Cardinal Laboratories is accredited through Texas NELAP under certificate number T104704398-16-8. Accreditation applies to drinking water, non-potable water and solid and chemical materials. All accredited analytes are denoted by an asterisk (\*). For a complete list of accredited analytes and matrices visit the TCEQ website at <a href="https://www.tceq.texas.gov/field/ga/lab">www.tceq.texas.gov/field/ga/lab</a> accred certif.html.

Cardinal Laboratories is accreditated through the State of Colorado Department of Public Health and Environment for:

Method EPA 552.2 Haloacetic Acids (HAA-5)
Method EPA 524.2 Total Trihalomethanes (TTHM)
Method EPA 524.4 Regulated VOCs (V1, V2, V3)

Celey D. Keene

Accreditation applies to public drinking water matrices.

This report meets NELAP requirements and is made up of a cover page, analytical results, and a copy of the original chain-of-custody. If you have any questions concerning this report, please feel free to contact me.

Sincerely,

Celey D. Keene

Lab Director/Quality Manager



BBC International, Inc.

Cliff Brunson P.O. Box 805 Hobbs NM, 88241

Fax To: (575) 397-0397

Received: 06/07/2017 Sampling Date: 06/06/2017

Reported: 06/13/2017 Sampling Type: Soil

Project Name: BRAVO DOME LEG #5 Sampling Condition: Cool & Intact
Project Number: NOT GIVEN Sample Received By: Tamara Oldaker

Project Location: OXY

#### Sample ID: SB1 @ SURFACE (H701505-01)

Chloride, SM4500CI-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	4560	16.0	06/09/2017	ND	448	112	400	0.00	
Sample ID: SB1 @ 5' (H7	01505-02)								
Chloride, SM4500Cl-B	mg/kg		Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	240	16.0	06/09/2017	ND	448	112	400	0.00	
Sample ID: SB1 @ 10' (H	701505-03)								
Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	4160	16.0	06/09/2017	ND	448	112	400	0.00	
Sample ID: SB1 @ 15' (H	701505-04)								
Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	784	16.0	06/09/2017	ND	448	112	400	0.00	

#### Cardinal Laboratories \*=Accredited Analyte

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BBC International, Inc.

Cliff Brunson P.O. Box 805 Hobbs NM, 88241

Fax To: (575) 397-0397

Received: 06/07/2017 Sampling Date: 06/06/2017

Reported: 06/13/2017 Sampling Type: Soil

Project Name: BRAVO DOME LEG #5 Sampling Condition: Cool & Intact
Project Number: NOT GIVEN Sample Received By: Tamara Oldaker

Project Location: OXY

#### Sample ID: SB1 @ 17' (H701505-05)

mg,	/kg	Analyze	d By: AC					
Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
352	16.0	06/09/2017	ND	448	112	400	0.00	
L <b>505-06)</b>								
mg	/kg	Analyze	d By: AC					
Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
1280	16.0	06/09/2017	ND	448	112	400	0.00	
1505-07)								
mg	/kg	Analyze	d By: AC					
Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
160	16.0	06/09/2017	ND	448	112	400	0.00	
1505-08)								
mg,	/kg	Analyze	d By: AC					
Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
208	16.0	06/09/2017	ND	448	112	400	0.00	
(H701505-	-09)							
-	-	Analyze	d By: AC					
Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
	Result 352 L505-06) mg Result 1280 L505-07) mg Result 160 L505-08) mg Result 208 (H701505-mg	352 16.0  L505-06)  mg/kg  Result Reporting Limit 1280 16.0  L505-07)  mg/kg  Result Reporting Limit 160 16.0  L505-08)  mg/kg  Result Reporting Limit 208 16.0  (H701505-09)  mg/kg	Result         Reporting Limit         Analyzed           352         16.0         06/09/2017           L505-06)         Mg/kg         Analyzed           Result         Reporting Limit         Analyzed           1280         16.0         06/09/2017           L505-07)         Mg/kg         Analyzed           Result         Reporting Limit         Analyzed           160         16.0         06/09/2017           L505-08)         Mg/kg         Analyzed           Result         Reporting Limit         Analyzed           208         16.0         06/09/2017           (H701505-09)         Mg/kg         Analyzed           Analyzed         Analyzed         Analyzed	Result         Reporting Limit         Analyzed         Method Blank           352         16.0         06/09/2017         ND           L505-06)         May kg         Analyzed By: AC           Result         Reporting Limit         Analyzed         Method Blank           1280         16.0         06/09/2017         ND           L505-07)         May kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           Result         Reporting Limit         Analyzed Method Blank           208         16.0         06/09/2017         ND           (H701505-09)         Mg/kg         Analyzed By: AC	Result         Reporting Limit         Analyzed         Method Blank         BS           352         16.0         06/09/2017         ND         448           L505-06)         mg/kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           L505-07)         Mg/kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           L505-08)         Mg/kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           L505-08)         Mg/kg         Analyzed By: AC           (H701505-09)         Mg/kg         Analyzed By: AC	Result   Reporting Limit   Analyzed   Method Blank   BS   % Recovery	Result Reporting Limit Analyzed Method Blank BS % Recovery True Value QC 352 16.0 06/09/2017 ND 448 112 400  L505-06)     mg/kg	Result         Reporting Limit         Analyzed         Method Blank         BS         % Recovery         True Value QC         RPD           352         16.0         06/09/2017         ND         448         112         400         0.00           L505-06)         mg/kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           L505-07)         mg/kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           L505-08)         mg/kg         Analyzed By: AC           Result         Reporting Limit         Analyzed By: AC           (H701505-09)         mg/kg         Analyzed By: AC

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BBC International, Inc.

Cliff Brunson P.O. Box 805 Hobbs NM, 88241

Fax To: (575) 397-0397

Received: 06/07/2017 Sampling Date: 06/06/2017

Reported: 06/13/2017 Sampling Type: Soil
Project Name: BRAVO DOME LEG #5 Sampling Condition: Cool

Project Name: BRAVO DOME LEG #5 Sampling Condition: Cool & Intact
Project Number: NOT GIVEN Sample Received By: Tamara Oldaker

Project Location: OXY

#### Sample ID: SB2 @ 5' (H701505-10)

Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	64.0	16.0	06/09/2017	ND	448	112	400	0.00	
Sample ID: SB2 @ 10' (H	701505-11)								
Sample ID: SB2 @ 10' (H Chloride, SM4500Cl-B	-	/kg	Analyze	d By: AC					
•	-	<b>/kg</b> Reporting Limit	<b>Analyze</b> Analyzed	d By: AC  Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier

#### Sample ID: SB3 @ SURFACE (H701505-12)

Chloride, SM4500Cl-B	mg/kg			Analyzed By: AC							
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier		
Chloride	4080	16.0	06/09/2017	ND	432	108	400	3.77	QM-07		

#### Sample ID: SB3 @ 5' (H701505-13)

Chloride, SM4500Cl-B	mg,	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	2200	16.0	06/09/2017	ND	432	108	400	3.77	

#### Sample ID: SB3 @ 10' (H701505-14)

	,								
Chloride, SM4500Cl-B	mg	/kg	Analyze	d By: AC					
Analyte	Result	Reporting Limit	Analyzed	Method Blank	BS	% Recovery	True Value QC	RPD	Qualifier
Chloride	1660	16.0	06/09/2017	ND	432	108	400	3.77	

Cardinal Laboratories \*=Accredited Analyte

PLEASE NOTE: Liability and Damages. Cardinal's liability and client's exclusive remedy for any claim arising, whether based in contract or tort, shall be limited to the amount paid by client for analyses. All claims, including those for negligence and any other cause whistoever shall be deemed waived unless made in writing and received by Cardinal within thirty (30) days after completion of the applicable service. In no event shall Cardinal be liable for incidental or consequential damages, including, without limitation, business interruptions, loss of use, or loss of profits incurred by client, its subsidiaries, affiliates or successors arising out of or related to the performance of the services hereunder by Cardinal, regardless of whether such claim is based upon any of the above stated reasons or otherwise. Results related only to the samples identified above. This report shall not be reproduced except in full with written approval of Cardinal Laboratories.



BBC International, Inc.

Cliff Brunson P.O. Box 805 Hobbs NM, 88241

Fax To: (575) 397-0397

Received: 06/07/2017 Sampling Date: 06/06/2017

06/09/2017

Reported: 06/13/2017 Sampling Type: Soil

Project Name: BRAVO DOME LEG #5 Sampling Condition: Cool & Intact Project Number: Sample Received By: NOT GIVEN Tamara Oldaker

Project Location: OXY

Sample ID: SB3 @ 15' (H701505-15)

Chloride, SM4500Cl-B mg/kg Analyzed By: AC Analyte Result Reporting Limit Analyzed Method Blank BS % Recovery True Value QC RPD Qualifier

ND

432

108

400

3.77

16.0

304

Sample ID: SB3 @ 17' (H701505-16)

Chloride

Chloride, SM4500Cl-B mg/kg Analyzed By: AC Reporting Limit Analyzed Method Blank BS True Value QC RPD Qualifier Analyte Result % Recovery Chloride 32.0 16.0 06/09/2017 432 400 3.77 ND 108

Sample ID: SB3 @ 22' (H701505-17)

Chloride, SM4500Cl-B mg/kg Analyzed By: AC Analyte Result Reporting Limit Analyzed Method Blank BS % Recovery True Value QC RPD Qualifier Chloride 32.0 06/09/2017 ND 400 16.0 432 108 3.77

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#### **Notes and Definitions**

QM-07 The spike recovery was outside acceptance limits for the MS and/or MSD. The batch was accepted based on acceptable LCS

recovery.

ND Analyte NOT DETECTED at or above the reporting limit

RPD Relative Percent Difference

\*\* Samples not received at proper temperature of 6°C or below.

\*\*\* Insufficient time to reach temperature.

Chloride by SM4500Cl-B does not require samples be received at or below 6°C

Samples reported on an as received basis (wet) unless otherwise noted on report

Cardinal Laboratories \*=Accredited Analyte

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Celey D. Keine

E		
CE.	ARDINAL LABORATORI	ES
4	101 East Marland, Hobbs, NM	88240

# CHAIN-OF-CUSTODY AND ANALYSIS REQUEST

	(505) 393-2326 FAX (505) 393-2476			_		ALTERIA		. =-		ANALYSIS REQUEST										
	BBC International	, Inc.				_			IL	L TO					ANA	LYSIS	KEC	JUES		_
	: Cliff Brunson					-	P.O. ‡	t:												
Address: P.O.	Box 805						Comp	any:												1 1
city: Hobbs		State: NM	ip:	882	41		Attn:													
Phone #: 575-3	397-6388	Fax #: 575-3	97-	0397	7		Addr	ess:												1 1
Project #:		Project Owner:	(	DKY	1		City:												1 1	
Project Name:	BRAVO DOME	LEG #5		0			State: Zip:											1 1		
Project Location	1:						Phone #:			ll								1 1		
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service. In no event shall C	ardinal be liable for incidental or consequence out of or related to the performance	uental damages, including v	vithout for	imitation, egardless	business into s of whether s	erruptions,	loss of us	e, or loss	of pro	fits incurred by	client, its subsidi asons or otherwi	aries, ise.								
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<sup>†</sup> Cardinal cannot accept verbal changes. Please fax written changes to 505-393-2476



# CHAIN-OF-CUSTODY AND ANALYSIS REQUEST

Company Name	ompany Name: BBC International, Inc.					9	BILL TO							ANA	LYSI	S RE	QUE	ST				
	: Cliff Brunson						P	.0.#						T								
Address: P.O.	Box 805						C	omp	any:													
city: Hobbs		State: NM	Zip:	. 8	8241		A	ttn:														
Phone #: 575-3	397-6388	Fax #: 575-	-397	-03	397		A	Address:														
Project #:		Project Owner	:	(	DKY		c	City:														
Project Name:	ERAVO DOME				1		s	State: Zip:														
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Sampler Name:		BURANDEZ					F	Fax #: ,									100					
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<sup>†</sup> Cardinal cannot accept verbal changes. Please fax written changes to 505-393-2476

District I
1625 N. French Dr., Hobbs, NM 88240
District II
811 S. First St., Artesia, NM 88210
District III
1000 Rio Brazos Road, Aztec, NM 87410
District IV

1220 S. St. Francis Dr., Santa Fe, NM 87505

#### State of New Mexico Energy Minerals and Natural Resources

Form C-141 Revised August 8, 2011

Oil Conservation Division 1220 South St. Francis Dr. Santa Fe, NM 87505 Submit 1 Copy to appropriate District Office in accordance with 19.15.29 NMAC.

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Unit Letter	Section	Township	Range	Feet from the	North/	South Line	Feet from the	East/Wes	East/West Line   County					
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regulations al public health should their o or the environ	I hereby certify that the information given above is true and complete to the best of my knowledge and understand that pursuant to NMOCD rules and regulations all operators are required to report and/or file certain release notifications and perform corrective actions for releases which may endanger public health or the environment. The acceptance of a C-141 report by the NMOCD marked as "Final Report" does not relieve the operator of liability should their operations have failed to adequately investigate and remediate contamination that pose a threat to ground water, surface water, human health or the environment. In addition, NMOCD acceptance of a C-141 report does not relieve the operator of responsibility for compliance with any other federal, state, or local laws and/or regulations.													
Signature:	Lity	K	>			200.00	OIL CONS	1	rion :	DIVISIO	ON 7	1		
Printed Name	: Eric Maes	tas			A	approved by I	Environmental Sp	ecialist:	10	ed)		Toul		
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E-mail Addres	1	estas@oxy.co	m		c	Conditions of	Approval:			Attached	D			
Date: 2/1	ate: z/15/17 Phone:575-420-7825													

CONDITIONS OF APPROVAL

#### Operator/Responsible Party,

The OCD has received the form C-141 you provided on State of the regarding an unauthorized release. The information contained on that form has been entered into our incident database and remediation case number 4RP-12 has been assigned. Please refer to this case number in all future correspondence.

It is the Division's obligation under both the Oil & Gas Act and Water Quality Act to provide for the protection of public health and the environment. Our regulations (19.15.29.11 NMAC) state the following,

The responsible person shall complete <u>division-approved corrective action</u> for releases that endanger public health or the environment. The responsible person shall address releases in accordance with a remediation plan submitted to and approved by the division or with an abatement plan submitted in accordance with 19.15.30 NMAC. [emphasis added]

Release characterization is the first phase of corrective action unless the release is ongoing or is of limited volume and all impacts can be immediately addressed. Proper and cost-effective remediation typically cannot occur without adequate characterization of the impacts of any release. Furthermore, the Division has the ability to impose reasonable conditions upon the efforts it oversees. As such, the Division is requiring a workplan for the characterization of impacts associated with this release be submitted to the OCD District office in on or before on or before on or before will be an associated deadline for submittal of the resultant investigation report. Modest extensions of time to these deadlines may be granted, but only with acceptable justification.

The goals of a characterization effort are: 1) determination of the lateral and vertical extents along with the magnitude of soil contamination. 2) determine if groundwater or surface waters have been impacted. 3) If groundwater or surface waters have been impacted, what are the extents and magnitude of that impact. 4) The characterization of any other adverse impacts that may have occurred (examples: impacts on vegetation, impacts on wildlife, air quality, loss of use of property, etc.). To meet these goals as quickly as possible, the following items must, at a minimum, be addressed in the release characterization workplan and subsequent reporting:

- $\bullet$  Horizontal delineation of soil impacts in each of the four cardinal compass directions. Adsorbed soil contamination must be characterized to the following concentrations: benzene 10 mg/kg, total BTEX 50 mg/kg, TPH (GRO+DRO+MRO; C<sub>6</sub> thru C<sub>36</sub>) 100 mg/kg, chloride 600 mg/kg. This is not an exclusive list of potential contaminants. Analyzed parameters should be modified based on the nature of the released substance(s). Soil sampling must be both within the impacted area and beyond.
- Vertical delineation of soil impacts. Adsorbed soil contamination must be characterized to the following concentrations: benzene 10 mg/kg, total BTEX 50 mg/kg, TPH (GRO+DRO+MRO; C<sub>6</sub> thru C<sub>36</sub>) 100 mg/kg, chloride 250 mg/kg. As above, this is not an exclusive list of potential contaminants and can be modified. Vertical characterization samples should be taken at depth intervals no greater than five feet apart. Lithologic description of encountered soils must also be provided. At least ten vertical feet of soils with contaminant concentrations at or below these values must be demonstrated as existing above the water table.
- No inference should be made concerning the minimum characterization concentrations expressed above as to the ultimate remediation levels which might be approved. Nominal detection limits for field and laboratory analyses must be provided.
- Composite sampling is not generally allowed.
- Field screening and assessment techniques are acceptable (headspace, titration, EC [include algorithm for validation purposes], EM, etc.), but the sampling and assay procedures must be clearly defined. Copies of field notes are highly desirable. A statistically significant set of split samples must be submitted for confirmatory laboratory analysis, including the laterally farthest and vertically deepest sets of soil samples. Make sure there are at least two soil samples submitted

for laboratory analysis from each borehole or test pit (highest observed contamination and deepest depth investigated). Copies of the actual laboratory results must be provided including chain of custody documentation.

- •Probable depth to shallowest groundwater and lateral distance to nearest surface water. If there is an estimate of groundwater depth, the information used to arrive at that estimate must be provided. If there is a reasonable assumption that the depth to water is 50 feet or less, the responsible party should anticipate the need for at least one groundwater monitoring well to be installed in the area of likely maximum contamination.
- If groundwater contamination is encountered, an additional investigation workplan may be required to determine the extents of that contamination. Groundwater and/or surface water samples, if any, must be analyzed by a competent laboratory for volatile organic hydrocarbons (typically Method 8260 full list), total dissolved solids, pH, major anions and cations including chloride and sulfate, dissolved iron, and dissolved manganese. The investigation workplan must provide the groundwater sampling method(s) and sample handling protocols. To the fullest extent possible, aqueous analyses must be undertaken using nominal method detection limits. As with the soil analyses, copies of the actual laboratory results must be provided including chain of custody documentation.
- Accurately scaled and well-drafted site maps must be provided providing the location of borings, test pits, monitoring
  wells, potentially impacted areas, and significant surface features including roads and site infrastructure that might limit
  either the release characterization or remedial efforts. Field sketches may be included in subsequent reporting, but should
  not be considered stand-alone documentation of the site's layout. Digital photographic documentation of the location
  and fieldwork is recommended, especially if unusual circumstances are encountered.

Nothing herein should be interpreted to preclude emergency response actions or to imply immediate remediation by removal cannot proceed as warranted. Nonetheless, characterization of impacts and confirmation of the effectiveness of remedial efforts must still be provided to the OCD before any release incident will be closed.

Jim Griswold
OCD Environmental Bureau Chief
1220 South St. Francis Drive
Santa Fe, New Mexico 87505
505-476-3465
jim.griswold@state.nm.us

#### Bayliss, Randolph, EMNRD

From:

Lowe, Leonard, EMNRD

Sent:

Friday, February 17, 2017 11:40 AM

To:

Bayliss, Randolph, EMNRD

Subject:

FW: OXY Bravo Dome Produced water spill 2152017

Attachments:

Scanned from a Xerox multifunction device001.pdf

Mr. Bayliss,

Leonard Lowe
Engineering Bureau
Oil Conservation Division
Energy Minerals and Natural Resources Department
1220 South St. Frances
Santa Fe, New Mexico 87004

Office: 505-476-3492 Cell: 505-930-6717 Fax: 505-476-3462

E-mail: leonard.lowe@state.nm.us

Website: http://www.emnrd.state.nm.us/ocd/

----Original Message----

From: Eric\_Maestas@oxy.com [mailto:Eric\_Maestas@oxy.com]

Sent: Wednesday, February 15, 2017 9:59 AM

To: Jones, William V, EMNRD < William V.Jones@state.nm.us>; Lowe, Leonard, EMNRD < Leonard.Lowe@state.nm.us>

Cc: Sharon\_Reid@oxy.com; Eric\_Maestas@oxy.com; Charles\_Terry@oxy.com; Cole\_Wallin@oxy.com; Mike\_Kelly2@oxy.com; Tommy\_Pugh@oxy.com; Bradey\_Holland@oxy.com; Casey\_Summers@oxy.com

Subject: OXY Bravo Dome Produced water spill 2152017

Mr. Jones,

A produced water spill was reported today on the leg 5 lateral of the Bravo Dome field. An internal corrosion leak occurred spilling and estimated 7bbls of produced water. Attached is the C-141 for the 7bbl produced water spill that occurred today. Please let me know if you have any questions or comments.

Thank you,

Eric Maestas HES Ops Coordinator Bravo Dome Sheep Mountain cell: (575)420-7825

# Environmental Impacts of BRINE (Produced Water)

Miranda Meehan, Extension Livestock Environmental Stewardship Specialist Kevin Sedivec, Extension Rangeland Management Specialist Thomas DeSutter, Soil Scientist, NDSU School of Natural Resource Sciences Chris Augustin, Extension Area Soil Health Specialist Aaron Daigh, Soil Scientist, NDSU School of Natural Resource Sciences

A higher quantity of brine will need to be stored, transported and disposed of as the result of increased energy development. These larger quantities can lead to greater risks for spills. Brine spills negatively affect the soil and vegetation, impairing their ability to produce crops and forage (Figure 1).

#### What is Brine?

Brine, or produced water, is a byproduct of oil and gas production. It consists of water from the geologic formation, injection water, oil and salts.

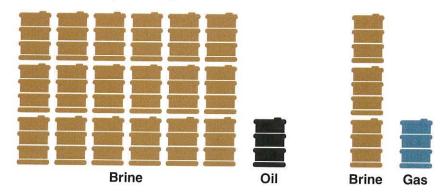
Brine has a high salt concentration that has been recorded up to 10 times the salinity of ocean water. Brine solutions can have electrical conductivities (EC) in excess of 200 deciSiemens per meter (dS/m; 1 dS/m = 1 millimhos per centimeter [mmhos/cm]), sodium adsorption ratios (SAR) of more than 300 and total dissolved solids (TDS) concentrations of 100,000 parts per million.

The high salt concentrations in brine come from salt deposits in oil-producing formations, as seen in the Bakken and Three Forks formations in western North Dakota. However, the overall salinity and concentrations of sodium can vary widely by location and depth of extraction.

Figure 1. This is a 50-year-old brine spill in northwestern North Dakota.



**Figure 2.** The average well in North Dakota produces 18 barrels of brine per barrel of oil and three barrels of brine per barrel of gas.





June 2017

#### Brine Effects on Soil

The salts in brine alter the chemical and physical properties of soils. Due to the high amounts of soluble salts (predominately sodium chloride, NaCl), brine negatively impacts soils in many ways.

Chloride levels in and around the spill area are toxic to many biological species. Sodium is a natural dispersant and can cause soils to swell and disperse, but only if the total salt level in the soil falls below a flocculation threshold limit. A flocculant binds the soil together and helps create soil structure.

For most soils in the region, when the SAR from a saturated paste extract (assume that at values of less than 50, the SAR  $\approx$  exchangeable sodium percentage  $\approx$  % sodium) is 5 or more and the EC of the saturated paste is 2 dS/m or less, soils will swell and/or disperse (Figure 3). Thus, remediation strategies should focus on reducing the concentration of sodium (a known dispersant), increasing the concentration of calcium (a known flocculant), and maintaining EC levels above the threshold at which swelling and dispersion will occur.

Swelling soils will retain their natural structure, but soil structure will be lost once dispersion occurs. This loss of structure impedes the ability of water to infiltrate and move through the soil, increasing the potential for erosion.

# Brine Effects on Vegetation

Salts in brine impair plants' ability to take up water and nutrients. High salt concentrations in the soil restrict the plants' ability to take up water despite adequate water being available in the soil, causing the plant to exhibit symptoms of drought. This is due to an osmotic effect, which causes water to move from areas of low salt concentrations, in the roots, to areas of high salt concentrations, in the soil.

Due to the impacts of high salt concentrations on soil and vegetation, impacted sites suffer from a decline in plant growth. This is magnified by the inability of many seeds to germinate. Under these conditions, seeds have difficulty taking up water, causing damage to the embryo or dormancy in response to water stress.

In addition to the inability to take up water, excess sodium and chloride ions can interfere with the plants' ability to generate energy and reduce the uptake and/or use of key nutrients (Figure 4).

Plants exposed to brine often die due to salt stress resulting from the inability to take up water and key nutrients. Most plants will show signs of salt stress if sodium exceeds 70 milligrams per liter in water, 5 percent in plant tissue or 230 milligrams per liter in soil (saturated paste extract).

Chloride negatively impacts most plants when it exceeds 350 milligrams per liter in water, 1 percent in plant tissue or 250 milligrams per liter in soil (saturated paste extract). However, some plant species are salt-tolerant; they are called halophytes.

Halophytes are able to grow and reproduce in soils with EC values of 20 dS/m or more. In comparison, EC values above 2 dS/m negatively affect the growth of many row crops and small grains. Halophyte plants are able to survive due to adaptations that allow them to regulate, transport or store salts safely in special compartments of the plants' tissues.

**Figure 3.** Soil EC and sodium impact the structure of soils when swelling and dispersion occur, which impedes the ability of water to infiltrate through the soil.

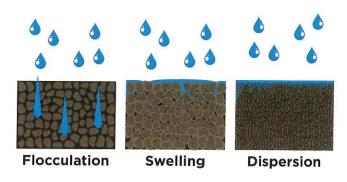


Figure 4. Effects of brine on vegetation.

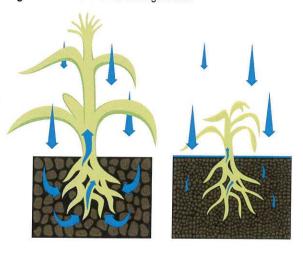


Table 1. Relative Saline Tolerance Levels (EC) of Agronomic Crops<sup>1,2</sup>.

Crop	EC (dS/m) Production Affected	Upper Limit	Tolerance Rating
Canola	10	14	High
Barley	8	16	High
Wheat (durum)	7	14	Moderate
Wheat (semidwarf)	7	14	Moderate
Sugar beets	7	14	Moderate
Sunflowers	6	14	Moderate
Safflowers	6	10	Moderate
Oats	4	8	Low
Soybeans	4	8	Low
Alfalfa	4	8	Low
Corn	3	6	Low
Flax	2	4	Low
Edible beans	1	2	Low

<sup>1</sup> Source: Ogle and St. John (2009).

<sup>&</sup>lt;sup>2</sup> Source: Franzen (2013).

#### Brine Spill Remediation

The goal of brine spill remediation is to remove or minimize salts in the soil, allowing for improved vegetation growth and establishment. Remediation can be accomplished through *ex situ* or *in situ* methods.

#### Ex Situ Remediation

Ex situ methods are most often utilized in North Dakota. During ex situ remediation, the topsoil or impacted depth is excavated from the site and moved to a landfill that is approved for the containment of oil-field wastes. New topsoil is brought in to replace the removed soil.

The new topsoil may have different chemical and physical properties, including a different seedbank, than the original soils. The new soil will not be contaminated with brine, but it should be managed to maintain a clean, weed-free seedbed for the reclamation process.

#### In Situ Remediation

*In situ* methods remove the salts from the topsoil while keeping the soil in place. The most commonly used methods include the application of chemical amendments, which can be supplemented with tile drainage.

Chemical amendments are used to replace sodium on the soil's exchange sites, allowing the sodium to be leached lower in the soil profile, where it does not impact plant growth and establishment.

Chemical amendments are typically calcium-based, such as gypsum. Gypsum is the most commonly applied amendment used for *in situ* remediation in North Dakota.

However, the use of gypsum has limitations because it is only effective to the depth to which it is incorporated into the soil. In addition, the particle size of the gypsum being applied can influence reclamation. Smaller gypsum particles have greater surface area, causing it to react more quickly than larger particles.

The use of tile drainage aids in permanently removing the leached waters containing sodium and chloride to offsite disposal areas. However, one of the main limitations to successful remediation is applying enough water to 1) solubilize the gypsum so that calcium can counteract the negative effects of the sodium, and to maintain soil EC; 2) move calcium down the soil profile; and 3) leach the sodium and chloride into the tile and collection tanks, or below the rooting zone.

The success of *in situ* remediation can be enhanced through the establishment of halophytic vegetation. Halophytes take up salts and store them in plant parts. Harvesting the above-ground biomass and removing it from the site can reduce salts in the soil.

Figure 5. A crew is doing ex situ remediation of a brine spill.



**Figure 6.** The topsoil was removed from this spill site as part of *ex situ* remediation.



#### Remediation Results

Remediation is a long and costly process, often with limited success. However, new research and technologies have greatly improved the success of remediation projects. Important factors to consider when tackling a remediation project include:

- who is responsible for cleaning up the spill
- the extent of the impacted area
- the soil EC and SAR levels
- estimated cost of cleanup
- the desired land use

Answering these questions will help you determine the method(s) best suited for your site.

Following any remediation project, continuing to monitor the site to document the success of the project is important. Pay close attention to soil structure, EC and SAR levels, vegetation cover and production.

Table 2. Relative Saline Tolerance Levels (EC) of Selected Range and Pasture Species<sup>1, 2</sup>.

	EC (dS/m) Production Affected – Seedling Stage	EC (dS/m) Production Affected – Vegetative Stage	EC (dS/m)  Plant Mortality (regardless of growth stage)	Tolerance Rating	Palatability
Grass		-			
Nuttall's alkaligrass	8	14	32	Very high	Medium
Inland saltgrass	12	16	32	Very high	Medium
Alkali sacaton	10	32	32	Very high	Medium
Beardless wildrye		13	26	Very high	Medium
Tall wheatgrass		13	26	Very high	Low
Green wheatgrass (Newhy)		13	26	Very high	High
Russian wildrye		13	24	Very high	Medium
Alkali cordgrass		12	24	Very high	_
Alkali bluegrass		12	24	Very high	_
Slender wheatgrass		10	22	Very high	Medium
Altai wildrye		10	20	Very high	Medium
Plains bluegrass		10	20	Very high	Medium
Tall fescue		8	18	High	Medium
Western wheatgrass	4	8	16	High	High
Crested wheatgrass		6	14	Moderate	High
Intermediate wheatgrass		6	12	Moderate	High
Little bluestem	6	6	10	Moderate	Medium
Smooth brome		5	10	Moderate	Highest
Meadow brome		4	10	Moderate	Highest
Switchgrass		=	6	Low	Medium
Blue grama	4	4	6	Low	Highest
Forbs and Shrubs					
Forage kochia		10	18+	High	Medium
Fourwing saltbush		10	18+	High	Medium
Winterfat		10	18+	High	High
Strawberry clover		6	16	High	Highest
Yellow sweetclover		5	10	Moderate	High
Cicer milkvetch	THE STATE OF THE S	4	10	Moderate	Highest
Birdsfoot trefoil		5	8	Low	High
Alfalfa		4	8	Low	Highest
Clovers (red, alsike, ladino)		3	4	Low	Highest

<sup>1</sup> Source: Ogle and St. John (2009).

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<sup>&</sup>lt;sup>2</sup> Source: Thomlinson, H. (2016).

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# REMEDIATION OF SALT AFFECTED SITES BY LEACHING

**Report Prepared for:** 

PETROLEUM TECHNOLOGY ALLIANCE CANADA

Prepared by:

MATRIX SOLUTIONS INC.

Nancy Finlayson, M.Sc., P.Ag.

**Principal Soil Scientist** 

reviewed by

Pat Reid, P.Ag.

**Principal Agrologist** 

June 2007 Edmonton, Alberta

#### **EXECUTIVE SUMMARY**

Sodium chloride (NaCl) based brine known as "produced water" is frequently produced along with petroleum hydrocarbons in western Canada. Remediation of soils impacted by produced water spills is an ongoing challenge since sodium chloride salts can have a negative impact on soil productivity, penetrate soils rapidly potentially affecting groundwater quality, and do not biodegrade.

The objective of this study was to evaluate current soil leaching technologies as a remediation tool for sodium chloride-impacted soils in western Canada. The study used existing spill monitoring data provided by a number of companies operating in western Canada. Data from 35 spills were included in the study. Because of the requirement for soil monitoring over several years, sites made available to the study tended to be larger or more persistent spills; they were not necessarily a typical cross-section of spills in Alberta or Western Canada.

Results indicated that leaching often moves salts downward very rapidly, particularly in the first several years after the spill. Produced salts can move through the soil profile to a depth of 5 m or more within 10 years, in permeable soil. Both engineered and passive systems can be effective in restoring good crop growth but there is some evidence that tile drainage may enhance the rate of salt leaching, particularly if the system is well maintained.

Leaching was not effective in removing salts from the topsoil at all spills. At about 10% of the passively remediated spills, electrical conductivity (EC) and sodium adsorption ratio (SAR) increased in topsoil between monitoring events. Resalinization can occur if there is upward movement of salts by capillary action from a high water table, or if the spill occurred in a groundwater discharge area.

Calcium (Ca) amendments appear to be very important to the leaching process. Because calcium applied as gypsum has a much lower solubility than sodium chloride and therefore moves more slowly through the soil profile, subsoil SAR sometimes increases during the leaching process, until sufficient applied calcium reaches subsoil. Data showed that calcium applied to the soil as gypsum can leach effectively through the soil profile to a depth of 1.0 m or more within 10 years despite its low solubility.



Sufficient water is needed to flush salts out of the root zone or into tile drains. Otherwise, salts can accumulate in subsoil at the maximum depth of water penetration resulting in a "bulge" in EC and/or SAR values. If the volume of leaching water is insufficient, additional time may not help move the salt "bulge" deeper into the soil profile. Spill remediation monitoring including yearly vegetation monitoring and less frequent soil sampling was recommended.



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#### 1.0 INTRODUCTION

Sodium chloride (NaCl) based brine known as "produced water" is frequently produced along with petroleum hydrocarbons (PHCs) in western Canada. Spills of produced water onto both agricultural and non-agricultural soils are common in many of western Canada's aging oil and gas producing fields. Remediation of soils impacted by produced water spills is an ongoing challenge since sodium chloride salts can have a negative impact on soil productivity, penetrate soils rapidly, potentially affecting groundwater quality, and do not biodegrade.

After a produced water release has occurred and initial spill clean-up is completed, the standard remediation practice for produced sodium chloride brine spills in western Canada is removal of the source followed by flushing of salts downward, out of the soil rooting zone. Calcium (Ca) amendments usually applied as calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>) or calcium sulphate (gypsum; CaSO<sub>4</sub>•2H<sub>2</sub>0) are frequently used to maintain soil physical properties so that leaching can effectively remove salts from the soil rooting zone.

Although leaching has been used extensively to remediate salt affected soils worldwide, information related to leaching rates of salts from sodium chloride spills in western Canada is lacking. It was concluded in a literature review of salt movement through soils disturbed during pipeline construction, that 8 to 11 years was sufficient time for naturally occurring soluble salts (primarily sodium sulphate) introduced into the rooting zone during construction to return to background levels (Finlayson, 1993). Since sodium chloride salts released in produced water spills are more soluble than the sodium sulphate salts redistributed during pipeline construction, produced water spills might be expected to return to background levels more quickly than soils disturbed by pipeline construction. However, soils impacted with produced water may contain levels of salts many times higher than found in naturally occurring saline soils.

Anecdotal evidence indicates 5 or more years may be required to restore agricultural capability of well-drained soils in east-central Alberta after a produced water spill. More than 10 years may be required to restore the agricultural capability of spills on poorly drained soils or soils with natural salts (Lowen et al., 2003). Restoration of agricultural capability may not be possible if continual upwelling of salts occurs in the shallow rooting zone or without active remediation (including possible source removal and applications of amendments to maintain soil



permeability and tilth). Leaching as a remediation tool is considered effective, but data on rates of leaching and remediation endpoints under different site and spill situations are lacking.

The objective of this study was to evaluate current soil leaching technologies as a remediation tool for sodium chloride-impacted soils in western Canada. In evaluating leaching technology, climate, landscape, and soil parameters as well as remediation history must be considered.

#### 1.1 Scope of Work

The following scope of work was undertaken:

- Approach major western Canadian oil and gas production companies for access to records
  or reports of salt spills or other salt impacted sites, which have been, or are currently being
  remediated using leaching techniques.
- Review records and reports made available on a confidential basis. Use this information to assess:
  - the reliability of leaching under different site and climate conditions;
  - the effectiveness of commonly applied amendments;
  - the effectiveness of systems constructed to collect leachate; and
  - the length of time required to complete remediation under different soil and climate conditions.
- Compare the relative costs and benefits of leaching enhancement techniques shown to be both effective and reliable.
- Prepare a report detailing results of the study and information needs.



#### 2.0 BACKGROUND

#### 2.1 Leaching Systems

The majority of produced salt spills are remediated passively, relying on the infiltration of natural precipitation to leach salts down through the soil profile and out of the root zone. Calciumbased amendments such as gypsum or Ca(NO<sub>3</sub>)<sub>2</sub> are commonly applied to prevent soil dispersion, which is an adverse effect of sodium on soil structure. Some spills are actively flushed with additional water to speed up the leaching process.

Engineered systems are sometimes employed on larger produced water spills to enhance the leaching process. Tile drainage is the most common engineered technique. Tile drains can be placed above or within the groundwater table, depending on site and spill characteristics, to remove leached salts from the soil system and to help prevent resalinization of the root zone soil. Resalinization can occur if there is upward movement of salts by capillary action from a high water table, or if the spill occurred in a groundwater discharge area. Leachate from the system must be collected and disposed of regularly to maximize the effectiveness of the system. A variation of tile drainage system is a trench intercept system that intercepts salts in soil or groundwater with a trench, bellhole or culvert placed to collect and facilitate disposal of leacheate. A third type of system, soil washing, aims to flush salts out of impacted soil by mixing the soil with clean water that is drained and then disposed.

#### 2.2 Requirements for Successful Leaching

For remediation of produced salt spills by leaching to be successful, the following conditions must be present:

#### Sufficient water available for leaching

If passive remedial leaching of a spill is attempted in areas where precipitation is too low to produce effective downward movement of soil water through the soil out of the rooting zone, leaching will not remediate the site effectively. In some situations, additional water can be applied through irrigation. Some spills may benefit from passive water trapping techniques



such as the use of snow fences in the winter, or re-contouring the site to collect additional runoff water.

#### Net downward movement of water

If sodium chloride salts are to leach downward out of the root zone during passive remediation, soils must have a net downward soil water flow. Remediation using passive leaching is unlikely to be successful in the presence of groundwater discharge or a net upward evapotranspirative flux. Leaching of salts out of the soil rooting zone may not be possible in areas with a high or fluctuating water table. Salts flushed from the root zone can resalinize root zone soils if the capillary fringe falls within the soil rooting zone at any time during the year.

#### Sufficiently permeable soil

The dispersive effect of sodium ions on clay-sized particles in soils is well known (see for example Sposito, 1989 or Bohn et al., 1985). The loss of soil structure and resulting decrease in permeability in a dispersed soil is a further impediment to efficient leaching of salts. This can be counterbalanced to some extent with the application of calcium-based amendments (see Sumner (1993) for an overview of the effect of sodium ions on soil properties).

#### Deep water table

Flushing salts from the soil rooting zone has the potential to impact groundwater resources under some conditions of high salt mass together with high water table and/or permeable soils.

#### 2.3 Methods

A total of 16 oil and gas companies were contacted with a request for information on salt-impacted sites that were remediated either with engineered leaching systems (engineered sites), or by passive remediation (passive sites). To be useful to the study, spills required comparable soil salinity data collected at a minimum of two points in time, ideally several years



apart. Nine companies supplied spill information, and data from seven companies were considered useful for this study. In total, file or data reviews were carried out for over 80 spills. Data from 35 spills were included in the study. Lack of consistency of sampling location or sampling depth between years, was the most common reason for rejecting data.

## 2.4 Evaluating Remediation Success

Various jurisdictions have developed guidelines or criteria to evaluate remediation success of salt spills. British Columbia has developed proposed risk-based guidelines specifically for salt-impacted soils (Royal Roads University, 2002). Saskatchewan's salt spill remediation guidelines are land use based (SPIGEC, 2000). Alberta's Salt Contamination and Remediation Guidelines (AENV, 2001) provide generic guidelines and procedures to develop site-specific risk-based criteria.

Alberta's generic soil quality guidelines for salts in soils were originally developed by Alberta Agriculture to assess soil materials for suitability as reclamation materials (Alberta Agriculture, 1987). They are based on the capability of the soils for use as a plant growth medium, not on actual vegetation parameters. The guidelines place soil into one of four categories based on a number of soil parameters including pH, electrical conductivity (EC), sodium adsorption ratio (SAR), saturation %, stone content, texture, consistency, organic carbon % and calcium carbonate (CaCO<sub>3</sub>) equivalent %. The four categories were:

Good None to slight soil limitations that affect use as a plant growth medium

Fair Moderate soil limitations that affect use, but which can be overcome by proper planning and good management

Poor Severe soil limitation that make use questionable

Unsuitable Chemical or physical properties of the soil are so severe that reclamation may not be feasible



For non-commercial/industrial land use, Alberta's generic guidelines for salt contaminated soil (AENV 2001) adapted these four categories, basing them on the soil parameters relating directly to salts i.e. EC and SAR. To meet guidelines, soils must fall into the same category (good, fair, poor and unsuitable) as background or pre-impact soils. Using these categories makes allowance for naturally saline and sodic background soils, which are common in many parts of Alberta. It is not realistic to assume all soils will be remediated to 'de minimus' criteria or in many cases to background conditions.

#### 2.5 Data Considerations

Data used for this study required comparable soil analytical data collected at more than one point in time, preferably several years apart. Because of the requirement for soil monitoring over several years, sites made available to the study tended to be larger or more persistent spills; they are not necessarily a typical cross-section of spills in Alberta or Western Canada.

#### 3.0 RESULTS AND DISCUSSION

Locations of spills used in this study are shown on Figure 1. Site and spill information is summarized in Appendix A for each spill. Of the five engineered sites, two are located in the Peace region of Alberta, one in east-central Alberta, one in central Alberta and one in southeast Saskatchewan. Of the 30 passive sites, four are located in central Alberta, five in southeast Saskatchewan, one in the Peace region of Alberta and 20 in east-central Alberta.

At spills with engineered systems, spill volumes ranged from about 30 to 720 m³ of produced water with impacted areas of 0.4 to 1.3 ha. Soil EC values in the spills ranged from less than 10 dS/m to as high as 70 dS/m and SAR values were as high as 25. Spills remediated passively ranged in volume from 1 to 1,000 m³ of produced water; impacted areas ranged from 0.01 to 5 ha in size. Of the 35 spills, eight can be considered large spills (>100 m³ brine released and/or >1 ha impacted). Spill volumes and areas of impact were not available in all spill information files.

Calcium amendments, usually Ca(NO<sub>3</sub>)<sub>2</sub> and gypsum, were used at most spills. In general, source material was removed at the more recent spills, but not necessarily from the older spills.



Fertilizer or straw additions were common. Unfortunately, details of rates, types and timing of amendments were often not completely documented in spill information files provided.

# 3.1 Engineered Sites

Of the five engineered systems reviewed, four were tile drainage systems and one was a soil washing system. A brief description of these engineered systems and results of soil monitoring follows.

# 3.1.1 Spill 6: Southeastern Saskatchewan Tile Drainage System

## 3.1.1.1 Background

Spill 6 with a tile drainage system located in an area under a cultivated crop rotation in southeastern Saskatchewan, had consistent soil salinity data that were collected over a period of 11 years. Of all the spill information reviewed for this project, this site had the most complete and consistent data set. Unfortunately, details of soil type, depth to groundwater and system installation details were not provided. The spill was the result of a pipeline break in 1993 on cultivated land. An estimated 720 m³ of produced water was released, affecting approximately 1.5 ha. Weeping tiles were installed after the initial spill clean-up. Tile drains were installed below 1 m depth and above the water table. The system was regularly maintained and soil samples were collected yearly. Approximately 75 m³ of source material was removed in 2000. The spill was irrigated with hauled-in water in dry years, and leachate was collected regularly; however, detailed information on volumes of water added or removed was not available for every year. Gypsum was applied as required; however, details of rates and timing were not available throughout the history of the spill.

The site was divided into three areas roughly equal in size and composite samples were taken from each area. Soils were sampled yearly to 1 m depth, and analyzed for salinity parameters including EC, SAR, chloride and sulphate anions. In 1998 and subsequent years, the three areas were subdivided, resulting in the collection of more composite samples for each area each year. Soil samples were collected at depths of 0-15, 15-50 and 50-100 cm at all sampling events. Table 1 provides a summary of the data used for this analysis.



#### 3.1.1.2 Results

Immediately after the spill, some areas had EC values up to 171 dS/m and SAR values up to 181 in the upper 15 cm of the soil. The most dramatic reduction in salinity throughout the 1 m monitored soil zone occurred within the first 3 years. After 3 years, the decrease in salinity was less dramatic but EC values continued to decline steadily in most parts of the spill. Figures 2a and 2b illustrate the decrease in average EC and SAR over time. Both EC and SAR dropped by more than half in the first 2 years of leaching, and even after 8 years, EC and SAR continued to decrease slowly. After 11 years, EC values in the upper 50 cm of the soil were less than 5 dS/m and SAR less than 3 at half the locations monitored in the spill area. Chloride concentrations (Figure 2c), show similar trends over time as EC and SAR.

Gypsum was applied to the impacted area regularly. Calcium concentrations through the soil profile in a control, and on the spill site at 1 and 11 years (1994 and 2004) after initial amendment are illustrated on Figure 2d. The increase in calcium compared to controls, and the decrease in calcium between 1994 and 2004 indicate that the much of the surface applied gypsum amendments have moved down the soil profile to at least 1 m.

In 2003, crop growth was reported as "fair" to "good" over more than 75% of the spill area. In 2004, chlorides were still being removed from the tile system in leachate water, an indication that remediation is continuing.

Soil samples were not collected below 1 m depth, so the effectiveness of the tile system in intercepting salts could not be assessed with the data available.

#### 3.1.1.3 Conclusions

- Surface applied gypsum amendments effectively moved through the soil profile to at least 1 m depth in a 10-year time period.
- Most of the leaching took place in the first 2 to 3 years, which emphasizes the need to recover spill fluids as soon as possible after the spill event to limit the depth of leaching of salts and the volume of soil impacted.



 With this well maintained tile drainage system, EC and SAR in surface soil decreased and good crop growth was restored over much of the site within 10 years.

# 3.1.2 Spills 15 and 16: Peace Region Flare Pit Tile Drainage Installations

### 3.1.2.1 Background

Spills 15 and 16 were both flare pit remediation projects on agricultural land. Both sites had fine-textured soils. In 1998, salt impacted soils were excavated from the flare pits. Tile drains and leachate collection systems were then installed in the excavation pits; the excavated soil was mixed with gypsum amendments and replaced. Leachate was collected and disposed of only sporadically. The sites were not irrigated.

### 3.1.2.2 Results

At Spill 15, two soil samples were collected from the excavated soil piles in 1998, prior to construction of the tile system. In 2003, after the system had been in operation for 5 years, soil samples were collected to a maximum depth of 1.5 m (Table 2). At Spill 16, two composite samples were collected in 1998; soils were sampled again in 2003 at eight points, also after 5 years of operation, to a depth of 1.5 m (Table 2).

After 5 years, EC was lower in the leached soils at both sites compared to initial sampling results (Figure 3a). The decrease in EC was more pronounced for Spill 15 compared to Spill 16, but both had substantially lower EC values after 5 years of leaching at all depths. The EC decrease was not constant at all depths; however, possibly indicating insufficient water moving through the soil to remove salts entirely from the system, and/or inadequate removal of leachate.

At Spill 15, SAR was substantially lower at all depths to 1.5 m (Figure 3b) after 5 years of leaching. At Spill 16 however, SAR was higher after 5 years of leaching compared to the initial SAR at all depths. Assuming SAR data accurately reflects soil conditions, the apparent increase in SAR after leaching may reflect the relocation of sodium in the profile during leaching coupled with insufficient calcium amendments.



From the information available, it was not possible to determine the volume of salts actually removed from the system. The system appears to have been attended only sporadically over the 5-year period, and the 2003 soil monitoring event does not appear to have reached the maximum depth of impact at either site.

#### 3.1.2.3 Conclusions

- Tile drainage successfully decreased EC at both spills to 150 cm depth. SAR increased at one sampling location, likely due to insufficient calcium amendments applied during the leaching process.
- The data illustrate the importance of sufficient water leaching through the soil profile to remove salts completely from the system and to prevent salt accumulation within the profile.

# 3.1.3 Spill 7: East-Central Alberta Tile Drainage System

## 3.1.3.1 Background

Spill 7 was at a battery in an agricultural area that was decommissioned in 1999. At that time (1999), elevated levels of salts were found near the flare pit, which had been remediated by excavation and disposal. Soil and groundwater information indicated that produced water had impacted the aquifer.

Groundwater remediation and weeping tile systems were installed in 2000 to remediate remaining salts and to prevent offsite migration of the salt plume. The tile system covered an area of approximately  $4{,}000~\text{m}^2$ .

In 2003, the spill was flood irrigated to more actively leach salts from the treatment area and an automated leachate and groundwater recovery system was installed. Two tons (1.8 tonnes) of  $Ca(NO_3)_2$  and 10 tons (9.1 tonnes) of gypsum were applied and incorporated into the treatment area. Approximately 1,200 m³ of fresh water was applied to the treatment area over a 3 month period. A total of 284 m³ of leachate was collected and hauled offsite for disposal. Quantab testing indicated disposed water contained chloride ions at levels greater than 4,000 mg/L.



Soil samples were collected from seven locations within the impacted area in 1999 prior to tile installation; unfortunately, samples were not analyzed above 150 cm, limiting their usefulness to this study. The 1999 data were not included for that reason. Soils were sampled twice at two different locations within the tile-drained area in 2003, once before irrigating and once after irrigating, using similar depth increments (Table 3), providing an interesting comparison.

#### 3.1.3.2 Results

Results of the 2003 leaching differed between locations 1 and 2 within the tile-drained area, shown on Figures 4a to 4d. Note that the lowest depth of each increment was graphed. The EC at both locations decreased in the 0-15 cm depth increment after irrigation (Figure 4a). At location 1, post-irrigation EC increases with depth below 15 cm, and exceeds pre-irrigation EC between approximately 30 and 150 cm depth. At 200 cm depth, post-irrigation EC is lower than the pre-irrigation value at location 1. At location 2, post-irrigation EC values decreased to about 60 cm, then began to increase with depth. Post-irrigation values remained lower than pre-irrigation to almost 150 cm depth.

A deeper EC "bulge" (increase in EC values) below 100 cm at location 2 compared to location 1 indicates more effective leaching than at location 1, where the EC "bulge" occurred between 50 and 100 cm. This difference could be due to a number of factors including differences in soil texture and micro topography between the locations, which could affect the volume of water moving through the soil.

Post-irrigation SAR values (Figure 4b) at location 1 were substantially higher than pre-irrigation below about 15 cm to the depth of assessment (200 cm), peaking at about 75 cm. The magnitude of the increase in SAR at location 1 is difficult to explain, but could be due in part to analytical differences since the location 1 pre-irrigation samples were analyzed by a different laboratory than post-irrigation location 1 samples and all location 2 samples. Alternatively, some unknown differences in sampling or handling may have had an effect. At location 2, post-irrigation SAR was lower than pre-irrigation values to about 75 cm; below 75 cm post-irrigation SAR values were higher than pre-irrigation values.

Data for sodium and chloride mirror the SAR results (Figures 4c and 4d). At location 1, both sodium and chloride concentrations increase substantially between about 15 and 175 cm



depths, after irrigation compared to before,. At location 2, post-irrigation sodium and chloride concentrations are lower than pre-irrigation values to a depth of almost 100 cm.

This tile drainage system with a single irrigation event moved salts down the soil profile but was not particularly effective in removing salts from the system as a whole. The volume of leachate collected and disposed (284 m³) was relatively small compared to the volume of water used to irrigate the spill (1,200 m³), indicating that much of the water applied did not leach through the soil into the tile system. Post-irrigation data indicate that salts are accumulating at various depths within the soil profile.

#### 3.1.3.3 Conclusions

- Salts move down the soil profile with the application of irrigation water, but the amount of salts and the depths to which they will leach can vary widely within a single, relatively homogeneous spill area.
- The depth at which salts will concentrate in a soil profile will depend on the volume of water available to move through the soil profile. If insufficient water is available to move salts through the profile and into the tile drainage system below, salts will accumulate higher in the soil profile. Differences in soil texture, structure, bulk density and even microtopography can affect the rate of salt leaching and the depth at which salts will accumulate in the soil at a given site.

# 3.1.4 Spill 2: Northeast of Edmonton Soil Washing Site

### 3.1.4.1 Background

At Spill 2, located northeast of Edmonton, soil washing was used to treat salt-impacted soils excavated from a flare pit as part of a remediation program. Approximately 3,500 m³ impacted soil material was placed into two lined wash pits, one constructed in the former flare pit, and a second adjacent to the flare pit. A wash water collection system was constructed which drained to an interception trench.



Soils were washed using surface water pumped from a nearby slough; soils and water in the pits were mixed three times and allowed to settle. Fluids were then pumped off and disposed down hole. Washing took place twice, once in July 1999 and again in July 2000. The washing process was reported to be slow and labour intensive. Gypsum and Ca(NO<sub>3</sub>)<sub>2</sub> amendments were added together and incorporated into the soil in the pits using a backhoe, after the second washing event in October 2000. In all, 11,000 kg gypsum and 1,150 kg Ca(NO<sub>3</sub>)<sub>2</sub> were mixed into soils in the pits.

Spill delineation information provided for this site indicated that soils in the spill-impacted area likely had EC values between 10 and 36 dS/m and SAR values between 20 and 90 prior to remediation. Analytical data for the soils actually placed into the washing pits were not available. Soils in the pits were monitored for salinity parameters after each washing event and after the amendments were added.

### 3.1.4.2 Results

Assuming starting EC values between 10 and 36 dS/m, the bulk of the decrease in EC likely occurred with the first washing event; EC after the first wash averaged 4.5 dS/m (Figure 5a; Table 4). After the second wash, soil sample EC values decreased from the first wash average of 4.5 dS/m to an average of 3.3 dS/m. Soil washing apparently resulted in a substantial decrease in EC, with values less than 5 dS/m after two wash events. However, EC after the addition of amendments was higher than values after the two washing events, averaging 8.9 dS/m.

The first soil washing event lowered soil SAR values to 26.2 and 19.4 in Pits 1 and 2, respectively (Table 4), from assumed initial SAR values ranging between 20 and 90. After the second soil washing event, SAR decreased further, but values remained relatively high, an average of 23.6 in Pit 1 and 9.5 in Pit 2. Gypsum and Ca(NO<sub>3</sub>)<sub>2</sub> amendments added after the second wash resulted in a further decrease in SAR to 9 in Pit 1 and 7.3 in Pit 2.

Amendments added after the second washing event resulted in a decrease in SAR as expected. However, from the data presented, amendment addition appears to have increased EC to levels higher than before washing, compromising remediation success. Changes in both sodium and chloride (Figure 5b) show the same trends as EC; a decrease between the two washing events



but an increase after amendment additions close to or higher than levels measured after the first washing event. There is no clear explanation for the increase in sodium and chloride after amendment additions, since neither was reported as having been added. Theoretically, an increase in sodium could have occurred as added calcium replaced sodium on the soil exchange complex. However, the increase in chloride cannot be explained in this way. It is possible that the single samples collected from each pit after amendment addition did not adequately reflect variability in the amended soil.

### 3.1.4.3 Conclusions

- Soil washing effectively reduced EC to near guideline levels, with by far the biggest reduction occurring in the first washing.
- Soil washing was less effective at reducing SAR than EC. Calcium amendments added after washing effectively further lowered SAR values, but the effect of the amendments on soil EC is not clear from the data for this site.

# 3.1.5 Engineered Sites - Summary

Well maintained tile drainage systems with adequate calcium amendments and sufficient water for leaching are effective in remediating soil EC and SAR to levels at which good crop growth can be restored within 10 years. Without sufficient calcium amendments however, SAR remains high or may increase in some parts of the soil profile with leaching. If insufficient leaching water moves through the soil, salts can accumulate within the soil profile, never reaching the underlying tile drainage system. However, even within a relatively small area, leaching success can vary widely, depending on various soil factors and micro topography. The key to successful leaching with a tile system would appear to be careful maintenance, adequate volumes of water applied to the site as irrigation, rainfall or collected runoff, timely removal of leachate and judicious application of calcium amendments.

Soil washing effectively speeded up the leaching process, reducing EC values to near guideline levels within two wash events. SAR was reduced but remained high after leaching, requiring the addition of calcium amendments. The effects of calcium amendments on soil EC was not clear from the data presented.



#### 3.2 Passive Sites

Data from 30 passively remediated spills were considered useful to this study. Of these, 20 spills were located in east-central Alberta, four were located in central Alberta, five were located in southeast Saskatchewan and one was located in the Peace region. Passively remediated spills ranged in age from 2 to 15 years from the spill date to the date of the most recent data available. Because not all spills were monitored immediately after the spill event, monitoring periods ranged from 2 to 9 years. Summary sheets with site and spill information as well as pertinent soil analytical data are presented in Appendix A. Data are summarized in Table 5.

Of the 30 passively remediated spills, most recent monitoring data indicated that:

- Topsoil EC decreased at 27 spills (90%) between the first and the last monitoring event; of those, 11 spills (41%) approached EC of 5 dS/m or less in the most recent monitoring event. Subsoil EC decreased at 17 of the 18 spills (94%) that had subsoil data; of those 6 spills (33%) approached EC of 5 dS/m or less in the most recent monitoring event.
- Topsoil SAR decreased at 28 of the 30 (93%) spills between the first and last monitoring event; of those, 11 spills (about 40%) approached SAR 8 or less in the most recent monitoring event. Subsoil SAR decreased at 15 of 18 spills (83%), with four of 18 (22%) approaching SAR 8 or less in the most recent monitoring event.

Spills which approached acceptable topsoil EC and SAR levels at the end of the monitoring period tended to be older spills, 5 to 11 years in age.

The EC and/or SAR increased over the monitoring period at seven of the 30 spills (23%). Net increases over time may have resulted from high or fluctuating water tables, or because the spill was located in a groundwater discharge area. Increases may also be a result of critical differences in sampling locations between years.



#### 3.3 Influence of Climate

Passive leaching depends on water from precipitation (P) infiltrating through the soil. However, to estimate the amount of precipitation potentially available to leach salts through the soil profile, evapotranspiration (ET), defined as the amount of water estimated to move from the soil-plant surfaces to the atmosphere, must be taken into consideration along with precipitation. Based on information available from Alberta Environmental Protection, (Bothe and Abraham, 1987 and 1993) the average areal ET for the Alberta spills in this study are presented in the following table. No equivalent data were available for the Saskatchewan spill area.

Region	Average Areal Evapotranspiration (ET)	Average Precipitation (P)	P-ET	Station Used
East- Central Alberta	401 mm	401 mm	0 mm	Coronation
Central Alberta	419 mm	482 mm	63 mm	Edmonton International Airport
Peace Region	321 mm	471 mm	150 mm	Fairview

Subtracting ET from average precipitation (P) gives a theoretical estimate of the amount of precipitation in an area that might be available to leach salts through the soil in an average year. For the passive spills examined in this study, the amount of water theoretically available for leaching (P-ET) varied from 0 mm in east-central Alberta to 150 mm in the Peace region; this suggests that spills in the Peace region should remediate faster than spills in eastern Alberta, when non-irrigated systems are used. Unfortunately, the data set in this study did not provide sufficient information to determine if a difference does in fact exist.

Other factors will also influence water availability for leaching. Depending on the slope and microtopography of the spill site, a substantial proportion of water potentially available for leaching may be lost in spring runoff. In relatively level landscapes, microtopography becomes particularly important in determining how much water will runoff the site and how much will be



available to leach into the soil. Vegetation transpiration rates will also affect the volume of water leaching through the soil. Any efforts to encourage leaching through the soil by trapping snow or holding water on a spill site will be beneficial to the passive remediation process.

## 3.4 Influence of Topography

Three spills (Spills 20, 21 and 22) all located in east-central Alberta, provided soil monitoring data for different slope positions (Table 6).

At Spill 20, soils were monitored at seven locations down a complex slope. Initial (2000) EC and SAR values varied widely between slope positions and depth increments, with no apparent relationships between the two. Four years after the spill, EC and SAR values and the variability between all slope positions were greatly reduced in the 0-15 cm depth increment (Figures 6a and 6b). After 4 years of leaching, EC values approached 5 dS/m in all slope positions. SAR remained over 10 after leaching at all upper to mid slope positions. Chloride concentrations in the 0-15 cm depth were less than about 200 mg/kg at all slope positions except the break site and upper slope position (Figure 6c) after 4 years of leaching.

In subsoil (60-100 cm) at Spill 20, EC decreased substantially after 4 years of leaching at all points assessed down the slope except at the break point and one mid slope point (Figure 6d). Subsoil SAR in the mid to lower slope positions was higher 4 years after the spill compared to before, possibly indicating inadequate calcium soil amendments at these location, or insufficient time for amendments to move through the soil (Figure 6e). Like EC, subsoil chloride concentrations remained elevated in 2004 at the break point and at one mid-slope location (Figure 6f).

At Spill 21, soils were monitored to a depth of 200 cm at mid-slope and lower slope positions in 2000 soon after the spill occurred, and again in 2004 (Figures 7a to 7c; Table 6). EC and chloride concentrations showed similar trends; 2004 values in topsoil are relatively low, indicating effective leaching of salts in surface soil at both slope positions. However, at the lower slope position, both EC levels and chloride concentrations have a "bulge" between 50 and 100 cm depth, indicating less effective leaching at the lower slope position compared to the mid-slope. SAR decreased in all slope positions after 4 years of leaching.



At Spill 22, soils were monitored to a depth of 100 cm, at upper, mid and lower slope positions in 2000 and again in 2004 (Figures 8a to 8c; Table 6). Trends were similar for EC, SAR and chloride concentrations. At the upper slope position (closest to the break point), EC, SAR and chloride concentration were lower after leaching in 2004 compared to 2000 to at least 100 cm depth. At the mid-slope position, these parameters were lower after leaching compared to before, to about 50 cm depth. At the lower slope position, EC, SAR and chloride concentrations at 100 cm depth were slightly higher after leaching in 2004 compared to before.

In summary, salts at lower slope positions tended to leach less deeply than those at upper and mid slopes after 4 years of leaching, resulting in increased EC and SAR values in the subsoil. The influence on leaching of higher water tables at lower slope positions may be a factor. In some cases, SAR remained relatively high after EC and chloride concentrations had been substantially reduced, possibly due to inadequate calcium amendment or insufficient time for amendments to move through the soil.

# 3.5 Effects of Soil Types

Very few of the spills included in this study had basic soils information such as soil texture or soil classification included with the salinity data. As a result, it was not possible to draw any conclusions regarding the effects of soil type on leaching from the data set.

#### 3.6 Effects of Time

Few of the spill data sets included soil salinity monitoring data starting soon after the spill event. Where such data does exist (for example Spills 6 and 19; Figures 9a and 9b), it points to a rapid decrease in EC and SAR within the first 2 to 3 years of leaching after the spill event. At both spills, leaching proceeded after the first 2 years at a much slower pace, but continued for more than 10 years.

Data collected regularly over more than 10 years were available for two spills: Spill 19, a passively remediated spill and Spill 6 a spill remediated with a tile drainage system. A comparison of the two data sets shows very different trends over multiple years. Figure 9a shows changes in surface soil EC (0-15 cm depth) over time at both spills. Surface soil EC decreased much more rapidly in the first 10 years of leaching at the tile-drained site compared



to the passively drained site. Even after 15 years of leaching, surface soil EC at the passive site remained much higher than at the tile-drained site. The best-fit trendline for the passively remediated spill was a logarithmic function; the best-fit trendline for the tile-drained spill proved to be a power function, both shown on Figure 9a. Both had R<sup>2</sup> values greater than 0.9.

Surface soil SAR at the passively remediated site decreased somewhat during the first 2 years of leaching, but remained relatively steady after that; even after 15 years or leaching the SAR value was not much lower than the SAR value after only 2 years of leaching. Surface soil SAR in the tile-drained system on the other hand, decreased very rapidly in the first 2 years of leaching, then continued to decrease at a slower but fairly consistent rate to 11 years.

It is difficult to determine exactly how much of the differences noted between these two spills are due to differences between the two leaching systems, passive-compared to tile-drained. Salts at the tile-drained spill leached faster than at the passive spill. The tile-drained spill was more closely managed over its 10 year history than the passively drained site, with additions of amendments as required, and occasional irrigation, which likely would have enhanced leaching rates with or without tile drainage. Other factors such as differences in climate, soil texture, precipitation and microtopography may also have affected rates of leaching at these two sites.

It is not possible to draw firm conclusions regarding salt leaching rates at tile-drained sites compared to passively drained sites from these two data sets alone. However, at these sites leaching is proceeding at a substantially faster rate at the tile-drained site compared to the passive site.

At Spill 42, soils were monitored to a depth of over 14 m, 10 years after the spill occurred. Information supplied identified soils at the site as silt and clay till from surface to approximately 5 m, and sand (or sandy) from approximately 5 m to the maximum depth of evaluation.

Results showed a dramatic decrease in surface soil EC and SAR after 10 years of leaching. A distinct "bulge" in EC, SAR, sodium and chloride occurred around the 0.75 m sample depth, decreasing rapidly by the 3.75 m sample depth (Figures 10a and 10b; Table 7). Deeper in the soil profile, chloride concentrations greater than 400 mg/L and sodium concentrations greater than 100 mg/L occurred to 10.5 m depth. EC values greater than 5 dS/m occurred to about 5 m



depth, and SAR values greater than 8 occurred to about 4 m depth. At present, salts appear to be moving down the soil profile at a rate of between 0.5 and 1 m per year.

Sulphate apparently applied as gypsum to the surface shows no "bulge" after 10 years of leaching and approaches background levels by the 3.75 m sample. Differences between parameters in depth of leaching after 10 years likely relates to relative solubilities of the salts in question.

Trendlines applied to EC, SAR, sodium, chloride and sulphate data collected to nearly 15 m depth after 10 years of leaching, show very good fits to a logarithmic function, with  $R^2$  values greater than 0.9 in both cases (Figures 10a and 10b). However, sulphate shows a relatively poor fit to a logarithmic function ( $R^2 = 0.37$ ), but a much better fit to an exponential function (shown on Figure 10b) with an  $R^2$  value of 0.86. The lower solubility of gypsum compared to sodium chloride likely accounts for this difference.

## 3.7 Effects of Remediation History

Most spills supplied for this study did not have complete remediation histories accompanying soil salinity monitoring data. Details of amendment application timing and rates were frequently missing, as were details of source removal. However, the review of available information indicates that calcium amendments, mainly gypsum and Ca(NO<sub>3</sub>)<sub>2</sub>, were very widely used for spill remediation. Some reports stated, for example, that amendments were applied "as required" or recommended specific rates and types of amendments, without indicating whether or not these rates were actually applied to the spill. As a result, it was not possible to gain any insight into optimal rates or timing of the application of amendments from this information.

The potential importance of calcium-based amendments to the leaching process, when added in sufficient quantities, was illustrated in data from several spills (for example Spills 7 and 16), where subsoil SAR was higher after leaching compared to before, but not subsoil EC. This was attributed to insufficient calcium amendments and/or lack of time for amendments to move through the soil profile.



At a number of spills, gypsum amendments were surprisingly effective in moving through the soil profile, despite gypsum's relatively low solubility. At Spill 6 for example, the decrease in calcium concentration 11 years after initial application relative to 1 year after initial application illustrates this point (Figure 2d). At Spill 21, after 4 years of remediation, sulphate concentration was highest in the 60-100 cm depth increment (Figure 11); below 1.0 m, sulphate levels decreased rapidly, but remain higher than pre-remediation levels to 2.0 m, indicating sulphate had moved through the soil profile at least to that depth. Because calcium can occur naturally in soils, especially at depth, it is difficult to track movement of applied calcium through the soil profile without sufficient comparable background data.

At Site 42, the lower solubility of gypsum compared to sodium chloride was apparent in the different data trends between sulphate and chloride concentrations with depth. The slower rate of movement of calcium from gypsum through the soil compared to sodium chloride can result in a situation where SAR can increase in subsoil as leaching of gypsum lags behind the leaching of sodium chloride salts.

### 3.8 Estimated Relative Costs

Detailed information on the costs of various leaching technologies was generally lacking in the files available to the study. Based on Matrix Solution's experience, approximate costs to remediate a spill passively and with a tile drainage system were estimated (2005 prices).

Approximate costs to passively remediate a 1 ha spill, excluding amendment delivery costs, equipment travel time and consulting fees:

- Gypsum (20 tonnes/ha) = 20 tonnes × \$265/tonne = \$5,300
- $Ca(NO_3)_2$  (400 kg/ha) = 400 kg × \$0.6/kg = \$240
- Spreading and incorporation of amendments by disc or rotospic = \$3,300/ha
- Total: \$8,850 for a one-time application of amendments not including amendment delivery costs, equipment travel time and consulting fees



Since passive remediation is frequently used in conjunction with source removal, costs involved in excavating, landfilling and replacing impacted soil would also need to be included. Ongoing costs for a passively remediated spill include soil and vegetation monitoring every few years to monitor remediation success and to determine if more amendments are required, additional amendment application costs if required, and ongoing lease payments to the landowner.

Approximate costs to install and maintain a 1 ha tile drainage system, excluding amendment delivery costs, equipment travel time and consulting fees:

- Installation of tiles \$25,000 for tiles ploughed in to a 1.5 m depth with a 5 m spacing.
   Installation costs could go up to \$40,000/ha if tiles need to be installed in trenches below
   1.5 m, or if the tile spacing must be reduced substantially.
- Cost for amendments is the same as for a passive spill (approximately \$8,850/ha).

Ongoing expenses for the system include:

- Hauling of leachate \$80 to \$120/hour depending location and availability of trucks and truck capacity (10 to 12 m³ capacity truck).
- Disposal of leachate \$25 to \$35/m³ (downhole disposal).

Regular monitoring of soil and groundwater is recommended for tile drainage systems.

Passive remediation is less expensive than remediation with tile drains. However, tile drainage systems are appropriate for large spills where salts need to be removed from the system to prevent impact to groundwater quality, quality of nearby soils, or other receptors.

#### 4.0 CONCLUSIONS

 Leaching can move salts downward very rapidly, particularly in the first several years after the spill, but this is not true for all spills. Many of the factors that appear to affect the rate of leaching are site specific, such as soil texture, topography, slope position and groundwater



conditions. However, there is evidence that tile drainage may enhance the rate of salt leaching, particularly if the system is well maintained. Both engineered and passive systems can be effective in remediating salt spills and restoring good crop growth. However, passive leaching was not effective in removing salts from the topsoil at all spills. At about 10% of the passively remediated spills, EC and SAR increased between monitoring events. These spills may be located in groundwater discharge situations, have high water tables, or sampling may not have been consistent between monitoring events.

- Salts originating from produced water spills can move through the soil profile to a depth of 5 m or more within 10 years in permeable soil.
- Calcium amendments appear to be very important to the leaching process. Gypsum worked
  into the soil surface as an amendment can leach effectively through the soil profile to a
  depth of 1.0 m or more within 10 years, despite its low solubility. However, slower leaching
  of gypsum compared to much more soluble sodium chloride can result in an increase in
  subsoil SAR, at least in the short-term.
- Sufficient water is needed to flush salts out of the root zone or into tile drains. Otherwise
  salts can accumulate in subsoil as a "bulge" in EC and/or SAR values. If leaching water is
  insufficient, additional time may not help move the salt "bulge" deeper into the soil profile.
- Data were insufficient to determine the effectiveness of tile drainage systems in removing salt mass from the soil/groundwater system.

## 5.0 RECOMMENDATIONS FOR SPILL MONITORING

This study highlighted the need for soil monitoring of a complete and consistent set of parameters, in consistent locations and depths, extending the complete depth of impact, and conducted at regular time intervals throughout the spill remediation process. Of the spills used in the study, adequate historical spill and site information documentation, including documentation of amendments and other remedial efforts was often lacking. Records of volumes and salt content of water removed from tile drains were often incomplete, so that the salt mass balance could not be assessed. Soil salinity analytical data including chloride and



sulphate anion concentrations were available for almost all of the spills, but other potentially useful parameters like cation exchange capacity, bulk density and soil texture were rarely available.

Sampling protocols and sampling locations frequently differed significantly between monitoring events, preventing meaningful comparisons. Very few of the data sets had accompanying vegetation data so that conclusions regarding the effects of salt levels on crop productivity could not be drawn. Similarly, few spills with soil monitoring data also had groundwater monitoring data so that the interactions between the two could not be examined. Data monitoring the salt levels in soils below tile drains were not available for any tile-drained site, so the effectiveness of tile drains at removing salts from the whole soil/groundwater system could not be evaluated.

The following guidelines for monitoring spills are recommended:

- Record spill information such as volume of spill, type of fluid spilled, whether the spill was surface or subsurface, and initial containment and recovery work completed. Record all initial clean-up and remediation measures implemented including dates, types and rates of amendment applications.
- Record spill site information such as the spill break point, its slope position, slope gradient, surface drainage direction, and vegetation types and quality, and location of any nearby surface water bodies.
- As soon as possible after completion of initial remediation measures, collect soil samples from the spill area and one or more background locations. Sample both surface soil and subsoil, since plant roots can extend to 1.5 m or deeper. Make sure that the same depths are sampled both on and off the spill to allow a valid comparison. At a minimum, analyze samples for pH, EC, SAR, cations, and chloride and sulphate anions all by the saturated paste method, and particle size analysis (soil texture) by the hydrometer method. Sample below the depth of impact to fully delineate the spill, followed by adequately sealing and grouting boreholes or wells to prevent migration of salts into previously unimpacted soil layers or groundwater.



- Ensure that sampling locations are accurately marked on a map drawn to scale, or with a GPS unit capable of ±1 m accuracy. Remember that the most common property of all soils is their variability; the effectiveness of any monitoring program will depend on the ability to collect soil samples from the same spot at each monitoring event and from the same depth increments. Normally background locations need to be sampled only once, unless monitoring has been carried out for more than 10+ years, since natural salts also can change over time.
- Collect vegetation data such as plant species, plant height, density, % cover or yield, from each sample location, including the background location, during each monitoring event.
   Vegetation data can be collected easily to provide a quick assessment of remediation progress.
- Soils do not normally need to be monitored each year. However, since the effectiveness of
  a remediation program depends on adequate and timely calcium amendments, it is wise to
  sample soils every 2 or 3 years, or if remediation problems become apparent in vegetation.
  Record dates, types and rates of any amendments applied.
- If a tile drainage system is being installed, ensure that tile drains can be located easily prior to soil sampling. Make sure soils are sampled periodically below the depth of tile installation to ascertain the potential salt concentration that is below the tile drain system and a potential source to groundwater. Salts below the tile drains may pre-exist the installation of the tile drain or/and be the result of salts bypassing the collection system. Keep a running record of water removed from the system and its chemical analysis.



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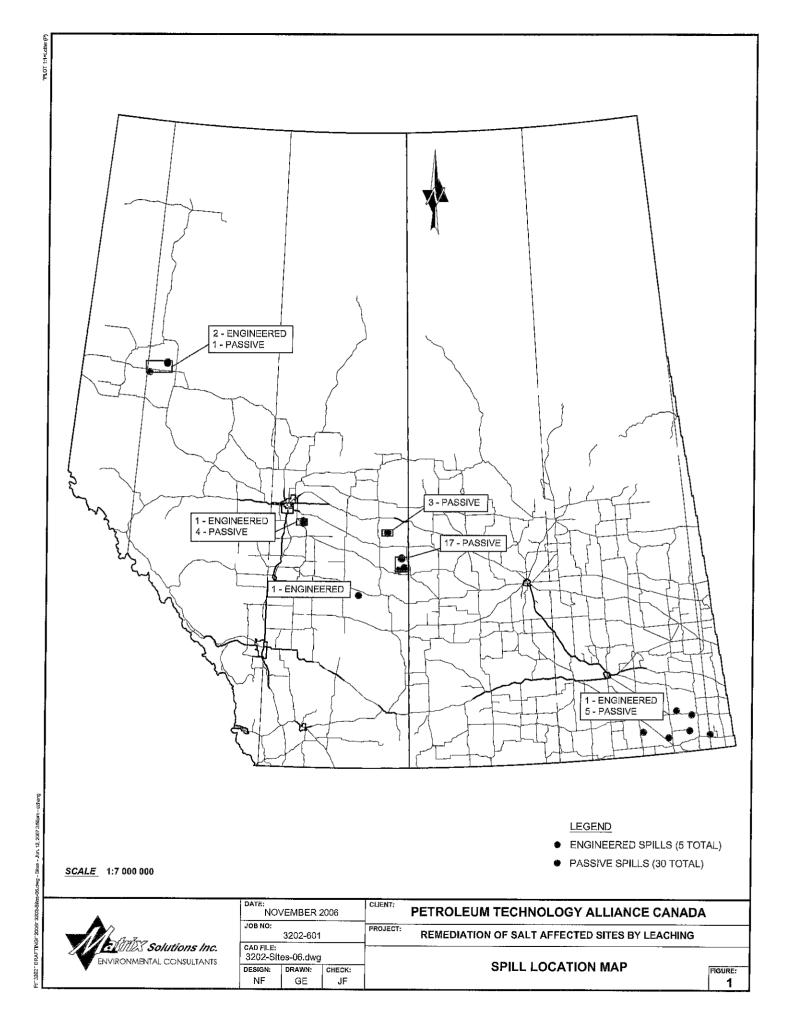
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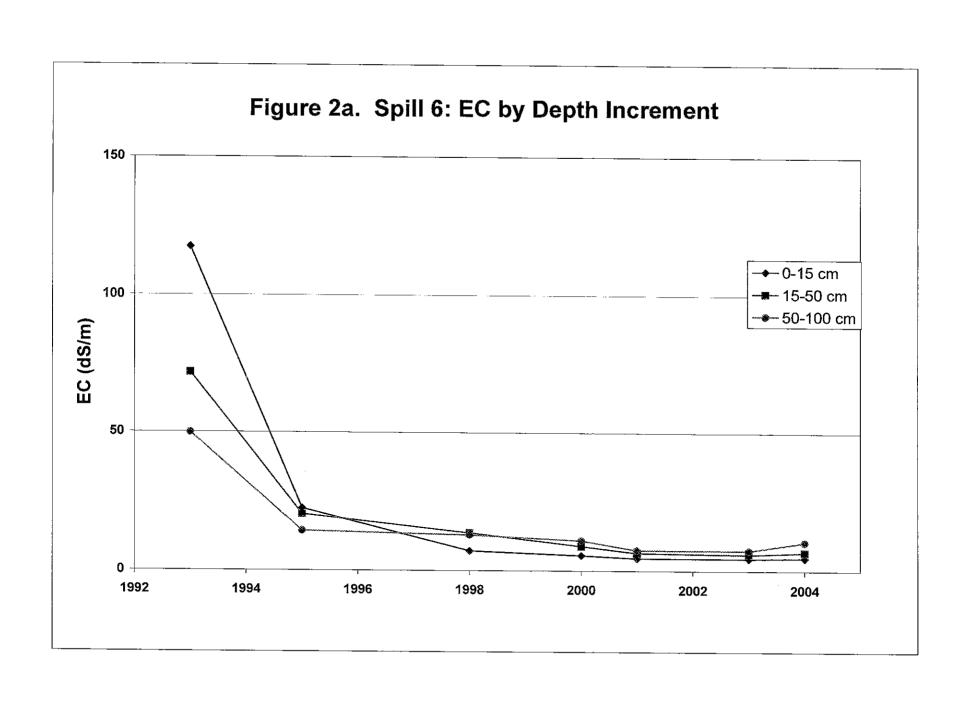
#### 7.0 LIMITATIONS

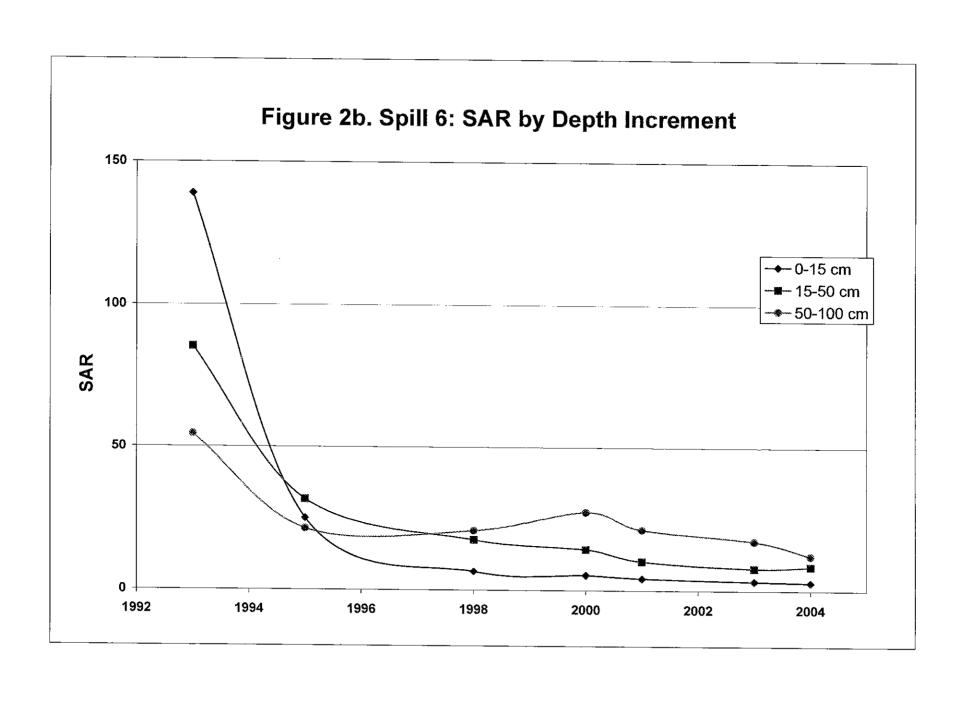
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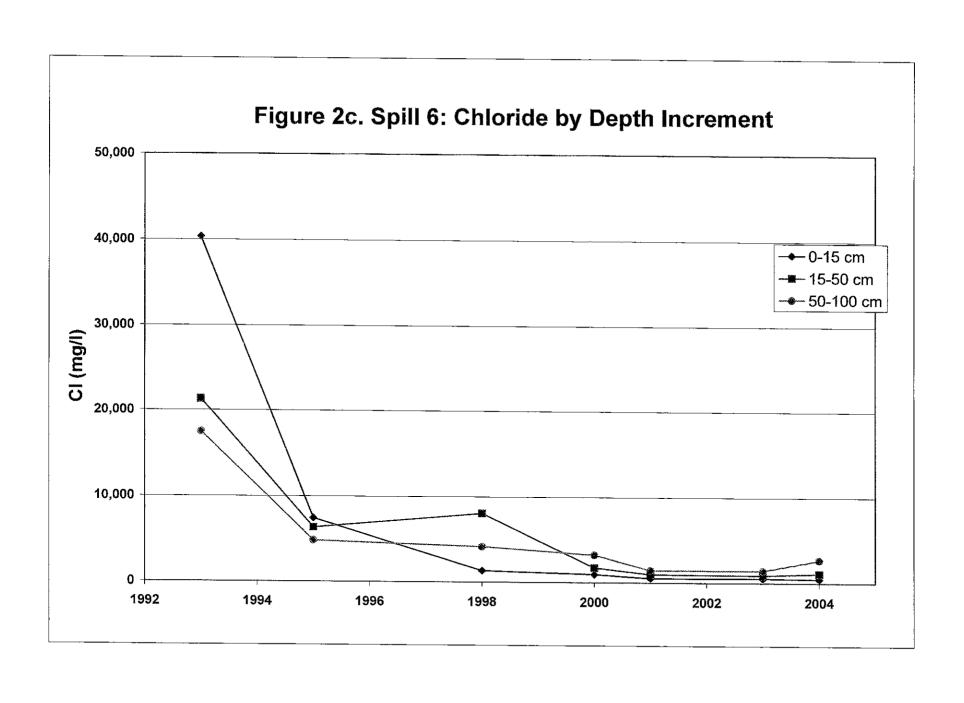
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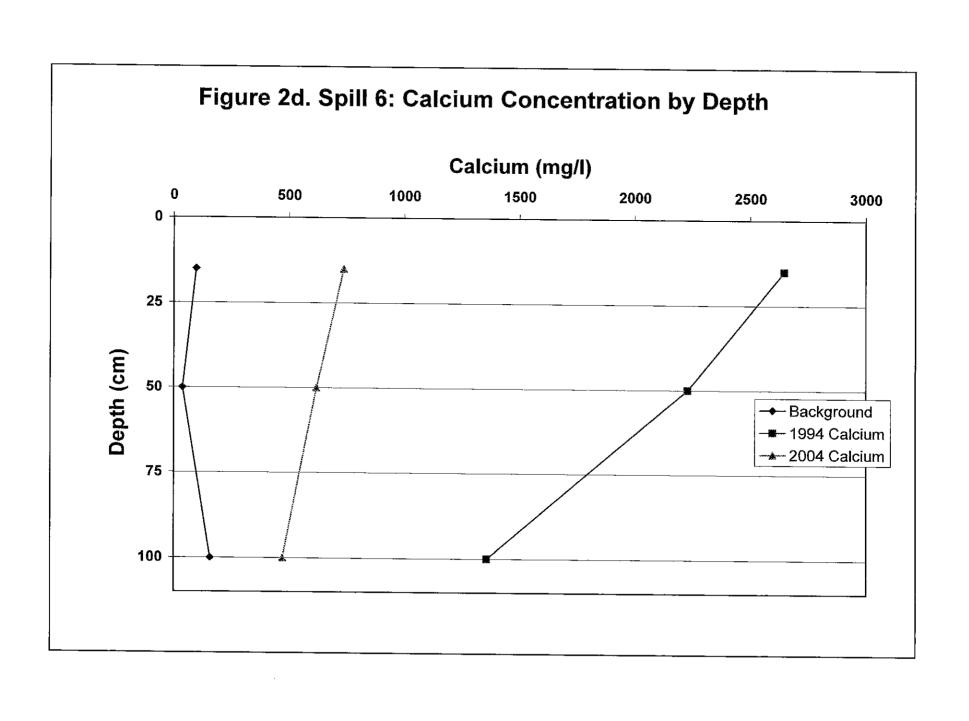


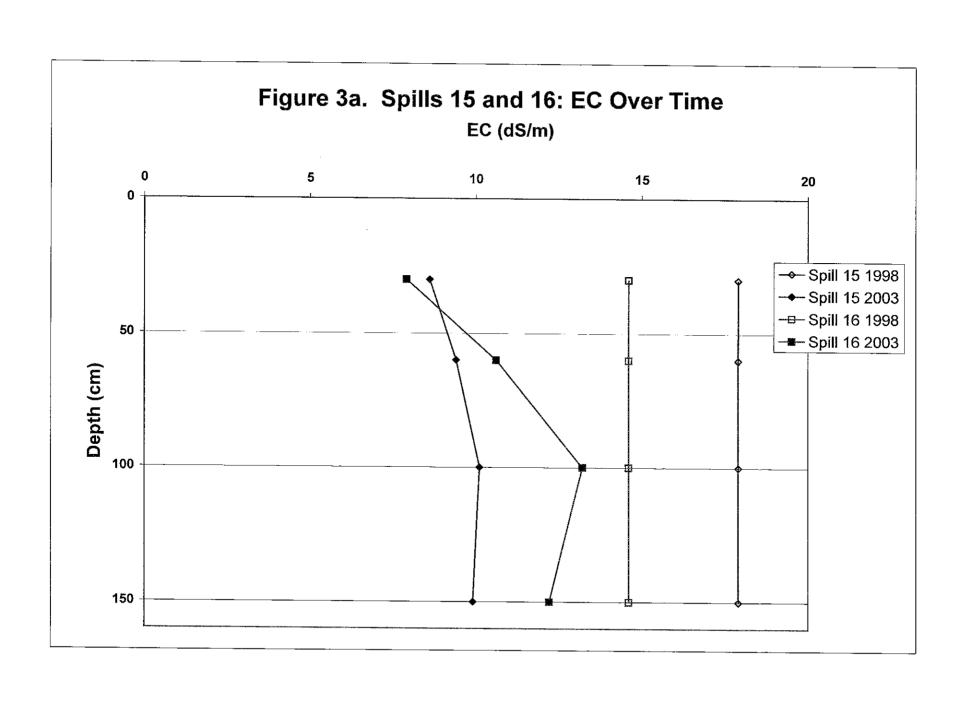


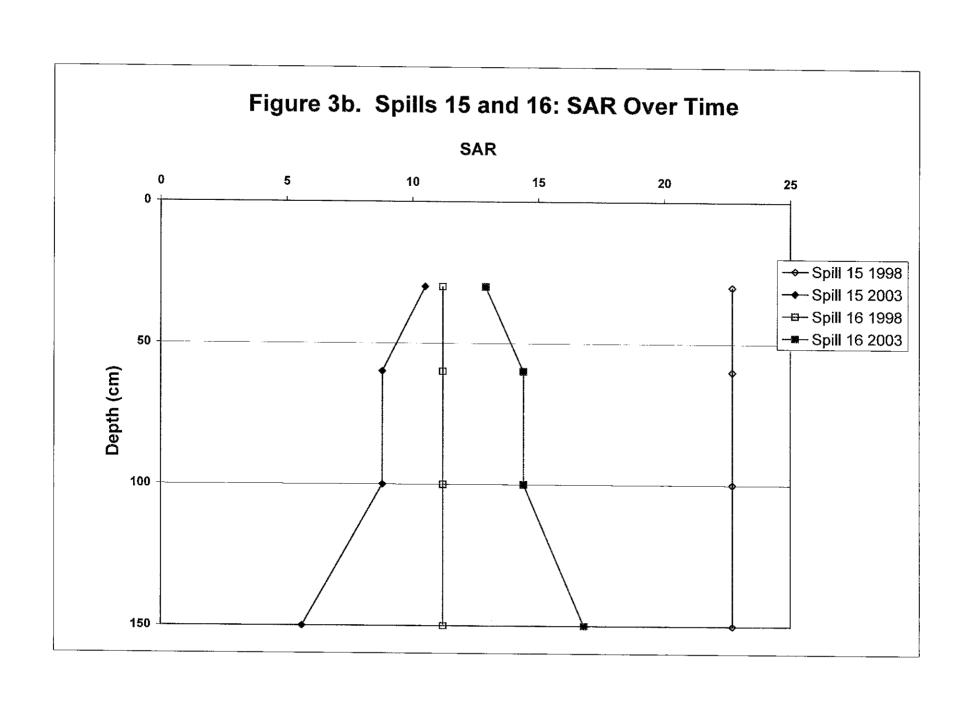


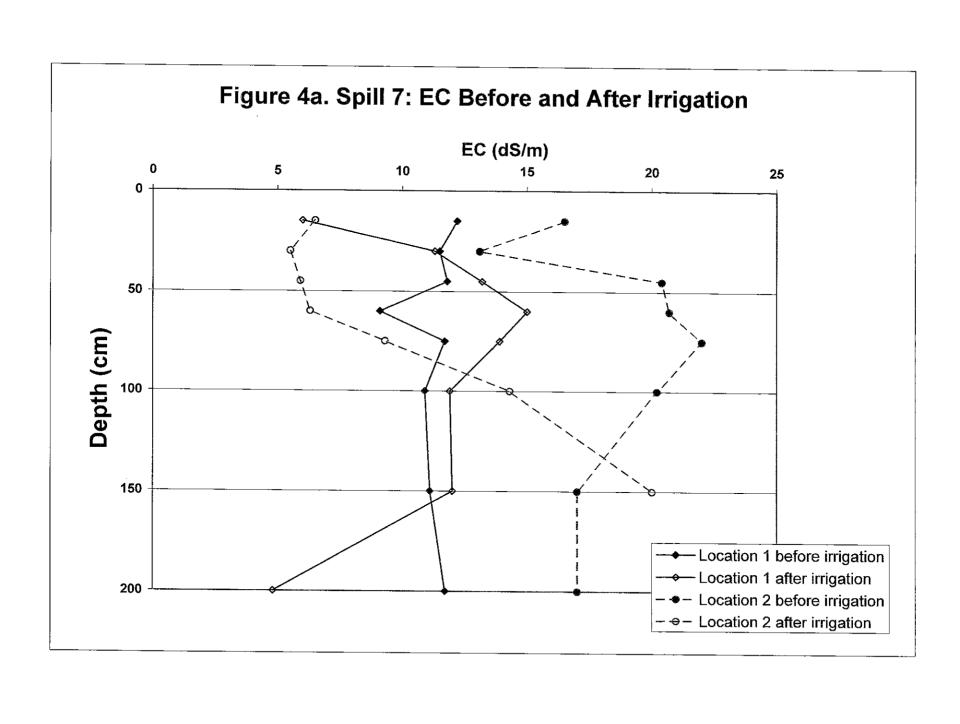


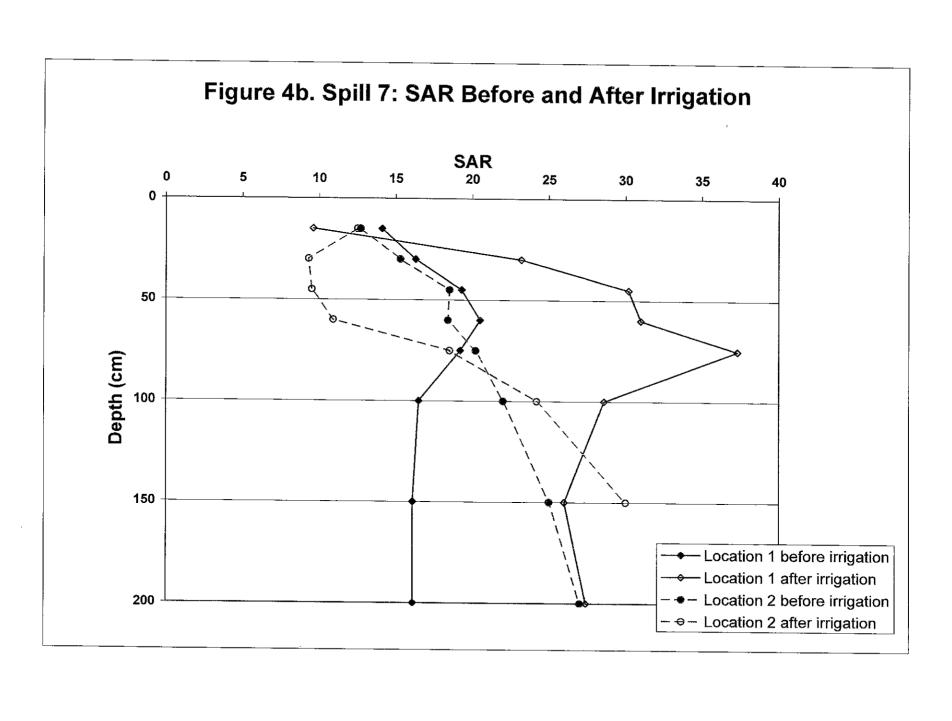


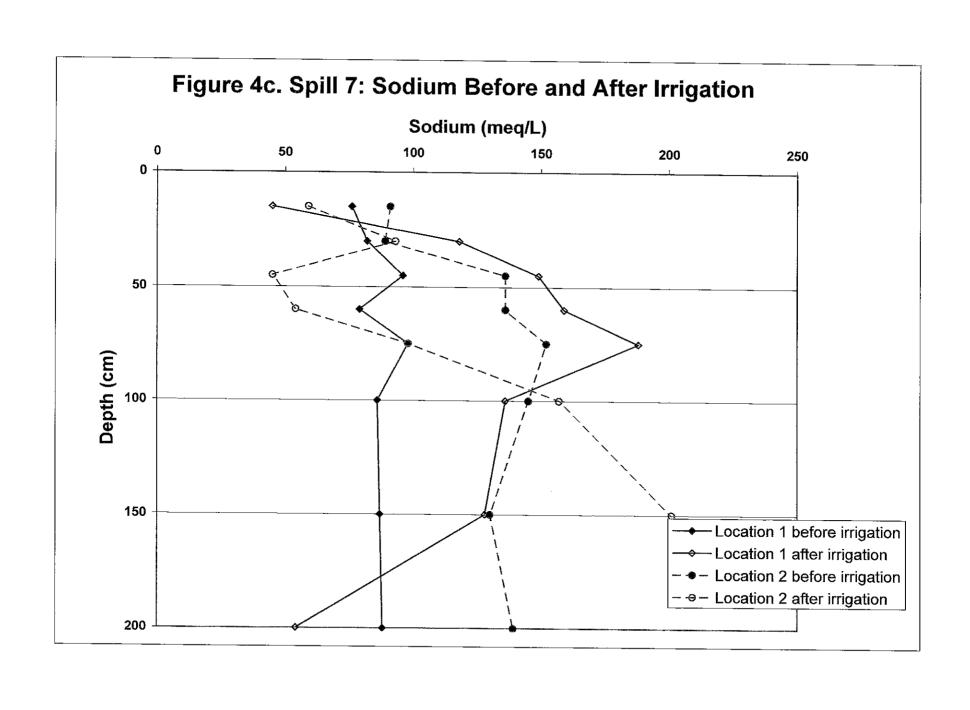


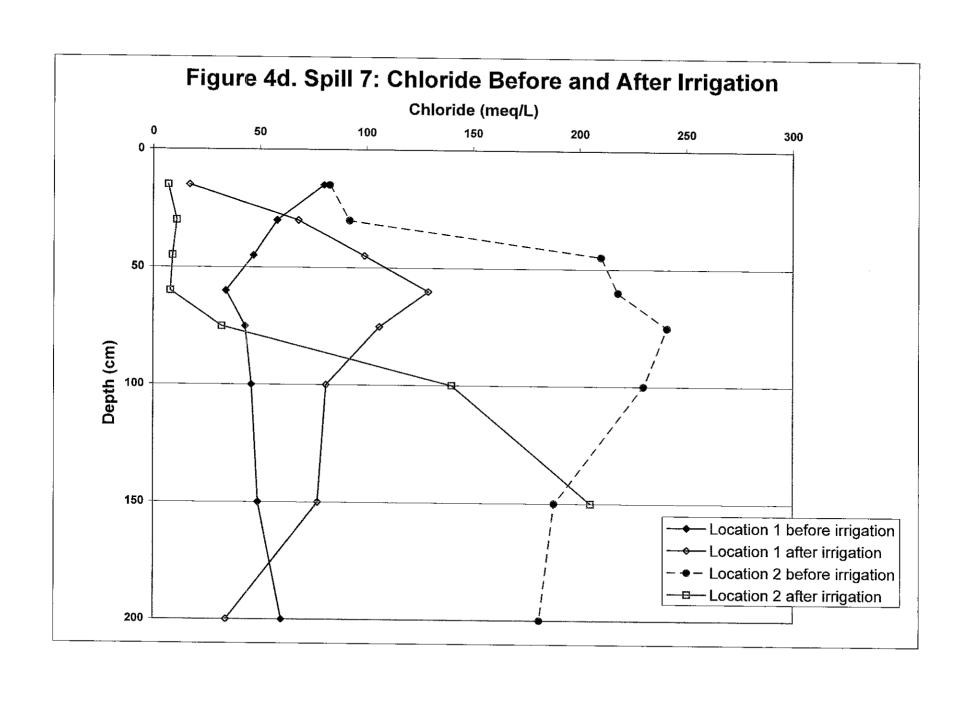


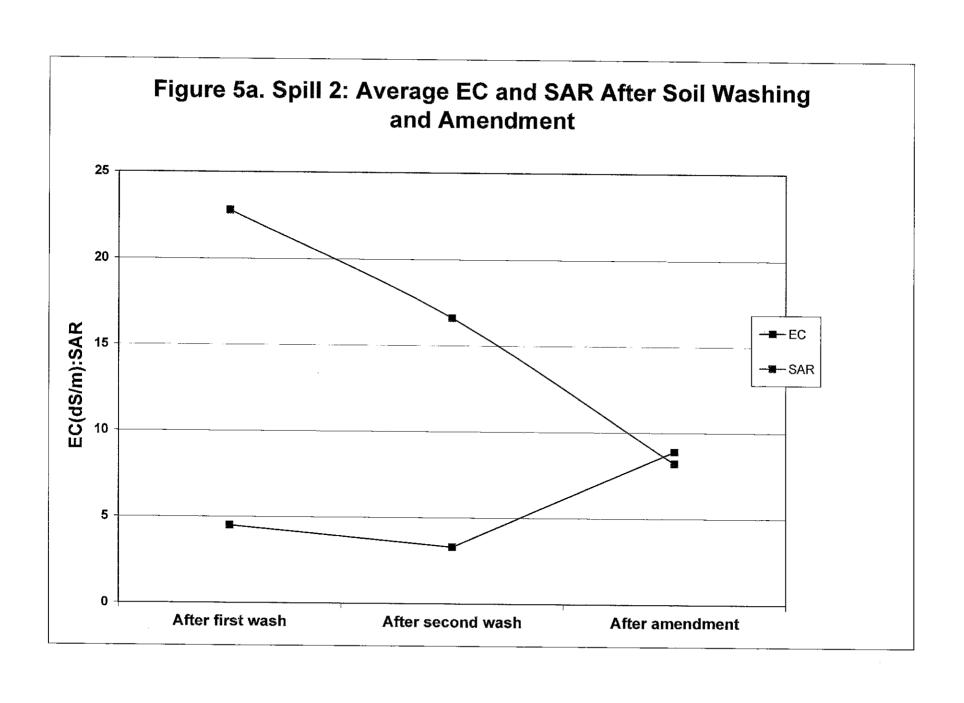


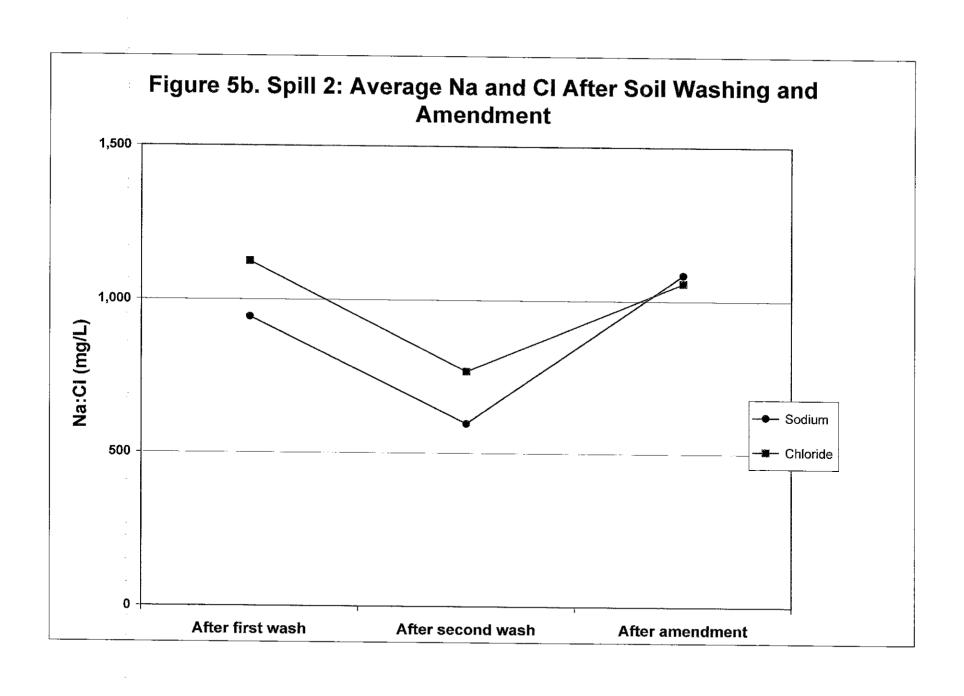


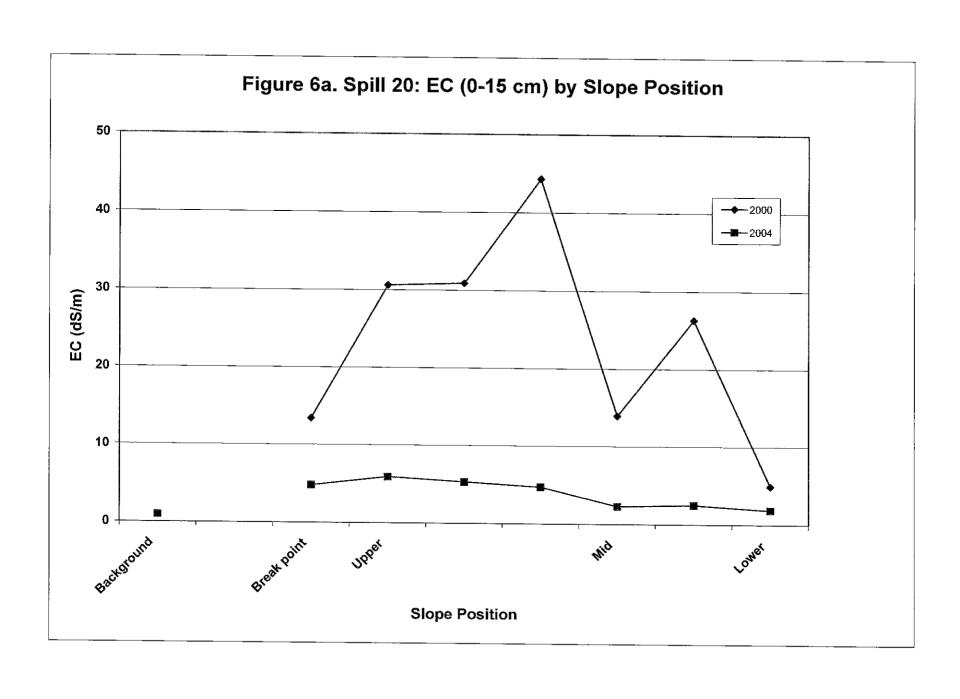


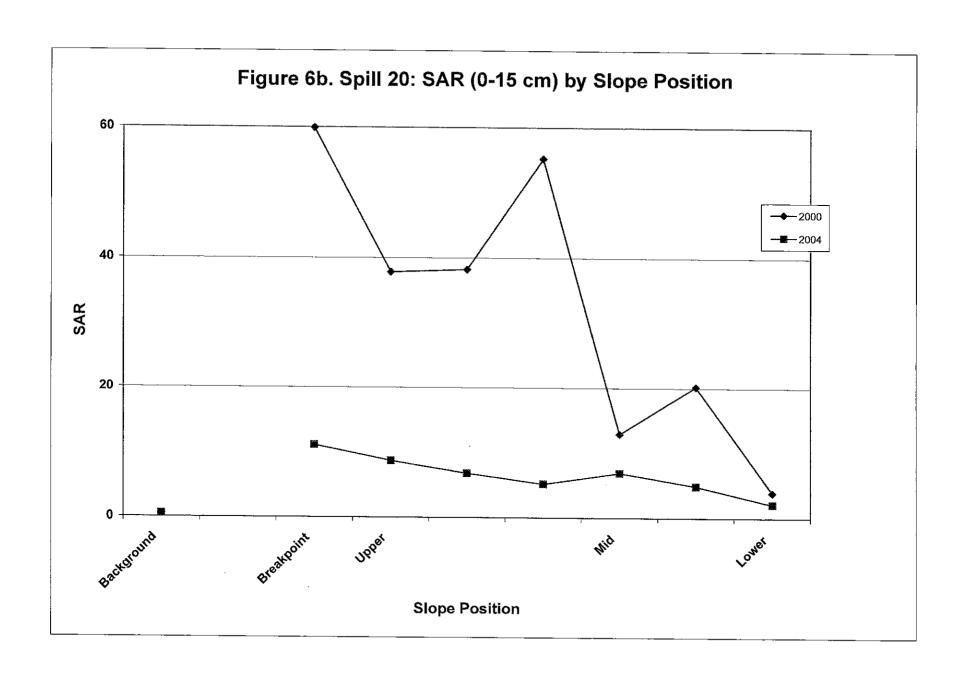


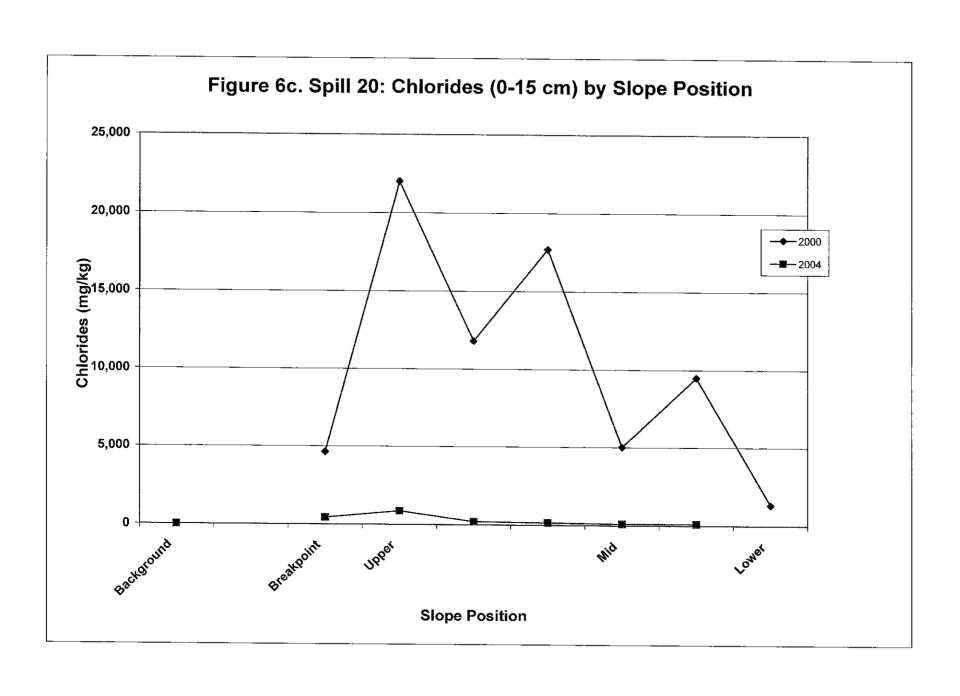


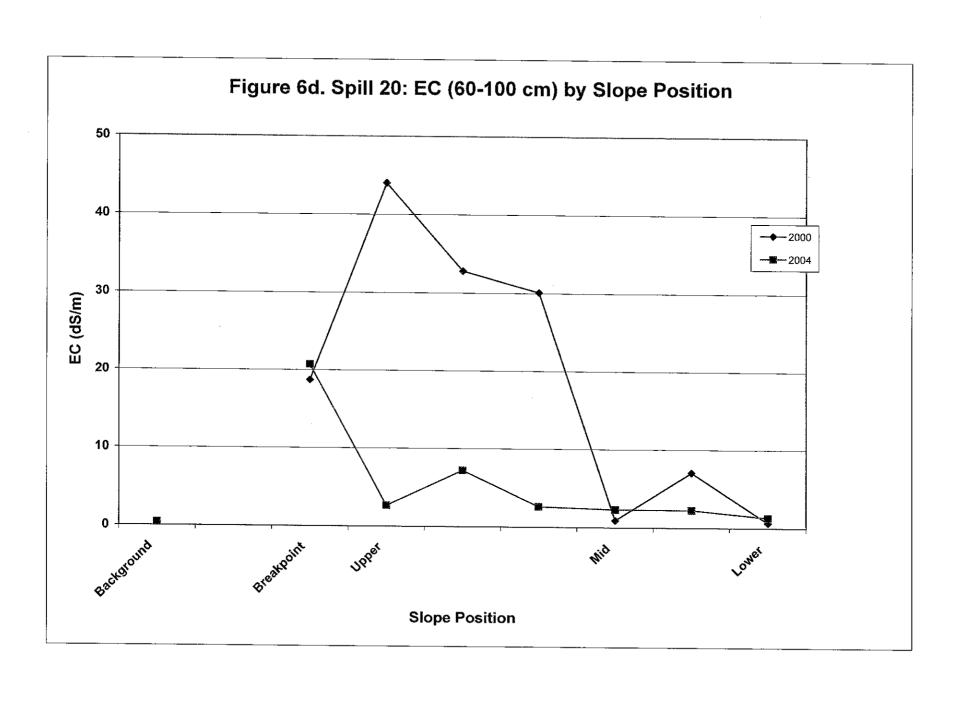


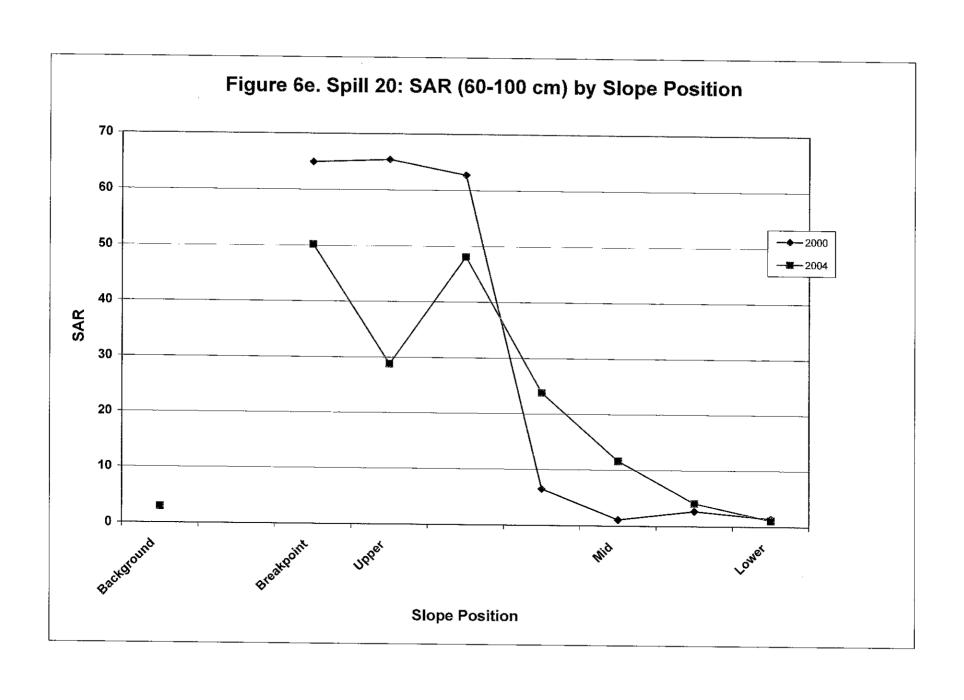


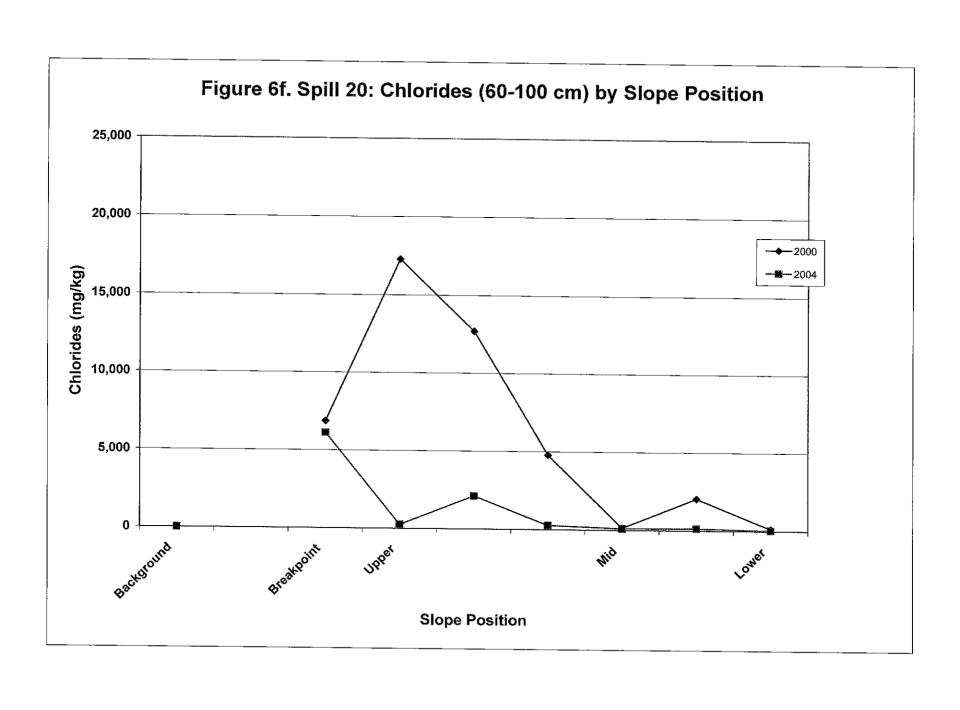


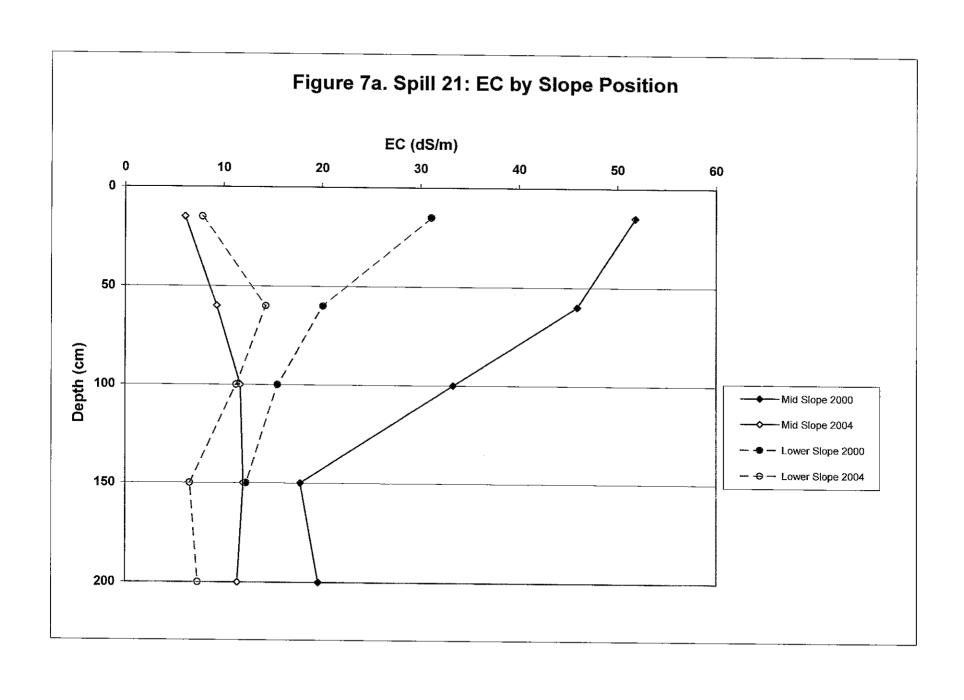


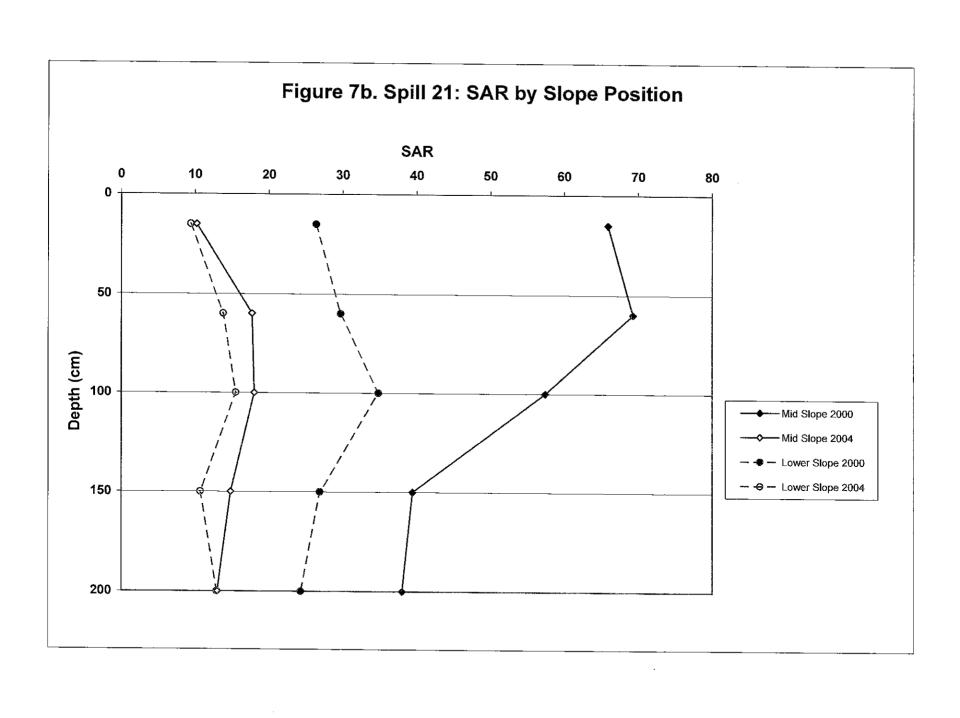


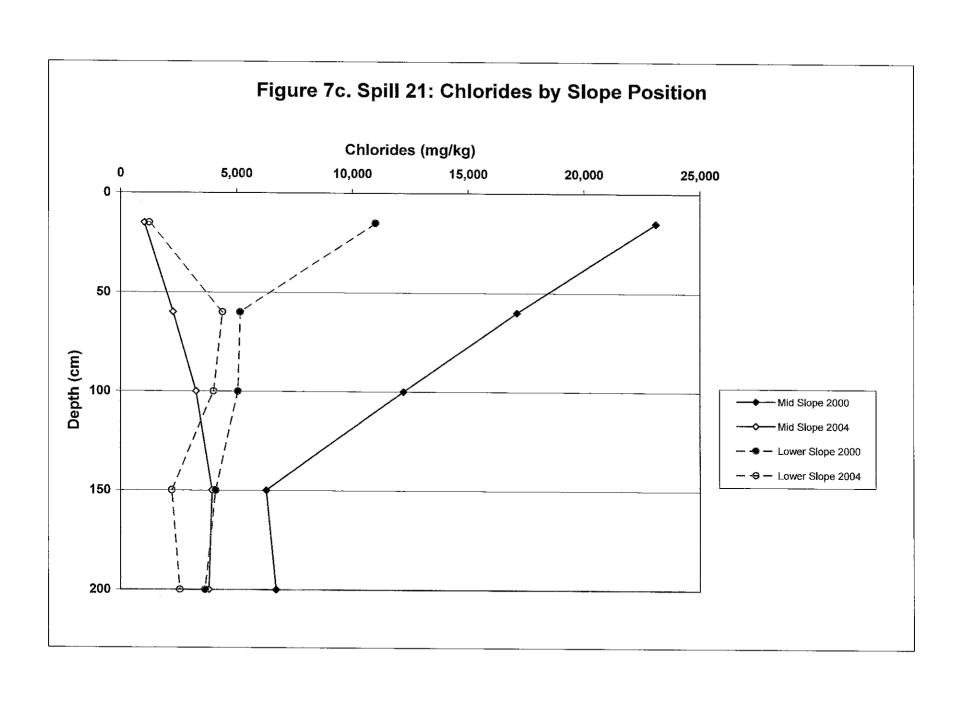


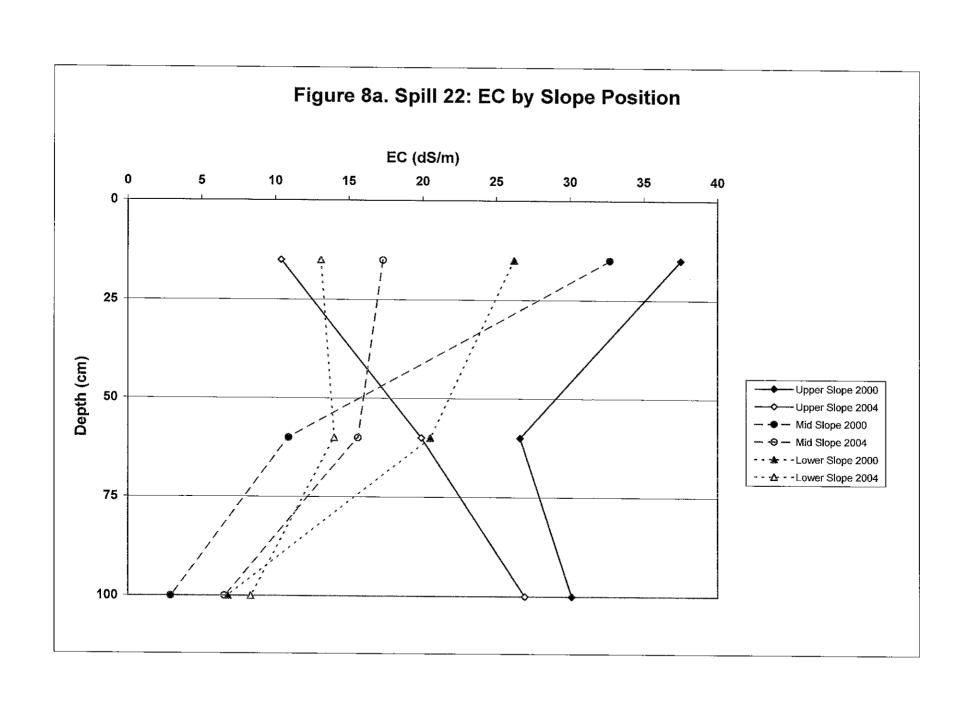


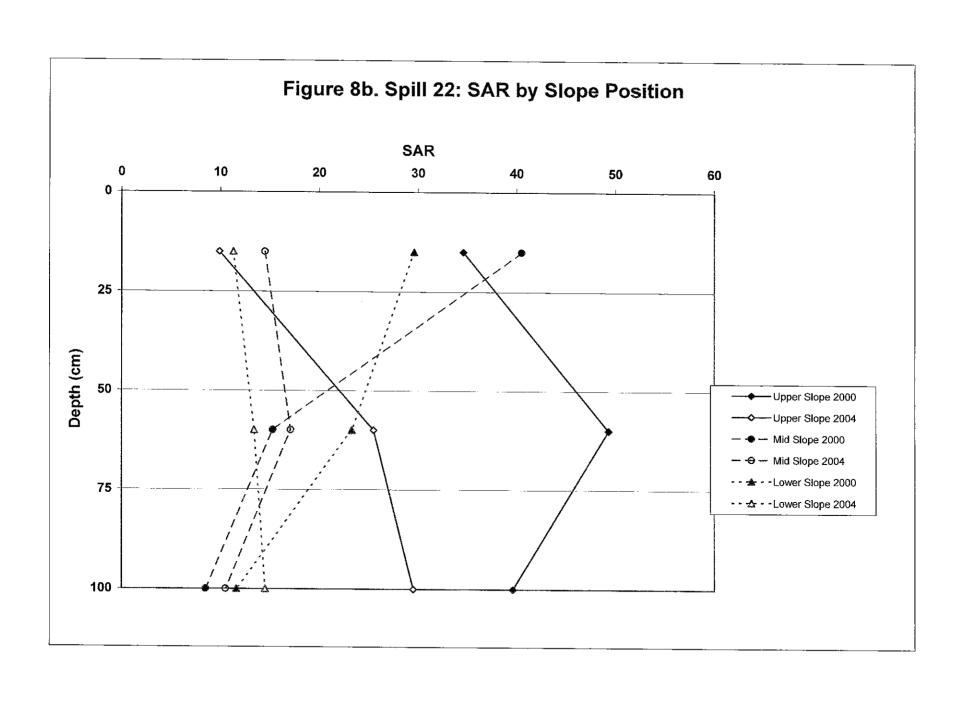


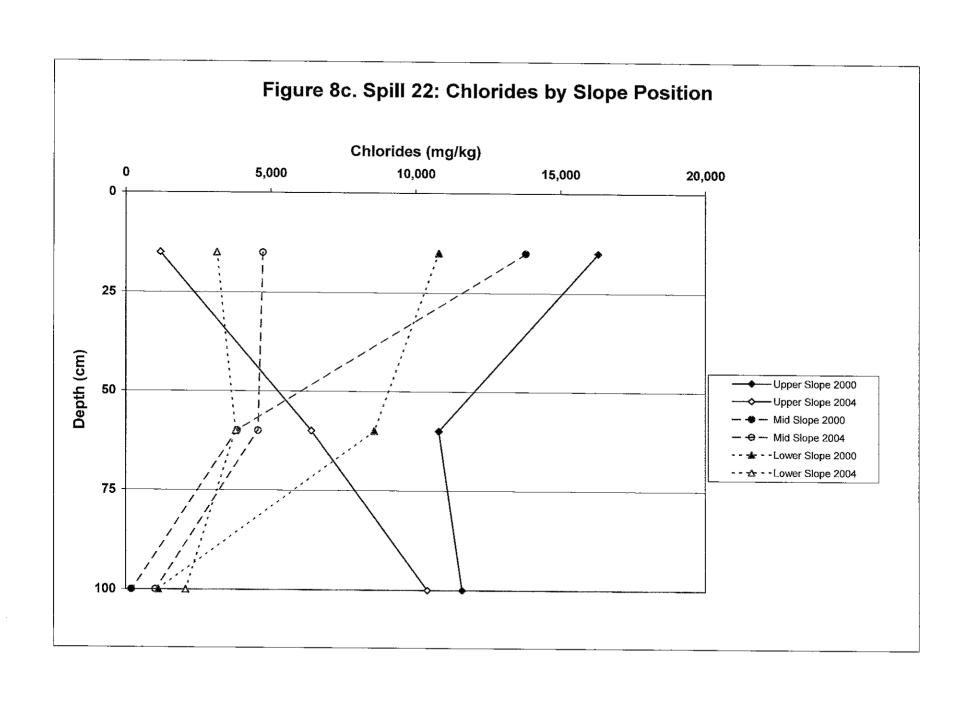


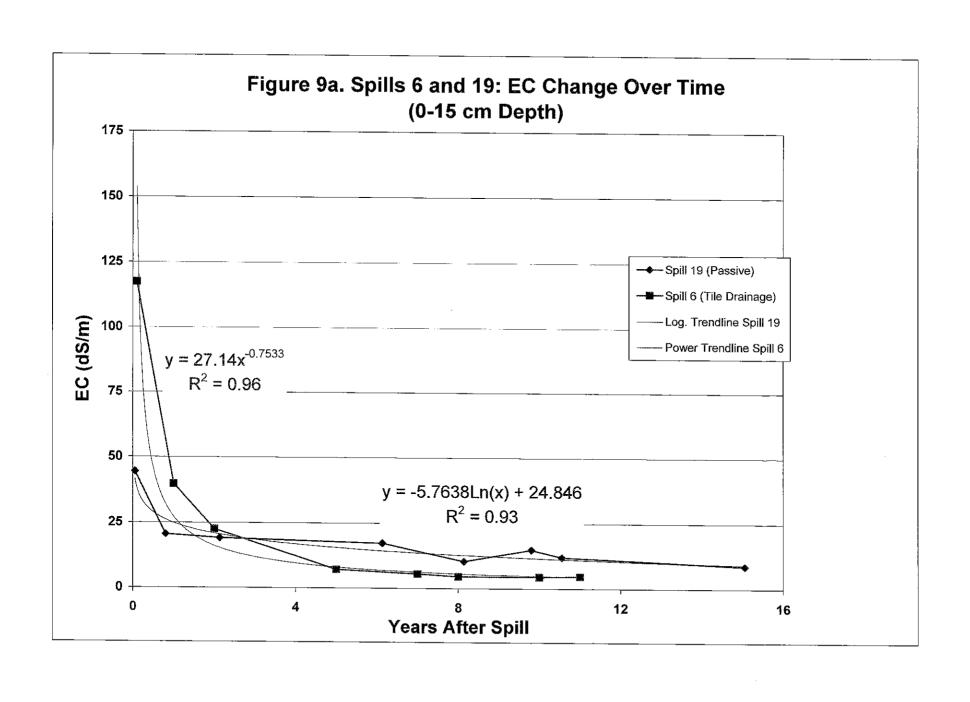


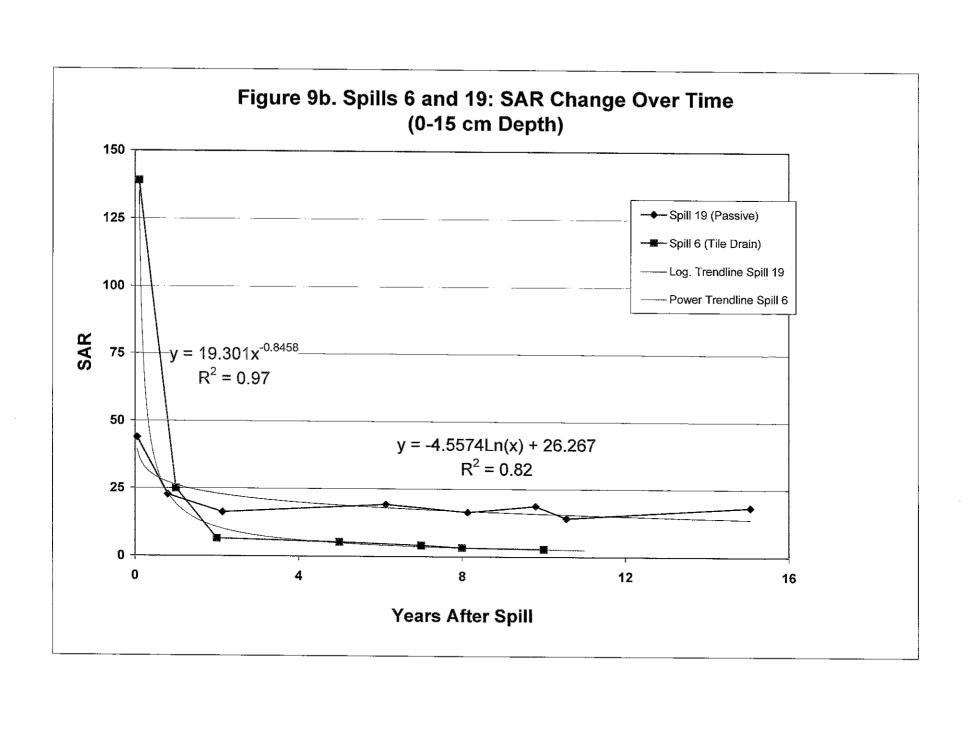












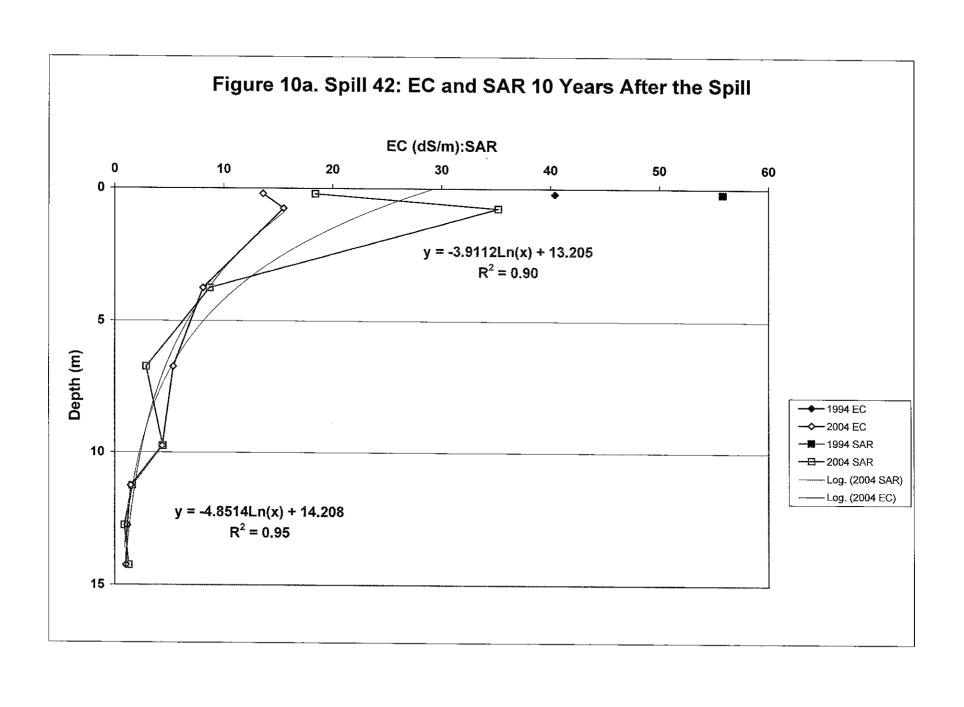


Figure 10b. Spill 42: Sodium, Chloride, Sulphate 10 Years After the Spill (2004) Na:CI:SO<sub>4</sub> (mg/kg) 1,000 0 2,000 3,000 4,000 5,000 6,000  $R^2 = 0.86$  $R^2 = 0.92$  $R^2 = 0.94$ 5 Depth (m) → Sodium - Chloride -
Sulphate ---Log. (Chloride) - Log. (Sodium) ---- Expon. (Sulphate) 10 -

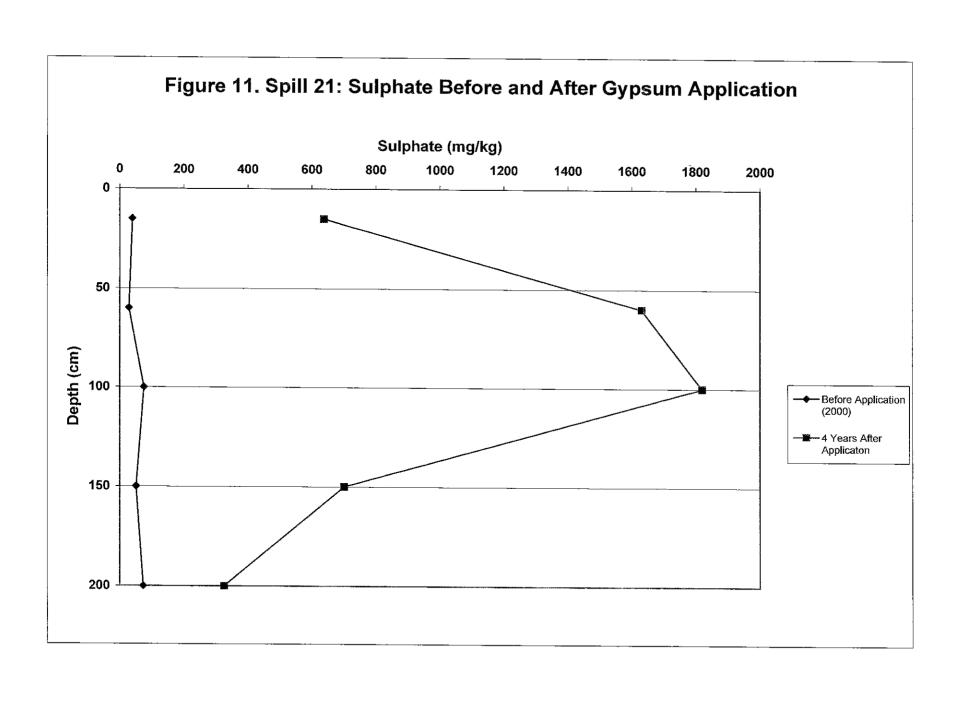


TABLE 1. SPILL 6: SOUTHEAST SASKATCHEWAN TILE DRAINAGE SYSTEM

EC (dS/m		1993	1994	1995		depth (cm)	1998	2000	2001	2003	2004
Area 2	0-15	63,8	22		Area 2a	0-15	7.1	3	2.8	3	3.5
	15-50	70.3	10.6	23.3		15-50	6.6	4.7	2.9	3.1	3.3
	50-100	35.8	13.1	14.2		50-100	7.4	3.6	2	4.7	5.3
					Area 2b	0-15	5.3	4.5.	3.4	3.3	4
	}				/ II QQ 2.5	15-50	13	8.5	5,6		6.1
1		- 1				50-100	22	12.8	8.1	6.4	12.3
Area 3	0-15	171	40.2	14.4	Area 3a	0-15	4.8	3.6	3.2	3,1	3.7
mica 3	15-50	73	55.1	9.4	1160 00	15-50	6.1	4.8	4,6	3.7	3.5
ì	50-100	63.8	32	7.3	]	50-100	6.5	4.1	2.8	5	4.4
		-			Area 3b	0-15	8.5	5.8	6.8	4.4	8 13.6
						15-50 50-100	18 19	10.5 14.9	8.7 12.2	6.7 7.9	16.5
	<del> </del>	<del></del>							-	<u> </u>	
Area 4	0-15	missing	56.6		Area 4a	0-15	3.2	4.8	3.2	3.2	3.9
	15-50		52.8	28.6		15-50	7.6	7.7	4	3,7	4.1
ļ	50-100		24.2	21.6		50-100		10.2	6.4	5.4	3,3
					Area 4b	0-15	14	12	8.2	10	5.3
						15-50	31	17.2	14	14	10.3
						50-100	9.6	20,3	13.2	15	20.8
Control	0-15				Control	0-15			0.7		
}	15-50					15-50	ня		5	им	
	50-100		~-			50-100			5,5		ww.
Control A	0-15		[		Control A	0-15			мм	1	1.6
CONTO	15-50	-			COMMON	15-50				0.8	0.6
	50-100	i				50-100	<u> </u>			0.5	0.9
Control B	0-15				Control B	0-15			page	1.2	0,5 0,5
	15-50 50-100	-		_		15-50 50-100	нн			1.7 2.5	2.4
SAR		1993	1994	1995		depth (cm)	1998	2000	2001	2003	2004
Area 2	0-15	56.6	51.8	23.7	Area 2a	0-15	1.6	0.8	0.3	0.3	0,3
	15-50	59.4	42.9	22.8		15~50	5.5	6.4	0.7	0.6	0.9
}	50-100								1		
		28.8	20	10.7		50-100	12	10	4	1.4	1.6
		28.8	20		Area 2b			10 3.5	4 1.9	1.4 1.7	1.6 2.1
		28,8  	20  		Area 2b	50-100	12				2.1 7.2
		28.8  	20   		Area 2b	50-100 0-15	12 5.2	3.5	1.9	1.7	2.1
Area 3	0-15	 		' 		50-100 0-15 15-50 50-100	12 5.2 20 32	3.5 14 31	1.9 8.9 19	1.7 6.3 21.7	2.1 7.2. 16.5
Area 3	0-15 15-50	   179.6	   43	  12.7	Area 2b Area 3a	50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3	3.5 14 31 1.7	1.9 8.9 19 1.7	1.7 6.3 21.7	2.1 7.2 16.5 0.6
Area 3	0-15 15-50 50-100	 		' 		50-100 0-15 15-50 50-100	12 5.2 20 32	3.5 14 31	1.9 8.9 19	1.7 6.3 21.7	2.1 7.2. 16.5
Area 3	15-50	   179.6 66.1	   43 54.3	12.7 31 27.7	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100	12 5.2 20 32 4.3 9.1 13	3.5 14. 31 1.7 6.4 16.	1.9 8.9 19 1.7 7.5 13	1.7 6.3 21.7 1.1 4.1 12.4	2.1 7.2 16.5 0.6 1.6 5.7
Area 3	15-50	179.6 66.1 56.6	  43 54.3 34.3	12.7 31 27.7	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13	3.5 14 31 1.7 6.4 16.	1.9 8.9 19 1.7 7.5 13: 8.6	1.7 6.3 21.7 1.1 4.1 12.4 4.9	2.1 7.2 16.5 0.6 1.6 5.7
Агеа 3	15-50	   179.6 66.1	   43 54.3	12.7 31 27.7	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50	12 5.2 20 32 4.3 9.1 13 10 26	3.5 14. 31 1.7 6.4 16.	1.9 8.9 19 1.7 7.5 13	1.7 6.3 21.7 1.1 4.1 12.4	2.1 7.2 16.5 0.6 1.6 5.7
	15-50 50-100	179.6 66.1 56.6	  43 54.3 34.3	12.7 31 27.7	Area 3a Area 3b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	12 5.2 20 32 4.3 9.1 13 10 26 32	3.5 14 31 1.7 6.4 16 6.4 17 33	1.9 8.9 19 1.7 7.5 13 8.6 15 38	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1
Area 4	15-50 50-100 0-15	179.6 66.1 56.6	  43 54.3 34.3   51.8	12.7 31 27.7 	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32	3.5 14 31 1.7 6.4 16 6.4 17 33	1.9 8.9 19 1.7 7.5 13 8.6 15 38	1.75 6.33 21.7 1.1 4.1 12.4 4.9 12.4 22.8	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1
Area 4	15-50 50-100 0-15 15-50	179.6 66.1 56.6	  43 54.3 34.3   51.8 42.9	12.7 31 27.7   38.7 40.9	Area 3a Area 3b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	12 5.2 20 32 4.3 9.1 13 10 26 32	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1 0.8 2.7
Area 4	15-50 50-100 0-15	179.6 66.1 56.6	  43 54.3 34.3   51.8	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4	2.1 7.2 16.5 0.6 1.6 5.7, 9 22.5 9.1 0.8 2.7 8.5
Area 4	15-50 50-100 0-15 15-50	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12	1.75 6.33 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1 0.8 2.7 8.5
Area 4	15-50 50-100 0-15 15-50	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12	1.75 6.33 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1 0.8 2.7 8.5 4.3 15.8
Area 4	15-50 50-100 0-15 15-50 50-100	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a	50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12	1.75 6.33 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1 0.8 2.7 8.5
Area 4	15-50 50-100 0-15 15-50 50-100	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a	50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12	1.75 6.33 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1 0.8 2.7 8.5 4.3 15.8
Area 4  Control	15-50 50-100 0-15 15-50 50-100 0-15 15-50	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a Area 4b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1 27.2	2.1 7.2 16.5 0.6 1.6 5.7 9 22.5 9.1 0.8 2.7 8.5 4.3 15.8
Area 4  Control	15-50 50-100 0-15 15-50 50-100	179.6 66.1 56.6 	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a Area 4b	50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12 11 25 41	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1 27.2	2.1 7.2 16.5 0.6 1.6 5.7, 9 22.5; 9.1 0.8 2.7 8.5 4.3 15.8 31.8
Area 4	15-50 50-100 0-15 15-50 50-100 0-15 15-50	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3a Area 3b Area 4a Area 4b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12 11 25 41	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1 27.2	2.1 7.2 16.5 0.6 1.6 5.7, 9 22.5; 9.1 0.8 2.7 8.5 4.3 15.8 31.8
Area 4  Control  Control A	15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3  51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3b  Area 4a  Area 4b  Control	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12 11 25 41	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1 27.2	2.1 7.2 16.5 0.6 1.8 5.7, 9 22.5 9.1 0.8 2.7 8.5 4.3 15.8 31.8
Area 4  Control  Control A	15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	179.6 66.1 56.6 	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7   38.7 40.9 25.9	Area 3b  Area 4a  Area 4b  Control	50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  0-15  0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11 17 34 15	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12 11 25 41	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1 27.2	2.1 7.2 16.5 0.6 1.8 5.7, 9 22.5; 9.1 0.8 2.7 8.5 4.3 15.8 31.8
Area 4  Control  Control A	15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50	179.6 66.1 56.6   180.7 129.9 78.2	43 54.3 34.3   51.8 42.9 20	12.7 31 27.7    38.7 40.9 25.9	Area 3b  Area 4a  Area 4b  Control	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	12 5.2 20 32 4.3 9.1 13 10 26 32 1.1 11 17 34 15	3.5 14 31 1.7 6.4 16 6.4 17 33 4.4 12 27 15 30 47	1.9 8.9 19 1.7 7.5 13 8.6 15 38 1.5 4.2 12 11 25 41	1.7 6.3 21.7 1.1 4.1 12.4 4.9 12.4 22.8 0.8 2.3 5.4 11 21.1 27.2	2.1 7.2 16.5 0.6 1.8 5.7, 9 22.5 9.1 0.8 2.7 8.5 4.3 15.8 31.8

not analysed

TABLE 1 (continued)

CI (mg/l)		1993	1994	1995	51	depth (cm)	1998	2000	2001	2003	2004
Area 2	0-15	27860				0-15	466	83	30		67
	15-50	30520	3808	7800		15-50	1300	207	26	73	210
	50-100	14560	5046	4800	)  	50-100	1670			720	86
	1			i	Area 2b	0-15	708	530	127	146	21
					" " " " " " " " " " " " " " " " " " "	15-50	3030	1	1	1	63
						50-100	8150	4380	1		294
Area 3	0-15	89900	15500	3120	Area 3a	0-15	448	127	57	107	4:
711040	15-50	31520	24000	2500		15-50	623	191	1	1	4
	50-100	27800	13400	2060		50-100	1100	477	1	1	6.
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	1				Area 3b	0-15 15-50	1960 6350	855 2400	1		1576 3336
					i	50-100	7150	5070	1		500
A 4	10.45			40700	t	· · · · · · · · · · · · · · · · · ·					
Area 4	0-15 15-50	3277.6	23200		Area 4a	0-15	116	627	73	1	14
	50-100	1909.6 1012.6	22000 7700	8750 7650	}	15-50 50-100	1050	1040 1900			108 78
	30-100	1012.0	7700	, 7000					i	700	
	1				Area 4b	0-15	4260	3480			824
		-	-			15-50	11800	5050			2310
	1	<del></del>		uu		50-100	2680	7100	3960	4610	7180
Area 5	0-15				Area 5	0-15		+			***
	15-50					15-50					
	50-100					50-100					
Control	0-15				Control	0-15		15	un.		New York
	15-50					15-50		17			
	50-100					50-100		20			
Control A	0-15				Control A	0-15		-	ни	53	23
	15-50				0011110171	15-50				52	14
	50-100					50-100				41	25
Control B	0-15		н-4		Control B	0-15				10	40
CONIDOLD	15-50				Control B	15-50				19 155	10 12
	50-100					50-100			P	111	9
SO <sub>4</sub> (mg/l	1)	1993	1994	1995		depth (cm)	1998	2000	2001	2003	2004
Area 2	0-15	200	2195		Area 2a	0-15	1650	1660	1430	1480	1770
	15-50	200	198	900		15-50	2240	2570	1620		
	50-100							2010	1020	1360	1890
	1	100	105	327		50-100	1660	1330	872	1730	
		100	105		Area 2h	50-100	1660	1330	872	1730	1900
		100 	105  		Area 2b	50-100 0-15	1660 1950	1330 1770	872 1590	1730. 1770	1900 1750
		  			Area 2b	50-100	1660	1330	872	1730	1900 1750 2220
Area 3	0-15			  		50-100 0-15 15-50 50-100	1660 1950 2560 1270	1330 1770 2600 795	872 1590 2350 3320	1730 1770 2310 2350	1900 1750 2220 1790
Area 3	0-15 15-50	   500	  2640	  1737	Area 2b —————Area 3a	50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020	1330 1770 2600 795 2000	872 1590 2350 3320 1730	1730 1770 2310 2350 1680	1900 1750 2220 1790
Area 3	0-15 15-50 50-100			  		50-100 0-15 15-50 50-100	1660 1950 2560 1270	1330 1770 2600 795	872 1590 2350 3320	1730 1770 2310 2350	1900 1750 2220 1790 1700 2170
Area 3	15-50	  500 200	   2640 290	  1737 626 296	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100	1660 1950 2560 1270 2020 2710 2190	1330 1770 2600 795 2000 2620 1240	872 1590 2350 3320 1730 2500	1730 1770 2310 2350 1680 1890 2270	1900 1750 2220 1790 1700 2170 2730
Area 3	15-50	500 200 280	  2640 290 119	1737 626 296		50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120	1330 1770 2600 795 2000 2620 1240	872 1590, 2350 3320 1730 2500	1730 1770 2310 2350 1680 1890 2270	1890 1900 1750 2220 1790 1700 2170 2730 1970
Area 3	15-50	  500 200	   2640 290	  1737 626 296	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50	1660 1950 2560 1270 2020 2710 2190 2120 2510	1330 1770 2600 795 2000 2620 1240 1840 2420	872 1590 2350 3320 1730 2500 1830 2340	1730 1770 2310 2350 1680 1890 2270 1980 2660	1900 1750 2220 1790 1700 2170 2730 1970 2640
	15-50 50-100	500 200 280	2640 290 119	1737 626 296	Area 3a Area 3b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	1660 1950 2560 1270 2020 2710 2190 2120 2510 520	1330 1770 2600- 795 2000 2620 1240 1840 2420 897	872 1590 2350 3320 1730 2500 1830 2340 816	1730 1770 2310 2350 1680 1890 2270 1980 2660 169	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240
Area 4	15-50 50-100 0-15	500 200 280 	2640 290 119 	1737 626 296   2590	Area 3a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520	1330 1770 2600- 795 2000 2620 1240 1840 2420 897	872 1590 2350 3320 1730 2500 1830 2340 816	1730 1770 2310 2350 1880 1890 2270 1980 2660 169	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240
Area 4	15-50 50-100 0-15 15-50	500 200 280   208 10.4	2640 290 119   2020 544	1737 626 296   2590 945	Area 3a Area 3b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	1660 1950 2560 1270 2020 2710 2190 2120 2510 520	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870	1730 1770 2310 2350 1880 1890 2270 1980 2660 169	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380
Area 4	15-50 50-100 0-15	500 200 280 	2640 290 119 	 1737 626 296   2590 945 515	Area 3a Area 3b Area 4a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130
Area 4	15-50 50-100 0-15 15-50	500 200 280 280   208 10.4 4.2	2640 290 119   2020 544 0.1	 1737 626 296   2590 945 515	Area 3a Area 3b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130
Area 4	15-50 50-100 0-15 15-50	500 200 280 280   208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515	Area 3a Area 3b Area 4a	50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590 1760 2400	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390
Area 4	15-50 50-100 0-15 15-50 50-100	500 200 280 280   208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515	Area 3a Area 3b Area 4a Area 4b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130
Area 4 Area 5	15-50 50-100 0-15 15-50 50-100	500 200 280 280 	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515	Area 3a Area 3b Area 4a	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-60 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390
Area 4 Area 5	15-50 50-100 0-15 15-50 50-100 0-15 15-50	500 200 280 280 	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515	Area 3a Area 3b Area 4a Area 4b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2510 520 1600 2600 2410 1910 1090	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400
Area 4 Area 5	15-50 50-100 0-15 15-50 50-100	500 200 280 280 	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515	Area 3a Area 3b Area 4a Area 4b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-60 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2240 1900 2380 2130 1850 2390 1400
Area 4 Area 5 Control	0-15 50-100 0-15 15-50 50-100 0-15 0-15	500 200 280 280 	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515  	Area 3a Area 3b Area 4a Area 4b	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-60 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2510 520 1600 2600 2410 1910 1090	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400
Area 4 Area 5 Control	0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-15	208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515  	Area 3a Area 3b Area 4a Area 4b Area 5	50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400
Area 4 Area 5 Control	0-15 50-100 0-15 15-50 50-100 0-15 0-15	500 200 280 280   208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515  	Area 3a Area 3b Area 4a Area 4b Area 5	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-60 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 2130 1850 2390 1400
Area 4 Area 5 Control	0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-15	208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515   	Area 3a Area 4a Area 4b Area 5	50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400
Area 4  Area 5  Control A	0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515   	Area 3a  Area 4a  Area 4b  Area 5  Control A	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600- 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400
Area 4  Area 5  Control A	0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515    	Area 3a Area 3b Area 4a Area 4b Area 5 Control	50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400 83.9
Area 4  Area 5  Control  Control A	0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100	208 10.4 4.2	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515     	Area 3a Area 4a Area 4b Area 5 Control A	50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100  0-15  15-50  50-100	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090 	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000   126 3120 3520   	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 2390 846 	1730 1770 2310 2350 1680 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2240 1900 2380 2130 1850 2390 1400 83.9 99.7 183
Area 4  Area 5  Control A  Control B	0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50 50-100 0-15 15-50	500 200 280 280 	2640 290 119   2020 544 0.1	1737 626 296   2590 945 515     	Area 3a  Area 3b  Area 4a  Area 4b  Area 5  Control A	50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15 15-50 50-100  0-15	1660 1950 2560 1270 2020 2710 2190 2120 2510 520 1600 2600 2410 1910 1090	1330 1770 2600 795 2000 2620 1240 1840 2420 897 1730 3020 2660 1840 2030 1000	872 1590 2350 3320 1730 2500 1830 2340 816 1550 1870 2600 1820 2390 846	1730 1770 2310 2350 1880 1890 2270 1980 2660 169 1580 2230 1590 1760 2400 1800	1900 1750 2220 1790 1700 2170 2730 1970 2640 2380 2130 1850 2390 1400

not analysed

**TABLE 2. PEACE REGION TILE SYSTEMS** 

Spill 15 Sample Point	Depth cm	Sample Date	EC dS/m	SAR	CI meq/L	SO₄-S meq/L
Control	0-30	1997	0.97	1.8	2.82	5.32
Control	30-60	1997	0.67	1.5	2.33	2.77
Control	60-100	1997	0.91	1.4	3.10	6.13
Pile 1	comp	1998	14.5	21.2	134	17.4
Pile 2	comp	1998	21.2	24.2	210	54.2
03-B1	0-30	2003	10.5	12.7	66.5	57.0
03-B1	30-60	2003	10.0	9.7	62.7	51.6
03-B1	60-100	2003	8.1	6.1	60.2	29.9
03-B2	0-30	2003	11.7	10.6	78.8	49.0
03-B2	30-100	2003	12.7	15.3	90.9	58.8
03-B2	60-100	2003	14.3	13.0	104	51.0
03-B2	100-140	2003	8.50	4.3	66.0	39.8
03-B3	0-30	2003	9.71	7.7	58.9	48.1
03-B3	30-60	2003	7.80	6.4	36.8	56.2
03-B3	60-100	2003	7.94	4.4	55.3	34.6
03-B3	100-130	2003	9.27	6.2	62.6	50.6
03-B4	0-30	2003	6.39	7.2	20.3	58.9
03-B4	30-60	2003	11.8	15.2	76.3	61.7
03-B4	60-100	2003	14.6	13.5	117	53.7
03-B4	100-150	2003	12.0	6.4	99.9	45.7
03-B5	0-30	2003	7.41	6.8	39.3	52.2
03-B5	30-60	2003	8.45	11.7	41.9	62.4
03-B5	60-100	2003	9.37	12.0	50.3	62.3
03-B6	0-30	2003	6.03	5.4	20.0	52.0
03-B6	30-60	2003	5.77	4.9	35.9	24.3
03-B6	60-100	2003	6.59	3.9	37.8	40.1

**TABLE 2 (continued)** 

Spill 16 Sample	Depth	Sample	EC dS/m	SAR	Na mag/l	Ca
Point  Control  Control	0-30 60-100	1997 1997	0.62 0.58	1.5 1.9	meq/L  	meg/L 
Composite		1998	21.2	15.6	12.9	54.7
Composite		1998	7.94	6.8	42.8	37.9
03-B1	0-30	2003	5.83	6.4	32.6	31.8
03-B1	30-60	2003	7.64	10.3	54.4	32.1
03-B1	60-100	2003	10.5	14.7	81.4	37.9
03-B1	100-150	2003	13.0	12.5	84.7	54.6
03-B2	0-30	2003	9.07	10.6	62.1	36.4
03-B2	30-60	2003	12.8	18.6	109	40.9
03-B2	60-100	2003	13.2	14.1	94.3	53.9
03-B2	100-150	2003	7.02	7.6	39.8	25.5
03-B3	0-30	2003	9.34	11.0	66	40.8
03-B3	30-60	2003	12.6	16.3	102	43.7
03-B3	60-100	2003	14.9	15.8	111	59
03-B3	100-150	2003	11.9	12.4	82.4	52.8
03-B4	0-30	2003	11.1	14.1	88.4	45.6
03-B4	30-60	2003	14.4	18.0	119	49
03-B4	60-100	2003	29.3	38.5	298	82
03-B4	100-150	2003	32.1	64.2	388	49.4
03-B5	0-30	2003	7.46	7.6	44	38.6
03-B5	30-60	2003	9.29	10.1	60.6	39
03-B5	60-100	2003	7.53	6.0	35.7	30.8
03-B6	0-30	2003	6.68	7.3	37.8	30.7
03-B6	30-60	2003	9.39	11.2	62.5	32.2
03-B6	60-100	2003	15.0	12.0	56.6	53
03-B6	100-150	2003	10.1	7.4	47.6	39.9
03-B7	0-30	2003	7.38	7.7	40.9	32.2
03-B7	30-60	2003	10.5	11.0	65.1	36.2
03-B7	60-100	2003	10.8	11.2	67.1	44
03-B7	100-150	2003	8.42	11.3	55.3	26.3
03-B8	0-30	2003	6.16	6.1	32.8	35.2
03-B8	30-60	2003	8.53	7.9	45	42.7
03-B8	60-100	2003	4.58	3.10	14.5	24.9
03-B8	100-150	2003	2.73	1.90	6.46	12.8

TABLE 3. SPILL 7: EAST-CENTRAL ALBERTA TILE SYSTEM (2003)

		EC (d	dS/m)	SA	AR	Calcium	(meq/L)	Sodium	(meq/L)	Sulphate	e (meq/L)	Chloride	(meq/L)
Sample	Depth	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Point	(cm)	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation	Irrigation
l 1	0-15	12.2	6	14.1	9.6	35	32	76	45			80	<u> </u>
	15-30	11.5					34		118			58	
	30-45	11.8		19.3			31	96	149		81	47	99
	45-60	9.1	15	20.5	l i	14	34	E I	159			34	
	60-75	11.7	13.9	19.2			32		188		79	43	
	75-100	10.9					29		136			46	
	100-150	11.1	12	16.1	T .	27	30		128		86	49	
	150-200	11.7	4.8	16.1	27.4		5				1		
2	0-15	16.5	6.5	12.7	12.5	G.E.	20			-			
	15-30	13.1	5.5	15.3	12.5 9.3			91	59			82.7	ľ
	30-45	20.4		18.5			28	89	93		i '	1	
	45-60	20.7	6.3	18.4			26 29	136 136			i .	210	
1	60-75	22	9.3	20.2			29 28	152					
	75-100	20.2						1			1		I .
	100-125		20		18	30	16		79		35	230	140 217
	125-150	17	20	25	30	22	39			34	i	i	1
<u> </u>	150-200	17		27		26		139		41		181	1

TABLE 4. SPILL 2: SOIL WASHING SITE

Sample Point	Sample Date	рН	EC dS/m	SAR	Na mg/L	CI mg/L
First Wash						
Pit 1	July 1999	7.6	4.5	26.2	948	1130
Pit 2	July 1999	7.5	4.55	19.4	940	1120
Second Wash						
Pit 1	July 2000	8.3	3.36	25	718	559
	July 2000	8.3	3.16	23.5	652	827
	July 2000	7.4	3.08	17.5	618	665
	July 2000	8.5	2.49	28.2	573	661
Pit 2	July 2000	6.8	3.57	9.4	549	926
	July 2000	6.8	3.45	9.5	543	848
<b> </b>	July 2000	6.9	3.44	9.8	580	817
ļ	July 2000	6.8	3.44	9.5	539	838
	July 2000	6.8	3.41	9.5	546	848
Amendment A	l ddition					
Pit 1	Oct. 2000	7.6	7.2	9	1040	755
Pit 2	Oct. 2000	7	10.6	7.3	1130	1360

Age of spill M	Monitoring	Averag	Average Topsoil EC (dS/m)	EC (qS/m)	Ave	Average Subsoil* EC	oil* EC	Ave	Average Topsoil SAR	oil SAR	Ave	Average Subsoil* SAR	il* SAR
Period (yrs)	<u>ه</u>	starting	ending	Background	starting	ending	Background	starfing	ending	Background	starting	ending	Background
~		11.7	8.3	2.3	4.7	5.5	7.7	20.7	14	10	99	7.4	12.8
.,	~	23.2	7.3	2.5	7.6	7.4	5.3	40.5	8	1.8	12.5	7.2	00
•	2	3.9	1,4	0.4	!	ì	1	18.1	œ	0.4	1	1	<u> </u>
	7	13	12.3	0.79	1	ŀ	ı	57.2	24.6	0.5	ı	l	ļ
	2	13	2.8	li	8.9	3.7		11.8	છ	1	9.3	4.6	l
	2	11.6	14.8	ı	ł	l	1	23.6	21.1	1	ı	     	
	2	2.5	_	i	1	ŀ	ı	12.8	6,8	i	I	ł	I
	2	9.4	6.3	ì	ı	ı	1	57.9	25.4	ŀ	1	ł	ı
	2	6.4	0.5	ì	!	ı	ı	10.5	9.0	ŀ	ł	I	1
	2	17.4	15.3	ı	1	Ι	_	56	23.9	ŀ	l	I	I
	7	7.8	3.5	ŀ	ł	ı	-	33.7	10.6	;	ł	1	ı
	က	18.6	14.3	ı	20.9	10.1	ì	21.1	22.9	1	21.8	19.4	1
	7	2.7	5.6	ı	I	1	ı	111.3	34.2	ł	I	I	1
	7	20.5	12	ı	16.3	14.2	1	22.7	14.2	ł	18.9	14.3	l
Į	4	22	3.9	_	15.3	4	9.0	32.6	6.5	0.5	21.7	13.4	1.6
	4	41.5	7	0.3	33	11.8	0.2	46.2	9.8	0.3	49.5	15.8	0.4
	4	32.1	13.6	0.5	19.3	16.5	0.5	34.9	11.9	6.4	29.3	18.7	6.6
	4	10.8	6.3	4.0	5.9	4.7	0.3	21.1	9.9	0.5	6.6	11.1	3.1
	ഗ	7.1	<del>;</del>	9.0	2.7	2.3	0.2	33.6	2.3	2.1	39.5	7.2	2.2
- 1	3	2.2	6.7	0.7	10.1	9.6	4.7	18	15.1	0.3	25.3	14.4	0.9
	4	10.8	12.3	5.2	29.7	8.6	7	27.7	15	3.2	37.5	15	9
	2	8.7	2.3	1.2	1	I	ı	Ф	12.7	9.0	l	!	ı
	က	124	36.3	1.7	85.2	43.2	2	126	36.3	რ	94.8	43.2	21.3
	2	8.5	5.8	1.2	10.1	6.4	l	14	8.9	0.3	16.8	6.6	ŀ
- [	6	16.9	14.2	0.4	19.6	13.7	0.4	19	15.1	0.5	25.8	24.8	0.2
	5	14.9	-	0.5	14	1,5	0.3	21.6	4,9	9.0	16.3	21.5	0,7
	9	39.3	2.4	ı	25.2	S	ı	66.1	6.6	1	28.5	21.9	ļ
	9	14.5	4.4	I	19.2	6.7	ı	58.4	7.3	í	64.1	48	1
	ω <del>ζ</del>	8.4	1.2	ı	ł	1 0	1	15.1	5.6	į	l	1	l
ļ	2	40.4	14.2	1	-	10./	1	55.8	24.7	;	1	33.4	1

<sup>no data
Depth increment immediately below topsoil</sup> 

TABLE 6. SPILLS 20, 21 and 22

Spill 20					·	
Sample	Depth	Sample	EC	SAR	Ci	SO <sup>4</sup> -S
Point	(cm)	Date	(dS/m)		(mg/kg)	(mg/kg)
Breaksite	0-15	2000	13.4	59.9	4620	53
Breaksite	15-60	2000	31.8	69.4	11900	30
Breaksite	60-100	2000	18.7	64.9	6850	36
Breaksite	0-15	2004	4.81	11.1	439	1640
Breaksite	15-60	2004	10.1	25.6	1770	2420
Breaksite	60-100	2004	20.7	50.2	6100	4400
2	0-15	2000	30.6	37.8	22000	80
2	15-60	2000	32.3	17.2	12900	30
2	60-100	2000	44	65.4	17300	30
2	0-15	2004	5.85	8.7	869	327
2	15-60	2004	3.18	19.1	193	861
2	60-100	2004	2.65	28.8	251	965
3	0-15	2000	30.9	38.2	11800	60
3	15-60	2000	11.9	54.1	4040	78
3	60-100	2000	32.8	62.7	12700	30
3	0-15	2004	5.3	6.8	209	2560
3	15-60	2004	6.0 <b>5</b>	19.8	627	2100
3	60-100	2004	7.18	48.1	2120	453
4	0-15	2000	44.3	55.2	17700	40
4	15-60	2000	26.6	7.7	3990	14
4	60-100	2000	30.1	6.5	4770	22
4	0-15	2004	4.68	5.2	158	2320
4	15-60	2004	2.75	13.0	167	898
4	60-100	2004	2.62	23.8	279	559
5	0-15	2000	13.9	12.9	5020	23
5	15-60	2000	1.1	0.7	182	23.5
5	60-100	2000	0.92	1.1	133	21.7
5	0-15	2004	2.26	6.9	95	565
5	15-60	2004	2.06	9.8	78	553
5	60-100	2004	2.3	11.6	113	602
6	0-15	2000	26.3	20.2	9480	60
6	15-60	2000	2.28	0.9	465	42
6	60-100	2000	7.05	2.7	2040	49
6	0-15	2004	2.48	4.9	94	785
6	15-60	2004	2.44	5.0	115	890
6	60-100	2004	2.06	4.1	138	660
lower	0-15	2000	4.92	3.9	1320	45.1
lower	15-60	2000	1.4	1.7	367	12.6
lower	60-100	2000	0.67	1.4	119	13.7
lower	0-15	2004	1.86	2.1	76	230
lower	15-60	2004	1.43	1.8	46	175
lower	60-100	2004	1.34	1.1	38	124
Background	15-60	2000	0.96	0.5	13	31.6
Background		2000	0.59	1.6	16	50.9
Background		2000	0.41	2.9	10	30.8

TABLE 6 (continued)

Spill 21						
Sample Point	Depth (cm)	Sample Date	EC (dS/m)	SAR	CI (mg/kg)	SO <sup>4</sup> -S (mg/kg)
Midslope	0-15	2000	51.8	65.9	23100	39.3
Midslope	15-60	2000	45.9	69.3	17100	28.1
Midslope	60-100	2000	33.3	57.4	12200	75.4
Midslope	100-150	2000	17.8	39.4	6280	50.9
Midslope	150-200	2000	19.6	38	6700	73.1
Midslope	0-15	2004	6.11	10.2	1030	638
Midslope	15-60	2004	9.31	17.7	2260	1630
Midslope	60-100	2004	11.7	18.0	3260	1820
Midslope	100-150	2004	12	14.8	3940	701
Midslope	150-200	2004	11.4	13.0	3810	325
Downslope Downslope	0-15 15-60	2000 2000	31.1 20.1	26.4 29.7	11000 5160	1470 496
Downslope	60-100	2000	15.5	34.8	5060	118
Downslope	100-150	2000	12.3	26.9	4100	126
Downslope	150-200	2000	10.9	24.3	3640	149
Downslope Downslope Downslope Downslope Downslope	0-15 15-60 60-100 100-150 150-200	2004 2004 2004 2004 2004	7.86 14.3 11.3 6.59 7.38	9.4 13.8 15.5 10.7 12.9	1240 4400 4010 2210 2560	1380 2060 332 53.3 42.5
Control Control Control	0-15 15-60 60-100	2000 2000 2000	0.26 0.21 0.12	0.3 0.4 0.6	28 10 15	11.5 26.8 8.9

Spill 22						
Sample	Depth	Sample	EC	SAR	CI	SO⁴-S
Point	(cm)	Date	(dS/m)		(mg/kg)	(mg/kg)
Upslope	0-15	2000	37.5	34.6	16300	205
Upslope	15-60	2000	26.6	49.3	10800	296
Upslope	60-100	2000	30.1	39.6	11600	2400
Upslope	0-15	2004	10.4	9.9	1190	1880
Upslope Upslope	15-60 60-100	2004 2004 2004	19.9 26.9	25.5 29.5	6400 10400	2330 2420
Midslope	0-15	2000	32.7	40.5	13800	97.3
Midslope	15-60	2000	10.9	15.3	3840	872
Midslope	60-100	2000	2.89	8.5	196	1280
Midslope	0-15	2004	17.3	14.5	4730	2010
Midslope	15-60	2004	15.6	17.1	4560	1930
Midslope	60-100	2004	6.54	10.5	1020	1870
Downslope	0-15	2000	26.2	29.6	10800	99.7
Downslope	15-60	2000	20.5	23.3	8570	346
Downslope	60-100	2000	6.77	11.6	1120	2740
Downslope	0-15	2004	13.1	11.3	3140	1850
Downslope	15-60	2004	14	13.4	3790	1970
Downslope	60-100	2004	8.31	14.5	2060	1280
Control	0-15	2000	0.53	6.4	91	74.2
Control	15-60	2000	0.49	6.6	45	77
Control	60-100	2000	3.22	17.4	523	762

TABLE 7. SPILL 42: EAST-CENTRAL ALBERTA

	Depth	Sample	EC	SAR	Na	CI	SO₄-
Sample point	cm	Date	dS/m		mg/L	mg/L	mg/L
After Similar Spill	Surface	2003	40.4	55.8			
(average of 4 points)							
1994 spill area							
Site 1	0-20	2003	13.6	18.8	2300	4150	1630
	20-100	2003	18.8	32.6	3650	6530	800
Site 2	0-20	2003	13.6	17.9	2250	3960	1870
	40-100	2003	18.7	34.1	3640	6470	704
Site 3	0-75	2003	15.5	35.2	3540	5760	681
	300-375	2003	8.09	8.7	894	3040	69.1
	600-675	2003	5.37	2.9	295	1860	6.6
	900-975	2003	4.36	4,4	356	1450	18.7
	1050-1125	2003	1.48	1.6	80	387	26.8
	1200-1275	2003	1.16	0.9	45	309	23.7
	1350-1425	2003	1.04	1.3	60	196	151

<sup>--</sup> no data

### APPENDIX A

### SITE SUMMARIES FOR

Spill 1	Spill 12e	Spill 28
Spill 2	Spill 12f	Spill 29
Spill 4	Spill 13f	Spill 30
Spill 6	Spill 14	Spill 31
Spill 7	Spill 15	Spill 32
Spill 8	Spill 16	Spill 35
Spill 9	Spill 19	Spill 36
Spill 10	Spill 20	Spill 37
Spill 11	Spill 21	Spill 38
Spill 12b	Spill 22	Spill 40
Spill 12c	Spill 23	Spill 42
Spill 12d	Spill 24	

### Spill 1

	Site Description	Remediation Efforts
Location:	Central Alberta	Remediation system: Passive
Natural region:	Central Parkland	Source removal details: Source removed, details unknown
Soil texture:	Unknown	Amendment details:
Soil Classification:	Unknown	Site was initially flushed with 2800 bbls water amended with 29.5 bags calcium nitrate. During
Depth to groundwater:	Unknown	remediation 118 bags calcium nitrate, 96 bags gypsum, 68 bags lime, and 56 bales straw worked in.
Discharge or recharge?	Unknown	
	Spill Description	Monitoring
Brine source:	Unknown	Sampling events (dates): 2001 and 2002
Year of release:	2001	Control data? yes
Brine origin (formation):	Nisku Devonian	Parameters analysed: detailed salinity
Spill volume:	225 m <sup>3</sup>	Sample points: 9 including 2 controls
Size of impacted area:	0.73 ha	Groundwater monitoring? No
Max investigation depth:	1.0 m	Details of EM surveys: None
Maximum impact depth:	> 1 m	
		Overview:

Site was a large spill, located on what appears to be naturally saline Solonetzic soils. The spill was remediated by flushing and amending with calcium products. Controls appear to be poorly chosen to represent pre-spill conditions since EC, SAR and sulphate values of control subsoil are higher than averages in the spill area. Topsoil EC, SAR and chlorides have decreased dramatically between the first and second years.

Spill 1

The Data

			<del>,</del>	ı <del></del>		<del>,                                      </del>		Data							
L	Depth				Depth			CI	Depth			SO <sub>4</sub> -S	Depth		
EC (dS/m)		2001	2002	SAR	(cm)	2001	2002	(mg/kg)	(cm)	2001	2002	(mg/kg)	(cm)	2001	2002
Profile 1	0-15	12.3	10.2	Profile 1	0-15	18.4	13.2	Profile 1	0-15	4410	2410	Profile 1	0-15	647	1200
	15-50	7.6	3,8		15-50	13.1	10.3	<b>i</b> [	15-50	1440	1240		15-50	2270	1070
	50-100	6,8	5.4		50-100	14.9	7.3		50-100	346	113		50-100	3930	3060
Profile 2	0-15	16,2	12.8	Profile 2	0-15	40.9	20.2	Profile 2	0-15	5860	3500	Profile 2	0-15	300	1830
	15-50	8.1	8.5		15-50	9	9.4	] []	15-50	1600	1600		15-50	2440	2330
	50-100	6.3	5.8		50~100	8.2	7.3		50-100	712	296		50-100	2810	2770
Profile 3	0-15	13	8.9	Profile 3	0-15	22.3	14.2	Profile 3	0-15	4650	2130	Profile 3	0-15	432	1290
	15-50	2.9	4.3		15-50	4.4	5.5		15-50	578	1010		15-50	579	313
	50-100	3,2	2.4		50-100	3.3	3.5		50-100	107	264		50-100	2210	791
Profile 4	0-15	15.7	7.9	Profile 4	0-15	27.2	12.9	Profile 4	0-15	5890	2220	Profile 4	0-15	100	624
	15-50	3.3	5.9	1	15-50	5.2	8.4		15-50	907	1810		15-50	285	194
	50-100	2.2	2.8		50-100	5.2	6.1		50-100	569	691		50-100	270	268
Profile 5	0-15	13.2	6,8	Profile 5	0-15	22.1	14.2	Profile 5	0-15	5240	1510	Profile 5	0-15	76.4	825
	15-50	3.6	6.1		15-50	5.1	6,7		15-50	1100	1350		15-50	213	543
	50-100	4.3	4.8		50-100	3.5	4		50-100	337	652		50-100	2310	1720
Profile 6	0-15	9.2	4.4	Profile 6	0-15	12.4	14.4	Profile 6	0-15	2710	1050	Profile 6	0-15	1410	178
	15-50	5.5	7.1		15-50	7	8.6		15-50	557	1290		15-50	2710	2470
	50-100	4.5	5.6	.	50-100	3.1	6.7		50-100	194	561		50-100	2860	2440
Profile 7	0-15	2.3	7.2	Profile 7	0-15	1.8	8.8	Profile 7	0-15			Profile 7	0-15		
	15-50	2	2.6		15-50	2.1	3.1		15-50		_		15-50		
	50-100	1.1	4.6		50-100	2.3	3.9	.	50-100				50-100		
Control 1	0-15	1.9	_	Control 1	0-15	8.1		Control 1	0-15	40	_	Control 1	0-15	734	
İ	15-50	7.7			15-50	11.6			15-50	20			15-50	5180	
	50-100	9.2			50-100	14.1	-		50-100	93			50-100	5800	-
Control 2	0-15	2.7		Control 2	0-15	11.9		Control 2	0-15	16		Control 2	0-15	1220	
	15-50	7.7			15-50	13.9	–	1	15-50	5			15-50	5190	
<u></u>	50-100	8.7	<u> </u>	<del> </del>	50-100	15.4			50-100	8			50-100	6060	

<sup>---</sup> no data

### Spill 2

Remediation system: Source removal details: Amendment details:	Soil washing system with leachate collection 175 m <sup>3</sup> removed in 1999 11,000 kg gypsum and 1150 kg calcium nitrate added after soil washing treatment
	11,000 kg gypsum and 1150 kg calcium nitrate added after soil washing
Amendment details:	
	treatment
	Monitoring
Sampling events (dates):	1999 and 2000 after washing events
Control data?	No
Parameters analysed:	Detailed salinity
Groundwater monitoring?	References to Piezometers installed, but no data available
Sample points:	4 to 5 samples
Details of EM surveys:	Done in 1994; no information available
1	

Soil washing was used to remediate salt affected soils at this flare pit. Soil was washed twice, once in 1999 and once in 2000. Report indicates first washing removed 72% of chlorides and 63% of sodium. EC was reduced by a factor of 2.9. Initial EC and SAR of the soil going into the soil washing pits are not given, but data from the initial flare pit investigation (1994) shows EC up to 36 and SAR up to 90. In September 2000, after the second wash, 4000 kg of gypsum and 460 kg of calcium nitrate was added to Pit 1 and 7000 kg of gypsum and 690 dm of calcium nitrate was added to Pit 2.

T	he	Data	

Event	Sample Point	Sample Date	рН	EC dS/m	SAR	Na mg/L	CI mg/L
						9	9/
First wash	Pit 1	1999	7.6	4.5	26.2	948	1130
	Pit 2	1999	7,5	4.6	19.4	940	1120
	Pit 1	Jul-00	8.3	3.4	25	718	559
Second wash		Jul-00	8.3	3.2	23.5	652	827
		Jul-00	7.4	3.1	17.5	618	665
		Jul-00	8.5	2.5	28.2	573	661
	Pit 2	Aug-00	6.8	3.6	9.4	549	926
		Aug-00	6.8	3.5	9.5	543	848
		Aug-00	6.9	3.4	9.8	580	817
		Aug-00	6.8	3.4	9.5	539	838
		Aug-00	6.8	3.4	9.5	546	848
Amendment	Pit 1	Oct-00	7.6	7.2	9		
Addition	Pit 2	Oct-00	7	10.6	9.3		

# Spill 4

	Site Description	Remediation Efforts
Location:	Central Alberta	Remediation system: Passive
Natural region:	Dry Mixedwood	Source removal details: None
Soil texture:	Unknown	Amendment details:
Soil Classification:	Unknown	Applied 6 barrels of calcium amendment with initial flushing plus 76 bags calcium nitrate, 122 bags gypsum, 180 bags line and 80 bales of straw
Depth to groundwater:	Unknown	
Discharge or recharge?	Unknown	
	Spill Description	Monitoring
Brine source:	Unknown	Sampling events (dates): 2001, 2002, 2003
Year of release:	2000	Control data? Yes
Brine origin (formation):	Nisku Devonian	Parameters analysed: Detailed salinity
Spill volume:	Unknown	Groundwater monitoring? No
Size of impacted area:	0.31 ha	Sample points: 5 including control
Max investigation depth:	1.0 m	Details of EM surveys: None
Maximum impact depth:	> 1.0 m	
		Overview:
Soil remediation in this haylar impacted by natural salinity.	nd/pasture site was effected in 2001 and 2002. Re Vegetation growth remained poor in the spill area.	ports note a substantial decrease in salt concentrations after the 2002 remediation efforts. Soil quality in the area is also

The Data

	<del></del>				Data				
EC (dS/m)	Depth (cm)	2001	2002	2003	SAR	Depth (cm)	2001	2002	2003
Profile 1	0-15	24.1	13.9	5.9	Profile 1	0-15	43	27.3	8.5
	15-50	13.2	13.7	4		15-50	32.4	14.2	6.2
	50-100	11	11.4	4.7		50-100	24.8	10.7	3.2
Profile 2	0-15	33.8	10.5	5.6	Profile 2	0-15	55.5	12.5	6.9
	15-50	4.5	7.4	6.2		15-50	5	8.5	7.1
	50-100	2.4	5.7	5.8		50-100	5.2	6.6	6.6
Profile 3	0-15	18.4	17.2	10.3	Profile 3	0-15	34.9	31	16.4
	15-50	8	8.3	12.6		15-50	9.7	10.3	15.4
	50-100	5.6	3.4	5.11		50-100	7	4.9	5.1
Profile 4	0-15	16.6	6.5	7.2	Profile 4	0-15	28.4	7.8	0.4
	15-50	4.8	5.2	6.7		15-50	3	0.1	0.1
	50-100	11.5	4.7	4.6		50-100	8.7	3.8	0.2
Control 1	0-15	2.5	_	****	Control 1	0-15	1.8		
	15~50	5.3				15-50	6.8	_	
	50-100	5.3				50-100	8.1	_	

CI	Depth				SO <sub>4</sub> -S	Depth	<u> </u>		
(mg/kg)	(cm)	2001	2002	2003	(mg/kg)	(cm)	2001	2002	2003
Profile 1	0-15	11700	3900	843	Profile 1	0-15	2000	2170	2220
	15-50	5350	4770	307		15-50	866	1480	1910
	50-100	4190	3420	630		50-100	720	1590	1820
Profile 2	0-15	19200	2560	929	Profile 2	0-15	540	1770	1910
	15-50	1300	1500	982		15-50	738	2350	2450
	50-100	507	608	570		50-100	596	2780	2910
Profile 3	0-15	8810	5510	2660	Profile 3	0-15	369	1210	2130
	15-50	1160	2090	4560		15-50	2360	1040	1990
	50-100	720	469	696		50-100	3560	2180	2490
Profile 4	0-15	7830	1280	1640	Profile 4	0-15	435	1640	1850
[]	15-50	1040	650	2060		15-50	1950	2060	2670
	50-100	4750	172	2720		50-100	1810	2720	2790
Control 1	0-15	47			Control 1	0-15	1680		_
	15-50	168				15-50	3600		
	50-100	47				50-100	3710		

<sup>-</sup> no data

### Spill 6

	Site Description		Remediation Efforts	
Location:	Southeast Saskatchewan	Remediation system:	Tile drainage system installed in 1993	
Natural region:	Unknown	Source removal details:	75 m <sup>3</sup> removed in 2000	
Soil texture:	Unknown	Amendment details:	Amendments applied regularly	
Soil Classification:	Unknown		5	
Depth to groundwater:	> 1m			
Discharge or recharge?	Recharge			
	Spill Description		Monitoring	
Brine source:	Pipeline break	Sampling events (dates):	Yearly 1993 to 2004	
Year of release:	1993	Control data?	Yes	
Brine origin (formation):	Winnipegosis	Parameters analysed:	Detailed salinity	
Spill volume:	720 m <sup>3</sup>	Groundwater monitoring?	No	
Size of impacted area:	1.3 ha	Sample points:	7 including control (composite sampling)	
Max investigation depth:	1.0 m	Details of EM surveys:	No survey	
• · · · · · · · · · · · · · · · · · · ·		1	•	

Tiles and a collection system were installed and soils monitored to 1 m yearly. Most dramatic reduction in salinity occurred within the first 3 years. After that the decrease was slower but steady. After 10 years salts in parts of the spill area approach guidelines but not everywhere. No information below 1 m was collected, so it is not known how much salt was actually removed from the system with the tile drainage system. Slow leaching of gypsum amendments down the soil profile is clear in sulphate data.

The Data

### Spill 7

	Site Description		Remediation Efforts		
Location:	East Central Alberta	Remediation system:	Tile drainage system installed in 2000		
Natural region:	Northern Fescue	Source removal details:	Hydrocarbon impacted materials landfilled		
Soil texture:	Fine, some sandy lenses	Amendment details:	Two tons calcium nitrate and 10 tons gypsum		
Soil Classification:	Unknown		331		
Depth to groundwater:	1.5 to 2.5 m				
Discharge or recharge?	Unknown				
	Spill Description		Monitoring		
Brine source:	Flare pit	Sampling events (dates):	1999 and 2003		
Year of release:	Site decommissioned in 1999	Control data?	Yes		
Brine origin (formation):	Viking	Parameters analysed:	Detailed salinity		
Spill volume:	Unknown	Groundwater monitoring?	Yes		
Size of impacted area:	4,000 m <sup>2</sup>	Sample points:	Numerous, not all directly comparable		
Max investigation depth:	6 m	Details of EM surveys:	EM 38 and EM 31 surveys completed		
Maximum impact depth:	< 2.0 m		, <u>-</u>		

#### Overview:

Elevated salinity was noted in the flare pit area of this site after excavation of hydrocarbon impacted materials. A detailed groundwater and soil investigation was carried out to delineate the extent of residu salt impact. Assessment included EM surveys. Once constructed, the tile area was irrigated and leacheate recovered. As the soil data was collected for delineation purposes and not impact monitoring, little of the information was directly comparable. However, data before and after irrigation is interesting in that EC and SAR were lower in subsoil at Sample Point 2, but higher in subsoil at Sample Point 1 after irrigation compared to before.

The Data See Table 3

## Spill 8

	Site Description		Remediation Efforts		
Location:	East-Central Alberta	Remediation system:	Passive		
Natural region:	Central Parkland	Source removal details:	No source removal		
Soil texture:	Moderately fine textured	Amendment details:			
Soil Classification:	Unknown	1 ton gypsum and sixteen 23	kg bags of calcium nitrate applied in 2001. Fertilized at a ratio of 20-100		
Depth to groundwater:	Unknown	120-0 lbs/acre including 73 kg of phosphate and 73 kg of potash. The area was paratilled to a 50 cm and then lightly worked with a rotospic.			
Discharge or recharge?	Unknown				
	Spill Description		Monitoring		
Brine source:	Surface rupture	Sampling events (dates):	2001 and 2003		
Year of release:	1994	Control data?	Yes		
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity		
Spill volume:	50 m <sup>3</sup>	Groundwater monitoring?	None		
Size of impacted area:	209 m <sup>2</sup>	Sample points:	2 including control		
Max investigation depth:	1.0 m	Details of EM surveys:	None		
Maximum impact depth:	0.7 m				
	Ove	erview:			
A surface spill occurred in 19 was completed. EC has decre	94. Soil was amended with gypsum, calcium nitrate, and fertilizer in 20 eased to near background levels, but SAR remains elevated.	001. Sampling occurred in 2001	and 2003. Background data was also collected and vertical delineation		

Sample Point	Depth cm	Sample Date	EC dS/m	SAR	CI meg/L	SO <sub>4</sub> -S meq/L
Spill area	0-30	2001	3.89	18.1	19.0	2.40
Spill area	0-15	2003	0.86	6.9	1.14	4.31
	15-30	2003	1.95	9.1	6.11	9.39
	70-100	2003	0.83	1.7	2.66	2.64
Control	0-15	2003	0.39	0.3	0.29	0.72
	15-30	2003	0.46	0.5	0.33	0.80
	70-100	2003	0.58	8.0	0.22	3.61

## Spill 9

	Site Description		Remediation Efforts
Location:	East Central Alberta	Remediation system:	Passive
Natural region:	Central Parkland	Source removal details:	No source removal
Soil texture:	Sandy clay loam	Amendment details:	
Soil Classification:	Unknown	3 tonnes of gypsum and two:	23 kg bags of calcium nitrate applied in 2001. Fertilized at a ratio of 20-
Depth to groundwater:	unknown	100-120-0, including 18 kg of	phosphate and 18 kg of potash.
Discharge or recharge?	Unknown		
	Spill Description		Monitoring
Brine source:	Surface rupture	Sampling events (dates):	2001 and2003
Year of release:	1998	Control data?	Yes
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity
Spill volume:	10 m <sup>3</sup>	Groundwater monitoring?	None
Size of impacted area:	1090 m <sup>2</sup>	Sample points:	2 including control
Max investigation depth:	1.0 m	Details of EM surveys:	None
Maximum impact depth:	Unknown		
		Overview:	
Vertical and horizontal exter	it was not determined. Salinity impact still in place.		

Sample	Depth	Sample	EC	SAR	CI	SO <sub>4</sub> -S
Point	cm	Date	dS/m		meq/L	meq/L
Spill area	0-30	2001	12.98	57.2	111	31.3
Spill area	0-15	2003	11.5	15.2	89,8	60.8
	15-30	2003	13.1	33.9	124	15.1
	30-50	2003	13.0	23.3	115	38.2
	50-100	2003	14.9	27.1	146	23.6
Control	0-15	2003	0.67	0.5	0,89	1.59
	15-30	2003	0.91	0.5	0,42	1.79
	70-100	2003	0.82	3.5	0,63	2.56

## Spill 10

	Site Description		Remediation Efforts
Location:	East-Central Alberta	Remediation system:	Passive
Natural region:	Central Parkland	Source removal details:	Unknown
Soil texture:	Clay loam	Amendment details:	480 lbs of calcium nitrate and 1120 lbs of gypsum added in 2000.
Soil Classification:	Unknown		
Depth to groundwater:	unknown	Ļ	
Discharge or recharge?	Unknown		
	Spill Description		Monitoring
Brine source:	Pipeline break	Sampling events (dates):	2000 and 2003
Year of release:	1999	Control data?	none
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity
Spill volume:	1000 m <sup>3</sup>	Groundwater monitoring?	None
Size of impacted area:	4400 m <sup>2</sup>	Sample points:	One
Max investigation depth:	1.0 m	Details of EM surveys:	None
Maximum impact depth:	Unknown		
	Ove	rview:	<u>.                                    </u>
Vertical and horizontal extent	was not determined. Salinity impact still in place. Movement of salts of	lown the soil profile over time is	evident from the data.

Sample	Depth	Sample	EC	SAR	Cl
Point	cm	Date	dS/m		meq/L
Spill area	0-15	2000	13	11.8	3477
	15-30	2000	8.9	9.3	2258
Spill area	0-15	2003	2.80	3.0	4.44
	15-30	2003	3.67	4.6	3.10
	50-100	2003	6.36	5.5	13.5

## Spill 11

	Site Description		Remediation Efforts		
Location:	East-Central Alberta	Remediation system:	Passive		
Natural region:	Central Parkland	Source removal details:	None		
Soil texture:	Moderately fine	Amendment details:			
Soil Classification:	Unknown	0.75 tons of gypsum, 80 lbs of paratilled to a depth of 40 cm	of calcium nitrate and 2 straw bales added in 2001. The area was and rotospiced to 10 cm.		
Depth to groundwater:	Unknown				
Discharge or recharge?	Unknown				
	Spill Description		Monitoring		
Brine source:	Subsurface line failure	Sampling events (dates):	2001 and 2003		
Year of release:	1997	Control data?	none		
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity		
Spill volume:	30 m <sup>3</sup>	Groundwater monitoring?	None		
Size of impacted area:	182 m <sup>2</sup>	Sample points:	One		
Max investigation depth:	1.0 m	Details of EM surveys:	None		
Maximum impact depth:	Unknown				
	•	Overview:			
Vertical and horizontal delineation was not completed. The salt impacted soil is still in place.					

Sample Point	Depth cm	Sample Date	EC dS/m	SAR	CI meq/L	SO₄-S meq/L
Spill area	0-30	2001	11.6	23.6	92	<b>25</b> .7
Spill area	0-15 15-30	2003 2003	13.50 16.1	18.5 23.7	106.00 138.00	52.6 70.6
ļ	50-100	2003	23.9	41.7	241.0	51.2

# Site Summary

SpH 20

Site De	cription	516 D	isoription	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		Remediation Efforts	
East Central Alb	Acception:	East Central A	Bertanuel Lucin Lyabi ki		Remediation system:	Passive	
Central Packland	Natural region:	Central Parkia	ridio statuli nest a Vastinia si se		Source removal details:	Unknown	
Moderately fine	Soil texture:	Moderately fine	<mark>s</mark> ∫ara satura pe		Amendment details:		
Unknown	Soil Classification:	Unknown	· · · · · · · · · · · · · · · · · · ·		in 2001, the spill was treated	with 300 lbs of calcium nitrated, 5 lbs of phosphate and 5 lbs of potash.	
Unknown	Depth to groundwater:	Unknown	Mitter of the Charles Higher Con-		Straw bales were spread across the site.		
Unknown	Discharge or recharge?	Unknown		_			
Split De	cription	Soill D	escription	art.	4 1 1 2 1	Monitoring	
Substitutes the	Brine source:	Subsurface line	a failure		Sampling events (dates):	2001 and 2003	
1992	Year of release:	1992	$e^{i\phi} = -i \epsilon A e^{i\phi}$		Control data?	None	
Mannville	Brine origin (formation):	Mannville	iga esektron tiber Aldiger och ko		Parameters analysed:	Detailed salinity	
6 m²	Spill volume:	6 m³	grant to be when		Groundwater monitoring?	None	
335 m	Size of impacted area:	339 m²	ing the second section of the s		Sample points:	1	
1,0 m	Max investigation depth:	1.0 m	in the second of the second		Details of EM surveys:	None	
Unknown	Maximum impact depth:	Unknown					
restorment their manufacturers of the state and the second		( ) :	a iya	Ove	rview:		
packgroene saugites	Spill not fully delineated. No	eckground sample	s collected. Subsoil SAR impact	remains after leach	ing,		

	1. 4.	- 5/4-	The Data					
Name of the			Sample Point	Depth cm	Sample Date	EC dS/m	SAR	CI mg/kg
galara   si	•		- Spill area	0-30	2001	2.5	12.8	220
indexan ( 1941) 1940	:		Spill area	0-15 15-30 50-100	2003 2003 2003	0.73 1.28 1.46	3.6 10.0 11.0	24.8 75.5 135,4

# Spill 12c

	Site Description		Remediation Efforts
Location:	East Central Alberta	Remediation system:	Passive
Natural region:	Central Parkland	Source removal details:	Unknown
Soil texture:	Moderately fine	Amendment details:	•
Soil Classification:	Unknown	In 2001 the impacted area wa	as treated with 5 tons of gypsum, 350 lbs of calcium nitrate, 70 lbs of
Depth to groundwater:	Unknown	tons/ac of gypsum was incorp	ish. Straw bales were incorporated into the spill area. In 2003 (or 04?) 5 porated.
Discharge or recharge?	Unknown	,	
	Spill Description		Monitoring
Brine source:	Subsurface line failure	Sampling events (dates):	2001 and 2003
Year of release:	1993	Control data?	None
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity
Spill volume:	52 m³	Groundwater monitoring?	None
Size of impacted area:	1912 m²	Sample points:	1
Max investigation depth:	1.0 m	Details of EM surveys:	None
Maximum impact depth:	Unknown	,	
		Overview:	
Spill not fully delineated. Mo	vement of salts through the profile evident from the data.		

	THE Data				
Sample	Depth	Sample	EC	SAR	CI
Point	cm	Date	dS/m		mg/kg
Spill area	0-30	2001	9.4	57.9	1270
Spill area	0-15	2003	6,60	13,7	279,3
	15-30	2003	5.9	37.0	872.1
	50-100	2003	11,8	13.4	3935.0

## Spill 12d

<u> </u>	Site Description		Remediation Efforts
Location:	East-Central Alberta	Remediation system:	Passive
Natural region:	Central Parkland	Source removal details:	Unknown
Soil texture:	Moderately fine	Amendment details:	
Soil Classification:	Unknown	The spill area was treated with	h 5 tons of gypsum, 150 lbs of calcium nitrate, 40 lbs of phosphate, and
Depth to groundwater:	Unknown	40 lbs of potash. Straw bales	were incorporated into the spill impacted area.
Discharge or recharge?	Unknown		
	Spill Description		Monitoring
Brine source:	Subsurface line failure	Sampling events (dates):	2001 and 2003
Year of release:	1994	Control data?	None
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity
Spill volume:	1 m <sup>3</sup>	Groundwater monitoring?	None
Size of impacted area:	274 m <sup>2</sup>	Sample points:	1
Max investigation depth:	1.0 m	Details of EM surveys:	None
Maximum impact depth:	Unknown		TO TO
		Overview:	
Remediation on this small sp	oill appears to be successful.		

Sample	Depth	Sample	EC	SAR	CI
Point	cm	Date	dS/m		mg/kg
Spill area	0-30	2001	6.4	10.5	469.0
Spill area	0-15	2003	0.5	0.5	16.6
	15-30	2003	0.4	0.6	3.9
	50-100	2003	0.6	1.5	26.3

## Spill 12e

	Site Description		Remediation Efforts
Location:	East Central Alberta	Remediation system:	Passive
Natural region:	Central Parkland	Source removal details:	Unknown
Soil texture:	Moderately fine	Amendment details:	CHARLOWIT
Soil Classification:	Unknown		m thick across the spill area. The soil was worked 40 cm deep with a
Depth to groundwater:	Unknown	paratill. Straw was incorporate	ed. 20 tons/ac of gypsum was incorporated in 2003 or 2004.
Discharge or recharge?	Unknowa		
	Spill Description		Monitoring
Brine source:	Subsurface line failure	Sampling events (dates):	2001 and 2003
Year of release:	1994	Control data?	None
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity
Spill volume:	1.5 m <sup>3</sup>	Groundwater monitoring?	None
Size of impacted area:	144 m <sup>3</sup>	Sample points:	1
Vlax investigation depth:	1.0 m	Details of EM surveys:	None
Maximum impact depth:	Unknown		MONE
<u> </u>		Overview:	
Jnlike 12d, this small spill ha	s not remediated well. There was little change in EC	C between sampling events, although SAR has decr	

Sample	Depth	Sample	EC	SAR	CI
Point	cm	Date	dS/m		mg/kg
Spill area	0-30	2001	17.4	56.0	4120
Spill area	0-15	2003	16.2	18.4	3899
	15-30	2003	14.4	29.4	3793
	50-100	2003	23.5	26.1	8083

## Spill 12f

_ocation:	East-Central Alberta	· · · · · · · · · · · · · · · · · · ·	
	Last-Central Alberta	Remediation system:	Passive
Natural region:	Central Parkland	Source removal details:	Unknown
Soil texture:	Moderately fine	Amendment details:	
Soil Classification:	Unknown	The soil was amended with 3	5 tons of gypsum, 300 lbs of calcium nitrate, 80 lbs of phosphate, 80 lbs
Depth to groundwater:	Unknown	or potash and straw. I ton/ac	of gypsum was incorporated in 2003 or 2004.
Discharge or recharge?	Unknown		
	Spill Description		Monitoring
Brine source:	Subsurface line failure	Sampling events (dates):	2001 and 2003
ear of release:	1994	Control data?	None
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity
Spill volume:	5 m <sup>3</sup>	Groundwater monitoring?	None
Size of impacted area:	786 m <sup>2</sup>	Sample points:	1
Max investigation depth:	1.0 m	Details of EM surveys:	None
Maximum impact depth:	Unknown		
		Overview:	
mall spill appears to be reme	diating well, but some impacts remain.		

Sample	Depth	Sample	EC	SAR	CI
Point	cm	Date	dS/m		mg/kg
Spill area	0-30	2001	7.8	33.7	1210
Spill area	0-15	2003	4.0	9.1	126
	15-30	2003	3.0	12.0	168
	50-100	2003	3.1	1.9	121

## Spill 13

	Site Description		Remediation Efforts	
Location:	East Central Alberta	Remediation system:	Passive	
Natural region:	Central Parkland	Source removal details:	Unknown	
Soil texture:	Clay loam to clay	Amendment details:		
Soil Classification:	Unknown		and 440 lbs of calcium nitrate added to the upper area and 11 tons nitrate added to the lower area. In 2004, 19,8 tons/acre gypsum and	
Depth to groundwater:	Unknown	400 lbs of calcium nitrate were		
Discharge or recharge?	Unknown			
	Spill Description		Monitoring	
Brine source:	Subsurface line failure	Sampling events (dates):	2000 and 2003	
Year of release:	1999	Control data?	None	
Brine origin (formation):	Mannville	Parameters analysed:	Detailed salinity	
Spill volume:	300 m <sup>3</sup>	Groundwater monitoring?	None	
Size of impacted area:	5450 m <sup>2</sup>	Sample points:	1	
Max investigation depth:	1.0 m	Details of EM surveys:	None	
Maximum impact depth:	Unknown			
		Overview:		
Complete horizontal and verti	Complete horizontal and vertical delineation not achieved. Spill impact has persisted.			

Sample Point	Depth cm	Sample Date	EC dS/m	SAR	CI mg/kg
Spill area	0-15	2000	18,6	21.1	4400
	15-30	2000	20.9	21.8	5720
Spill area	0-15	2003	14.3	22.9	4112
]	15-30	2003	10.1	19.4	2765
	50-100	2003	22.4	22,4	3534

# Spill 14

	Site Description	Remediation Efforts		
Location:	East-Central Alberta	Remediation system: Passive		
Natural region:	Central Parkland	Source removal details: None		
Soil texture:	Clay loam to clay	Amendment details:		
Soil Classification:	Unknown	0.5 tons/acre of gypsum and two 80 pound bags of calcium nitrate applied in 2001. The area was paratilled to a depth of 45 cm and was rotospiced to a depth of 10 cm.		
Depth to groundwater.	Unknown	paratition to a deptit of 40 off and was follospiced to a deptit of 10 cm.		
Discharge or recharge?	Unknown			
· · · · · · · · · · · · · · · · · · ·	Spill Description	Monitoring		
Brine source:	Surface spill	Sampling events (dates): 2001 and 2003		
Year of release:	1990	Control data? None		
Brine origin (formation):	Mannville	Parameters analysed: Detailed salinity		
Spill volume:	6 m <sup>3</sup>	Groundwater monitoring? None		
Size of impacted area:	600 m <sup>2</sup>	Sample points: 1		
Max investigation depth:	1.0 m	Details of EM surveys: None		
Maximum impact depth:	Unknown			
Overview:				

Sample Point	Depth cm	Sample Date	EC dS/m	SAR	CI meq/L
Spill area	0-30	2001	2.7	111.3	6.8
Spill area	0-15 15-30	2003 2003	5,6 5.7	16.3 52.0	14.9 30.2
	50-100	2003	8.1	60.0	68.4

### Spill 15

	Site Description		Remediation Efforts	
Location:	Peace Region	Remediation system:	Tile drainage system	
Natural region:	Dry Mixedwood	Source removal details:	Flare pit soils	
Soil texture:	Clay loam	Amendment details:	Gypsum applied during construction.	
Soil Classification:	Unknown		71	
Depth to groundwater:	2 to 3 m			
Discharge or recharge?	Unknown			
	Spill Description		Monitoring	
Brine source:	Flare pit	Sampling events (dates):	1998 and 2003	
Year of release:	Unknown	Control data?	Yes	
Brine origin (formation):	Debolt	Parameters analysed:	Detailed salinity	
Spill volume:	Unknown	Groundwater monitoring?	Yes	
Size of impacted area:	Unknown	Sample points:	6 in 2003	
Max investigation depth:	1.4 m	Details of EM surveys:	Completed in 1997	
Maximum impact depth:	Unknown		•	
		Overview:		
Flare pit soils were excavated guidelines, and soils were ex	Flare pit soils were excavated and placed into an LTA between 1991 and 1995. A tile drainage system was installed in the LTA to address soil salinity issues in 1998. By 2003, soils had not reached guidelines, and soils were excavated in 2004. Maintenance of the system while operating was sporadic.			

The Data

See Table 2

# A GUIDE FOR REMEDIATION

## **OF**

# SALT/HYDROCARBON

# **IMPACTED SOIL**

Distributed by:
North Dakota Industrial Commission
Department of Mineral Resources
Bismarck, ND 58505-0840

Funded by the Oil and Gas Research Council

Technical Author Len J. Gawel, Ph.D. BioRem Environmental Consultants 1601 Meadowbrook Dr. Ponca City, OK 74606 (580) 762-3805

# **Remediation Philosophy**

## Goal: Return the site to a state consistent with original land-use.

- Based on practical, accurate, and reproducible procedures.
- Use of select analyses, measurement of key indicators, recommended treatment, and a follow-up program.
- Remediation process presented is continually being evaluated and improved.
- Depending on various factors, plan on 3-4 year remediation duration.

"Remediation requires patience."

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## **Disclaimer**

This remediation guide is published to be used as an aid to the petroleum industry to remediate soil contaminated with salt water or petroleum hydrocarbons.

The author and contributors to the publication are not responsible for any consequences or results that occur upon implementing any recommendation stated in this guide or stated in any oral presentation of this guide.

# Tips For Use of the Field Guide:

- 1. Read and understand the various steps in the remediation guide before using the field guide.
- 2. Establish a record keeping system. Record all data, observations, and processes as soon as possible.
- 3. Maintain consistency in all tests and observations. Remember you are comparing data points to the control sample and to samples over time.
- 4. Always take the control sample first.
- 5. Accuracy and consistency will increase the rate of success.
- 6. The procedures used in this guide are designed to remediate a site over a 3 to 4 year period.

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### INTRODUCTION

The goal of this Remediation Guide is to assist field personnel in restoring impacted soil to a state consistent with the original land use. Sections I through IX of the guide are intended as a field reference for remediation of salt and/or hydrocarbon impacted soils. Documentation of basic soil science used to develop the field guide is included as appendices E (Soil Properties) and F (Soil Chemistry).

This remediation guide is based on practical, reproducible, and field-friendly procedures. The remediation method requires a limited amount of analytical data to formulate a remediation procedure. The analytical methods can be conducted in the field by a trained technician or in a local laboratory. A nominal investment of time and equipment are required to perform these analyses and obtain accurate data. Steps detailing these analyses are outlined in the guide.

When the impact of a produced water or hydrocarbon discharge is examined, a number of critical factors can indicate the immediate and long-term impacts on soil structure and fertility. The use of and response to these factors are key to a successful remediation.

Field experience has demonstrated a success rate greater than 80% when the methods in this guide are properly followed. The remediation is based on a 3 to 4 year duration, with the exception of difficult problem sites, where only partial remediation may be obtained. In these cases, additional remedial actions may be warranted.

The remediation method in this guide utilizes naturally occurring soil amendments, basic soil chemistry, and time to achieve success. Gypsum, the major remediation amendment, is a naturally occurring product in the earth's crust. Additionally, Humex<sup>TM</sup>, (also known as leonardite) is a secondary amendment that is also naturally-derived.

Cost of the remediation process is an important part of the remediation plan; however, cost may vary significantly from area to area. Therefore, costs are not included in this guide.

Record keeping can be tailored to the unique needs of each operator. There is an example of a record keeping form in Appendix D to help organize and archive site and remediation information. The record keeper may prefer to develop their own format and strategies for documentation depending on company requirements and data needs. The use of a GPS unit, a computer, and appropriate software will increase accuracy and reduce time spent on documentation.

### I. IMPACT OF SALT/HYDROCARBONS ON SOIL

#### A. Impact of Salt on Soil

There are three major impacts on soil and plants when salt water spills occur.

- Soil particles are dispersed which destroys aggregation
- Osmotic potential reduces the plants ability to up take water
- Ionic balance of the soil solution is impacted reducing nutrient absorption

#### 1. Impact of sodium on soil and plants

The Na<sup>+</sup> ion of sodium chloride causes the dispersion of the soil. Due to the large number of Na<sup>+</sup> ions available, the Na<sup>+</sup> ions are able to exchange with a sufficient number of the Ca<sup>++</sup> and Mg<sup>++</sup> ions. The Na<sup>+</sup> ion is a large ion therefore weakening the normal soil aggregate stability. The major impact of a salt water spill is the destruction of the soil aggregates by dispersion. Dispersion will occur when more than 15% of the cation exchange capacity sites on clays are occupied by sodium ions and when the total EC in the soil solution is low. The potential dispersion of a soil can be determined by the exchangeable sodium percentage (ESP).

Soil dispersion results in:

- Loss of soil structure
- Loss of pore structure
- Reduced air and water movement
- Reduced bioactivity
- Reduced nutrient transfer
- Increased water run off and erosion of soil

Due to the major impact of the Na<sup>+</sup> ion in the soil root zone, the remediation process is focused on restoring the soil aggregation. When the soil aggregation is restored the secondary impact due to osmotic pressure will also be reduced.

In the remediation process it is very important to treat the soil as soon as possible. Rain on the spill site before gypsum is added will increase the rate of soil dispersion.

As the salt (NaCl) concentration in the water solution increases, the change in osmotic potential makes the roots work harder to take in water. The amount of water intake by a plant will directly affect plant growth. As rain fall events occur salt in the water solution will be diluted. In most cases the first year rain fall (12-14 inches of rain) will significantly reduce the salt concentration in the soil solution.

#### 2. Impact of chloride on soil and plants

Depending on the chloride concentration in the spill event, direct chloride toxicity can occur at high levels of Cl<sup>-</sup> ions. Sensitivity to the Cl<sup>-</sup> ion will depend on the plant species. The Cl<sup>-</sup> ion in the soil water solution is usually flushed below the root zone by the first year of rain fall.

The Cl<sup>-</sup> ion, due to its negative charge, moves rapidly out of the root zone through the negatively charged soil aggregates. Chloride concentration does not have a direct impact on soil structure except for being one of the ions which increases the osmotic potential in the soil solution.

#### B. Impact of Hydrocarbon on Soil

When a hydrocarbon spill occurs, in most cases, salt water is also involved. These spills can be considered an emulsion spill. The impact from both sodium chloride and hydrocarbon affects soil structure and plant growth.

#### 1. Impact of hydrocarbon on soil structure

When hydrocarbons are spilled on soil, the light hydrocarbons will evaporate according to the type of hydrocarbon, temperature, and wind conditions. It is not uncommon to see 20 to 30% of the hydrocarbon evaporate. As might be expected, the higher the API gravity of the crude, the higher the evaporation rate.

The hydrocarbons which do not evaporate will move through the soil. Soil texture and moisture content will determine how fast and how far the hydrocarbons will migrate into the soil profile.

Hydrocarbons move rapidly in moist soil conditions. When soils are saturated (pores filled with water), hydrocarbon movement is reduced. Similarly, in dry soil conditions hydrocarbon movement through the soil will also be reduced. In general, hydrocarbon moves as a contact front through the soil matrix. As the soil wets, the hydrocarbon front moves forward. Hydrocarbon movement through soil is not homogeneous.

Hydrocarbon spills impact soil by:

- Affecting soil physical structure by coating soil aggregates
- Affecting soil water holding capacity
- Reducing and diverting water infiltration into the soil
- Obstructing air and water movement in the soil matrix
- Reducing cation/anion ion exchange on soil aggregates

At low hydrocarbon concentrations, the impact on plants is due to the physical impact on soil structure. Soils contaminated with 1 to 2% hydrocarbon can be remediated with the normal salt spill remediation process. At hydrocarbon concentrations of 4% or greater, some direct toxicity to plants occurs. At hydrocarbon concentrations of 7%, direct toxicity to plants occurs. These actual hydrocarbon concentrations will vary depending on the type of hydrocarbon, type of soil and the species of plants. At hydrocarbon concentrations greater than 2%, additional remediation steps are required which are described in the remediation amendments section.

#### 2. Impact of fresh water on salt water spills

During clean up of hydrocarbons, water or hot water is often used to assist the hydrocarbon removal. <u>DO NOT</u> USE FRESH WATER TO CLEAN UP HYDROCARBONS WITHOUT A CALCIUM AMENDMENT. The most efficient method is to add "BioCal" to the wash water. BioCal primarily contains calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>) and can be diluted with fresh water at a

ratio of one part BioCal to 50 parts of fresh water. If a large amount of washing is required the mix ratio can be increased to 1 to 100.

The calcium amendment can also be over sprayed with a 1 to 20 BioCal to fresh water solution before and periodically during the hydrocarbon clean up. If Bio Cal is not available, gypsum can be added at 5 tons/acre before hydrocarbon washing is initiated.

NOTE: WASHING EMULSION SPILLS OR RECEIVING RAIN PRIOR TO ADDITION OF A CALCIUM AMENDMENT CAN INCREASE THE RATE OF SOIL DISPERSION. THIS WILL ALSO MAKE REMEDIATION MORE DIFFICULT BY INCREASING AMENDMENT CONCENTRATION AND INCREASING REMEDIATION TIME.

Since BioCal is predominantly Ca(NO<sub>3</sub>)<sub>2</sub>, the use of BioCal is restricted in environmentally sensitive areas. Do not use BioCal near ponds or water ways. The nitrates in the BioCal mixture are highly soluble.

#### C. Process of Remediation

The primary goal of remediation is to reduce the amount of soil dispersion caused by the Na<sup>+</sup> ion. This is accomplished by adding calcium ions. Gypsum is a good source of Ca<sup>++</sup> ions in the form of calcium sulfate (CaSO<sub>4</sub>).

As stated earlier, it is important to add gypsum before washing or rainfall occurs on the site.

The first step is to prepare a suitable soil surface to receive the remediation amendments. Under normal conditions, work the top 4 inches of soil similar to a "seed bed." In some areas a layer of hard soil, "hard pan", will be encountered at 6-8 inches into the soil profile. When core tests indicate an impermeable "hard pan," the area should be tilled to 10-12 inches. It is important to have an area below the "active root zone" for flushing of the soluble salts out of the active root zone. For remediation purposes, this is considered below 6-8 inches.

Following the selection of remediation amendments, the amendment material is worked into the soil. In most cases, it is recommended to blend the amendments into the soil by working the top 2 inches of soil. Rototilling or disking are both acceptable methods for this process.

The most critical variable in the remediation process is rainfall. In most remediation processes it takes 12-14 inches of moisture to remediate 10,000 uS/cm of electrical conductivity (EC). This is of particular concern in North Dakota where the annual rainfall is a limiting factor. Ionic exchange can occur during winter months; however, the rate of remediation appears to be slower. This could be a function of temperature reducing reaction rates or the limited water movement under frozen conditions

It generally requires 3-4 years to complete remediation of a 30,000 uS/cm EC soil. This of course is a general estimate of the time required for remediation. Patience is required for a successful remediation.

#### 1. First year remediation

In the first year of remediation, repair to dispersed soil is beginning but may not yet be visually evident. The remediation rate during this first year is slow but accelerates as aggregation of the soil is restored. Close evaluation of the soil will reveal some restoration of the aggregate soil particles and weeds may be present. Soil sampling and testing is generally not required in the first year of remediation.

#### 2. Second year of remediation

In the second year of remediation, aggregation repair is evident and weeds will begin to appear. It may be possible to control weeds by mulching in mid summer to late summer. Weeds should be cut or mulched before seeds are formed.

Late in the second year the site should be sampled and EC and pH analyses conducted. In addition, aggregation and bio-activity should be evaluated. A 40 to 50% remediation improvement at the end of the second year should be expected. If good results are obtained, dormant seeding is recommended. Plant growth on the impacted site will aid the remediation process.

#### 3. Third year of remediation

At the end of the third year the site should be re-sampled and tested for EC, pH, percent aggregation, and bio-activity. A 70 to 90% remediation improvement should be observed. Depending on the site location, the landowner can be allowed to work or plant the site. If the site does not reach 70% of remediation and a cover crop was not planted in year 2, a dormant seeding is recommended. The decision to plant a cover crop and the type of cover crop planted should be approved by the state agencies and the land owner.

#### 4. Fourth year of remediation

By the end of the fourth year, the remediation process should be complete. If the remediation is not complete, additional amendments must be added. Determine the percentage of remediation not accomplished (subtract the current EC reading from the initial EC reading) and reapply this amount of amendment plus 10% to the site. If the EC remediation percentage is not determined, repeat the original amendment at 50% of the original concentration. If the remediation results are not successful it may be beneficial to review the history of the site and the original evaluation data.

### II. SITE EVALUATION

Proper protocol must be followed to identify and report spill occurrences involving salt water and/or hydrocarbon. The area supervisor or environmental technician must follow the prescribed procedure and rules to document the event. Each government agency and operator will have specific reporting procedures. Comprehensive and accurate record keeping is imperative during the remediation procedure.

Several examples of forms used in the remediation processes are provided in the appendices. These forms are provided as templates and can be modified as necessary.

#### A. Measurement of the Site

The process of remediation should begin as soon as possible following an incident. Any precipitation at the site prior to placement of amendments will increase the difficulty of an effective remediation. A thorough evaluation and accurate record-keeping are critical to remediation success. Measurement of the site should include the following steps:

- Determine the size of impact area by measuring the perimeter. The recommended method utilizes a global positioning system (GPS) unit. If a GPS unit is unavailable, a surface wheel will suffice.
- Rule of thumb: When measuring the perimeter, take the perimeter measurement 2 feet out from the impacted area to streamline irregularities in its shape.
- Calculate the square footage of the impact area.
- One acre = 208.71 ft x 208.71 ft = 43,560 sq ft.
- Secure area if necessary (fencing or flags).
- Document the initial site with pictures if possible.

### B. Type of Impact

Generally speaking, oil and gas environmental impacts can be viewed as either current or historical. With the exception of initial response, the approach to their respective remediation procedures is similar. However, in many cases, the historical site may be more difficult to remediate due to age of the impacted site.

Oil and gas environmental impacts are listed below by type. Some cases may require special remediation procedures:

- Salt water (brine)
- Hydrocarbons
- Salt water and hydrocarbons (emulsion)
- Erosion
- Weed control chemicals
- Old pits
- Decommissioning of site removal of base construction material

#### C. Area Topography

Site grade and direction should be recorded in both the permanent record and site sketch. Special attention should be devoted to topography adjacent to the impacted site at potentially sensitive areas.

Determine site grade and direction:

- Flat < 1%
- Slight 1-2%
- Moderate 2-5%
- Steep >5%

Examine the surrounding topography; record hills, valleys, bodies of water, and other significant land features.

Note how to access the impact area.

Communicate with the landowner regarding your remediation plans and address any landowner concerns.

Identify any erosion problems.

- Repair major erosion trails.
- Determine erosion causes and establish erosion prevention program if required.
- In most cases (accidental spills), it may not be possible to repair erosion trails before amendments are placed. Repair erosion problem during remediation.
- In historical remediations, site erosion and lease cover material should be addressed before amendments are applied.

#### D. Soil surface

Identify the general land use such as crop, summer fallow, pasture, etc., and the type and amount of plant growth.

Identify predominant soil types:

- Sand
- Silt
- Clay

Note whether scoria, gravel, or heavy clay removal is required. Will vary by location.

Before a decision is made to remove soils due to salt or hydrocarbon contamination, the following factors should be considered:

- Soil test results and depth of salt penetration if contained in top 1-2 inches removal may be the best option.
- Soil removal (and replacement) is generally recommended for soil conductivities exceeding 35,000 uS/cm.
- Consider sensitivity of area and time required to remediate.
- Hydrocarbon contamination depth and concentration.
- Replacement soil should have an electrical conductivity below 1,000 uS/cm.

Note uniformity of site. This information will be useful in determining sampling procedure.

#### E. Record Keeping

Samples of record keeping forms are located in the Appendices.

Note: Accurate record keeping is critical to remediation success.

## III. Soil Sampling

Three major factors must be considered when developing a sampling procedure for an impact site: number of samples, uniformity of soil surface, and method of obtaining samples.

#### A. Number and Location of Samples

- 1. Number of samples
  - 1/3 acre, 14,520 sq ft = 3 site samples, one control
  - 2/3 acre, 29,040 sq ft = 4 site samples, one control
  - 1 acre, 43,560 sq ft = 5 site samples, one control

Obtain the control sample first, approximately 150 ft from the area of impact. The control sample should represent the area soil. If in question, take an extra control sample and average the EC readings.

#### 2. Site uniformity

Adjust sample number according to site uniformity. Non-uniform features may include heavy clay, sand, heavy scoria, vegetated vs. non-vegetated areas, grade, and other areas significantly different from control:

- More than three non-uniform features add one sample point.
- Less than three non-uniform features reduce one sample point in sites greater than two thirds acre.

### **B.** Procedure for Taking Soil Samples

The technique for taking soil samples must be standardized from sample to sample and site to site. A standard procedure will enable accurate comparison of accumulated data.

- One inch diameter coring tube cut is the most useful soil sample. Sample depth is 6 inches (0-6) inch sample.
- If coring tube is not used, cut an 8 inch deep face with a tilling spade and use a spatula or garden trowel to obtain sample. The sample should be 6 inches deep, 1/2 inch wide and 3/8 inch thick.
- Select sample points to best represent the soil surface of the impact area. Mark location with flags or GPS. Mark location on site map. Sample the non-uniform area if it represents 1/4 of the site area.
- Place the soil sample in a pre-labeled plastic bag. Label bags with pertinent identifying information including:

Site
Date
Sample ID number
Technician's initials

- Roll the bag, eliminating any air trapped within. Do not leave samples in the sun.
- Conduct EC and pH tests within 72 hours if possible. Record results as you complete each analysis.

## IV. Procedure for Conducting Physical Evaluation of Soil

Four physical evaluations of the soil will aid in determining the impact of the incident. In addition, these evaluations will aid in determining the proper remediation procedure and in monitoring remediation progress.

#### A. Percent Aggregation

Determine the amount of aggregation by using the top 1-2 inches of the soil profile.

- Poor no aggregation.
- Fair small clumping but majority of loose particles.
- Good Moderate aggregation throughout soil sample.
- Excellent Consistent throughout sample garden quality soil.

### B. Biological Activity

Determine, by the sense of smell, the presence and amount of biological activity in the top 1-2 inches of soil. The relative amount of "earthy" odor will quantify the amount of biological activity.

- None No earthy odor.
- Fair Faint earthy odor.
- Good Obvious earthy odor.
- Excellent Heavy earthy odor.

#### C. Clay Content of Soil

The clay content of the soil can be determined by the "ribbon test," whereby a small amount of soil is squeezed and rolled between the thumb and forefingers to determine the relative clay content of the soil. Soil that remains intact but curls upon itself is considered to contain greater than 50% clay. Although the type of clay will impact the soil quality, clay type is not considered in the test matrix.

- < 35% normal productive soil
- 35 50% clay soil
- >50% predominantly clay

Note: If it is determined that the soil contains >50% clay, a 20% increase in gypsum should be considered.

#### D. Depth of Topsoil

Depth of top soil can be determined by measuring the soil profile from the core sample or from the sidewall cut. A thicker topsoil layer is ideal for supporting plant growth.

Shallow: 1-2 inchesModerate: 2-4 inchesProductive: 4-6 inches

#### Adjustments:

- Top soil 1-2 inches increase Humex<sup>TM</sup> concentration by 30%.
- Top soil 2-4 inches increase Humex<sup>TM</sup> concentration by 20%.
- Top soil 4-6 inches no increase required.

## V. Soil Analytical Tests

### A. Analytical Procedure to Determine the Electrical Conductivity (EC) of Soil:

- Soil sample preparation
  - a) Mix soil sample from 0-6 inch analysis.
  - b) If soil is "wet," reduce soil moisture content by air drying.
  - c) If soil is "damp," proceed with analysis.
- Measure a level tablespoon of soil into 60 ml of distilled water. This will result in a 1 to 5 dilution of soil, one part soil into four parts distilled water. The volume of one level tablespoon is 15 ml.
- Shake mixture for 2 minutes. After mixing, allow sample to stand for additional 2 minutes.
- Prepare the syringe with the millipore filter adaptor and draw the fluid sample (0.5 to 1 ml) into syringe.
- Place the fluid sample onto the instrument sensor and discard the first sample load. Repeat this "flushing" procedure, then test and record the third load.
- Calculate the EC by multiplying the EC reading on the meter by five.

#### 

- Wash the instrument sensor using a dedicated "wash syringe" and distilled water.
- Record results of the test and other information and disable and discard the syringe.
- Repeat procedure for additional depths, if necessary.

Note: Use the same fluid sample to measure the pH. No additional calculations are needed; pH is measured directly by the meter.

Note: Most EC units read as microsiemens per centimeter (uS/cm). In addition, high EC readings may read as millisiemens per centimeter (mS/cm). It should be noted one millisiemen (mS/cm) is equal to 1,000 microsiemens (uS/cm). Either unit may be used, but to compare data, choose one unit for all analyses, and convert all readings to the chosen unit. This remediation guide uses uS/cm.

A siemen is an inverse ohm (conductance = 1/resistance). The original siemen was measured though a distance of one meter. Most of the field equipment measure one centimeter unit (cm). Although not precise, one millimhos/cm is equal to one millisiemen/cm. For remediation purposes the field guide uses mS/cm or uS/cm.

#### B. Ribbon Test

- Take a sample of soil, add water, and make a ball (size of a golf ball).
- Work soil like putty.
- Squeeze out a ribbon between the thumb and forefinger.
- Sand will feel gritty, silt is smooth and silky, and clay is sticky and forms a ribbon.
- Ribbon of 2 in. or longer -- heavy clay -- 50% plus clay content.

### VI. Selection of Remediation Amendments

#### A. Generic Amendments

Quantity of required amendments can be selected from the generic table provided. The main criterion used in this table is electrical conductivity (EC) of the soil. The generic table is applicable for soils in most of the oil producing counties of North Dakota. Nevertheless, for some counties, the best results may require minor adjustments to amendment quantities.

To tailor chemical amendments most accurately, a set of guidelines are provided below. If the guidelines are not followed, total remediation time may be longer.

Using the EC values from the soil analysis, select the amount of gypsum and Humex<sup>TM</sup> required. The quantity of amendments is given as pounds/1000 sq ft or tons/acre. Note: there are 43,560 sq ft in one acre. EC values are obtained by calculating the average EC of samples in the impacted area.

The remediation procedure is designed to be completed in 3-4 years.

### **GENERIC AMENDMENTS TABLE**

Electrical Conductivity	Gypsum		Humex	
EC's (uS/cm)	lbs/1000 sq ft	tons/acre	lbs/1000 sq ft	tons/acre
0 - 5,000	180	4	100	2
5 - 7,000	227	5	136	3
7 - 10.000	272	6	180	4
10 - 13,000	318	7	250	5.5
13 - 16,000	364	8	318	7
16 - 20,000	450	10	364	8
20 - 25,000	450	10	364	8
25 - 30,000	450	10	364	8

#### **B.** Site Preparation

Depending on the impact on the site, soil preparations prior to the addition of amendments may be necessary. On historical sites, removal of scoria or heavy clay cover is often necessary. In some cases, repair of erosion trails and soil replacement may be required. In discharges of hydrocarbon, salt water, or emulsion, the first priority is fluid containment, recovery, and cleanup.

#### 1. Initial site preparation

- Conduct accidental discharge impact assessment and reporting procedure as required.
- Protect sensitive environments with berms and dikes.
- Initiate cleanup as soon as possible.
- Remove scoria if necessary. Remove heavy clay where used as cap material.
- Apply BioCal or gypsum stabilization amendments as soon as possible (if delay in remediation process seems likely).
- Spray with Ca(NO<sub>3</sub>)<sub>2</sub> solution (BioCal diluted with fresh water 30:1). Application rate of BioCal is 2 barrels of Ca(NO<sub>3</sub>)<sub>2</sub> per acre or treat area with gypsum at rate of 300 lbs/1000 sq ft or 4 tons/acre.
- Work top 2 inches of soil when possible.

Note: The success of any remediation will be significantly reduced if rain or other heavy precipitation occurs on site prior to the application of appropriate amendments and will increase the time and effort required to adequately restore a site to its original condition.

#### C. Addition of Amendments

- 1. Work soil to prepare for remediation amendments.
  - Work soil 4-6 inches.
  - Use disc or rototill equipment.
  - In some cases deeper spiking of the soil may be required to break down "hard pan" area of the soil profile.
- 2. Select amendment treatments from the generic table.
  - Gypsum, agricultural grade if possible.
  - Humex<sup>TM</sup>.
  - Fertilizer 10/20/10/10 or equivalent in area. (nitrogen, phosphorous, potassium, sulfur)
  - Sulfur if required.
- 3. Work soil to incorporate the amendment material to 2 inches.

#### D. Remediation Amendments

Except for commercial fertilizer, all amendments are naturally occurring products. The amendments, in addition to remediating the salt or hydrocarbon contamination, will improve the overall fertility of the soil. The generic amendment recommendation may not meet the requirement of every site and may require adjustments for a more tailored fit. Past experience has shown generic amendments were greater than 80% successful.

#### 1. Gypsum

There are several different grades of gypsum. If possible use agricultural grade gypsum which is more economical but not readily available in North Dakota. Agricultural grade gypsum contains particles ranging from very small dust to 3/8 of an inch. Solubility of gypsum depends on particle size and moisture content of the soil and plays a role in remediation time.

When wallboard gypsum is used, the particle size is uniformly small. Solubility will be more uniform as well. Wallboard grade gypsum will place more calcium in solution per unit of time at a constant moisture level; however, this grade of gypsum is more expensive.

### 2 Humex<sup>TM</sup>

Humex<sup>TM</sup> is the trade name for leonardite, a naturally occurring mineral closely related to soil humus. Humus is an important element of soil fertility. In addition to improving soil fertility, Humex<sup>TM</sup> can be used to reduce weed killer chemical toxicity. Add Humex<sup>TM</sup> according to the Generic Amendment table presented previously.

#### 3. Fertilizer

Fertilizer stimulates microbial growth and increases rate of hydrocarbon biodegradation.

Fertilizer should initially be applied at a rate of 5 lbs/1000 sq ft or 220 lbs/acre. Use 10/20/10/10 or equivalent (nitrogen, phosphate, potassium, sulfur). If hydrocarbon contamination is above 1%, increase fertilizer to 20 lbs/1000 sq ft or 880 lbs/acre.

If hydrocarbon is visible in the second year of remediation, reapply fertilizer at 10 lbs/1000 sq ft. Work soil to aerate and mix in fertilizer to 4 inches.

#### 4. Sulfur

A small amount of sulfur is included with regular fertilizer but more can be added to reduce pH.

2,200 lbs/acre of sulfur is required to reduce pH by one unit (50 lbs/1000 sq ft).

If pH is greater than 8.7, additional sulfur is needed.

Reduction in pH will increase solubility of gypsum and increase remediation rate.

Note: If sulfur is not used in cases where pH is high (>8.6), remediation time will be extended.

#### E. Adjustments of Amendments

Clay content

Clay heavy and content greater than 50% - increase gypsum concentration by 20%.

• Depth of top soil

Shallow (1-2 inches), increase Humex TM concentration by 30%.

Moderate (2-4 inches), increase Humex<sup>TM</sup> by 20%.

Productive (4-6 inches), no increase required.

• pH > 8.7

Increase gypsum by 25 lbs/1000 sq ft (1,100 lbs/acre).

#### F. Winter Remediation

The objective of remediation of produced fluid spills during the winter is containment and recovery. Very little useful remediation can be accomplished when the soil is frozen. The standard remediation process can commence when the soil is no longer frozen and the soil is dry enough to work with tools.

- Contain and recover as much spilled fluid as possible.
- **NEVER WASH A SPILL WITH FRESHWATER**. Doing so will set sodium (salt) on the clay particles and cause dispersion of the soil and will prolong the total

remediation process. To increase hydrocarbon recovery, wash area with a 50:1 solution of fresh water and Ca(NO<sub>3</sub>)<sub>2</sub> (Bio Cal).

- In cases where additional hydrocarbon recovery is not feasible, overspray with a 30:1 solution of freshwater and Ca(NO<sub>3</sub>)<sub>2</sub> (Bio Cal) at a rate of one 55 gal drum/acre.
- As soon as possible, after the soil has thawed, test the soil. If average soil EC is greater than 20,000 uS/cm, overspray with 20:1 freshwater and Ca(NO<sub>3</sub>)<sub>2</sub> (Bio Cal) at a rate of one 55 gallon drum/acre.
- When the area is dry and workable, conduct the regular generic remediation.
- Over spraying with Bio Cal can reduce the gypsum requirement by 30%.

### G. Hydrocarbon/Salt Water Spill Remediation

- Conduct initial containment, recovery, and cleanup as required.
- If hydrocarbon concentrations are less than 1%, no additional treatment is required.
- If hydrocarbons are greater than 1%, follow generic amendment table with the following adjustments:

Increase Humex<sup>TM</sup> by 30%.

Increase fertilizer by 20%.

Work area to 4 inches two to three times per year until remediation is complete.

Evaluate once per year. If required, repeat the Humex<sup>TM</sup> and fertilizer treatment and work soil two times per year.

When hydrocarbon contamination is >5% the remediation should be on a case by case basis.

## VII. ALTERNATIVE REMEDIATION OPTIONS

#### A. Soil Removal

• When the average EC of the 0-6 inch samples is greater than 35,000 uS/cm, soil removal and replacement may be more economical than treatment.

Additional EC measurements are required to determine precisely where the salt contamination is located within the soil profile. Use the same soil analysis procedures as presented previously; the only difference is that specific soil profile intervals are being tested.

Test EC at 0-1 inch

Test EC at 1-2 inches

Test EC at 2-3 inches

Test EC at 6-7 inches

If the EC tests indicate the majority of the salt is concentrated in the top of the soil profile, removal and replacement is the remediation of choice.

• When removal and replacement remediation is used, the quality of the soil replacement is important. Electrical conductivity of replacement soil should be 1,000 uS/cm or less. Test the replacement soil at the source before the soil arrives at the site.

Note: Landowner's consent is required for soil replacement.

#### **B.** Manure Amendments

Manure can be successfully applied as an amendment if a supply of 6 to 8 year old manure is available. Three inches of manure is equal to approximately 6 tons per acre of gypsum.

- Add 3 inches of manure and work material into top 4 inches of soil.
- Need landowners consent to use manure. In most cases, the manure has to come from the landowner's property.
- Manure can carry numerous weed seed species the number of live weed seeds is reduced by the aging process.
- Manure has a high nitrate content. Do not use manure near ponds, streams, water supplies, and residences.
- Work soil two times in the second and once in the third year to stimulate remediation and bacterial growth.
- Control weeds by mulching or mowing before weed seeds mature.
- Remediation time may be extended by one year if manure is used.

## VIII. Remediation Monitoring and Closure

During the remediation process, some monitoring should be conducted to determine the progress of the remediation. In the more difficult remediation sites, some adjustment may be necessary. Note, the remediation process normally requires 3 to 4 years to complete.

#### A. Monitoring

First year: monitoring is not required. In some cases, weed control may be required. Mow weeds before seeds drop.

Second year: conduct EC analysis, percent aggregation, and bioactivity at the original sample points. A 40-50% remediation improvement should be observed. Make any adjustments if required. Weed control is usually required; possibly 2-3 times per year. In some cases, cover crop should be seeded as dormant seeding.

Third year: conduct EC analysis, percent aggregation, and bioactivity at the original sample points. A 70-100% remediation improvement should be observed. Record plant type and growth. Make any adjustments required.

Fourth Year: remediation should be complete and all goals of the remediation process achieved. If remediation is not completed, the site requires re-evaluation and causes other than salt contamination should be considered. Additional treatments may be required. Repeat the original amendments at 50% concentration.

- 1. Incident factors affecting remediation
  - Concentration of salt.
  - Concentration of hydrocarbons.
  - Remediation is not a linear relationship to contamination concentration.
- 2. Environmental factors affecting remediation
  - Moisture (minimum requirement of 12 14 inches rain per year)
  - Soil type
  - Soil texture
  - Past usage
  - Grade/slope
  - Drainage
  - Temperature

#### B. Site Closure

- 1. Who determines site closure:
  - a) NDIC representative
  - b) Operator: Environmental Technician, Foremen, and Environmental Coordinator
  - c) Landowner
- 2. Closure Criteria

Evaluation and consensus determine when the remediation has been completed. Criteria used to determine completion of remediation include:

- Plant growth
- Aggregation of soil
- Bioactivity of soil
- Electrical Conductivity (EC)

EC guideline: 80% of control EC + control EC

Example: Control EC 600 uS/cm

80% control 480 uS/cm Endpoint 1080 uS/cm

Endpoint should be achieved in 4 years remediation.

### IX. SUMMARY OF REMEDIATION GUIDE

#### **Site Evaluation**

Measurement of site

Type of impact

Area topography and soil surface

### **Soil Sampling**

Number of samples

1/3 acre -3 site samples plus one control

2/3 acre – 4 site samples plus one control

1 acre - 5 site samples plus one control

Site non uniformity – more than three, add one sample point

#### **Take Soil Samples**

Coring tube or tilling spade

0-6" deep sample

Place soil in pre-labeled plastic bag

Roll bag to eliminate air, do not leave bag in sun

If soil is wet air dry

### **Conduct Physical Evaluation of Soil**

Percent Aggregation

Poor – no aggregation

Fair – few small clumps (25%)

Good – 60% aggregation

Excellent – garden quality soil

#### **Biological Activity**

None – no earthy smell

Fair – faint earthy smell

Good – obvious earthy smell

Excellent - heavy earthy smell

#### Clay Content (ribbon test)

< 35 % – normal productive soil

35 - 50 % - clay soil

50 % – predominantly clay

#### Depth of Top Soil

1 –2 inches – shallow

2-4 inches – moderate

4 - 6 inches – productive

#### **Soil EC Analysis**

One tablespoon of soil into 60 ml distilled water

Shake mixture for 2 minutes

Draw fluid through filter into syringe

Place fluid into instrument and test third load

Calculate the EC by multiplying by 5

#### Soil pH Analysis

Use same fluid as for EC test to measure pH

The pH measurement is a direct reading

## X. GLOSSARY

**Acid soil:** A soil with a preponderance of hydrogen ions, and probably aluminum, in proportion to hydroxyl ions. Specifically, soil with a pH value of less than 7.0; for most practical purposes, a soil with a pH value of less than 6.6.

**Adsorption:** The attachment of compounds or ionic parts of salts to a surface or another phase. Nutrients in solution (ions) carrying a positive charge become attached to (adsorbed by) negatively charged soil particles.

**Aggregate, soil:** Many fine particles held in a single mass or cluster. Natural soil aggregates, such as granules, blocks, or prisms, are called peds. Clods are aggregates produced by tillage.

**Alkali soil:** (1) A soil with a high degree of alkalinity (pH of 8.5 or higher) or with a high exchangeable sodium content (15% or more of the exchange capacity), or both. (2) A soil that contains sufficient alkali (sodium) to interfere with the growth of most crop plants.

**Alkaline soil:** Any soil whose pH is greater than 7.0.

**Capillary water:** The water held in the capillary, or small pores, of a soil, usually with a tension greater than 60 cm of water.

Cation exchange capacity (CEC): The total amount of exchangeable cations that can be held by the soil, expressed in terms of milliequivalents per 100 grams of soil at neutrality (pH 7.0) or at some other stated pH value. Soil clays and organic matter have a relatively large number of negative charge sites which retain cations in dynamic equilibrium with the soil solution. The number of cation positive charges retained by 100 grams of soil is called the cation exchange capacity.

**CEC:** See cation exchange capacity.

**Clay:** As a soil separate, the mineral soil particles less than 0.002 mm in diameter. As a soil textural class, soil material that is 40% or more clay, less than 45% sand, and less than 40% silt.

Colloid soil: "Colloid" refers to organic or inorganic matter with very small particle size and a correspondingly large surface area per unit of mass. Most colloidal particles are too small to be seen with the ordinary compound microscope. Soil colloids do not go into true solution as sugar or salt do, buy they may be dispersed into a relatively stable suspension, and thus, be carried in moving water. By treatment with salts and other chemicals, colloids may be flocculated, or aggregated, into small crumbs or granules that settle out of water. (Such small crumbs of aggregated colloids can be moved by rapidly moving water or air just as other particles can be.) Many mineral soil colloids are really tiny crystals, and the minerals can be identified with X-rays and in other ways.

**Disperse:** (1) To break up compound particles, such as aggregates, into the individual component particles. (2) To distribute or suspend fine particles, such as clay, in or throughout a dispersion medium, such as water. Dispersion is an electro-chemically induced process which

results in physical movement of clay particles. Dispersion in soil is the reverse process to aggregation. When freshwater is applied after a saltwater spill, it dilutes and leaches the total salt concentration in the soil solution leaving mostly sodium cations to balance electrically the cation exchange sites. This condition of dilute total salts consisting of predominantly sodium cations causes clay particles to repel from each other and migrate into pore spaces thereby clogging pores.

**Dispersed soil:** Soil in which the clay has dispersed. A dispersed soil consists of discrete soil particles which are not segregated into aggregates or structural peds. The soil macropores become clogged with particles and greatly restrict water and air movement into and through the soil.

**EC:** See electrical conductivity.

**Electrical conductivity (EC):** Conductivity measured directly in reciprocal units of resistance and reported in mmhos/cm. EC is an indirect measure of total dissolved solids (TDS).

**ESP:** See exchangeable sodium percentage.

**Exchangeable sodium percentage (ESP):** The extent to which the adsorption complex of a soil is occupied by sodium. Amount of exchangeable sodium expressed as a percentage of total exchangeable cations. Refer to discussion under exchangeable cation percentage. It is expressed as follows:

**Field capacity:** Water content of a soil after it has been saturated and allowed to drain freely, usually expressed as a percentage of its oven-dry weight or volume.

**Gravitational water:** Water that moves into, through, or out of the soil under the influence of gravity.

**Hardpan:** A hardened or cemented soil layer in the B or lower A soil horizon.

**Humus:** The well decomposed, more or less stable part of the organic matter in mineral soils.

**Lime, agricultural:** A soil amendment consisting principally of calcium carbonate, but including magnesium carbonate; used to furnish calcium and magnesium and to neutralize soil acidity.

**Loamy:** Intermediate in texture and properties between fine-textured and coarse-textured soils. Includes all textural classes with the word loam or loamy as a part of the class name, such as clay loam or loamy sand.

**Osmotic:** A type of pressure exerted in living bodies as a result of unequal concentration of salts in both sides of a cell wall or membrane. Water will move from the area that has the lesser salt

concentration through the membrane into the area that has the greater salt concentration; it therefore, exerts additional pressure on its side of the membrane.

**Pans:** Horizons or layers in the soils that are strongly compacted, indurated, or very high in clay content.

**pH, soil:** The negative logarithm of the hydrogen-ion activity of a soil. The degree of acidity (or alkalinity) of a soil as determined by means of a glass electrode or indicator at a specified moisture content of soil-water ratio and expressed in terms of the pH scale (see reaction, soil).

**Pore space:** The total space not occupied by soil particles in a bulk volume of soil.

**Porosity:** The volume percentage of the total bulk not occupied by solid particles.

**Saline-sodic:** (1) A soil containing sufficient exchangeable sodium to interfere with the growth of most crop plants and also containing appreciable quantities of soluble salts. (2) A soil in which the exchangeable sodium percentage (ESP) is greater than 15% and the conductivity of the saturation extract (EC) is greater than 4 mmhos/cm.

**Saline soil:** A nonsodic soil containing sufficient soluble salts to impair its productivity. The conductivity of the saturation extract is greater than 4 mmhos/cm (at 25°C) and the pH is usually less than 8.3.

**Salinity:** A term describing water solutions containing dissolved mineral solids. The U.S. Geological Survey has assigned terms for degrees of salinity for waters with the following dissolved-solids concentration ranges:

Slightly saline 1,000 to 3,000 mg/L
Moderately saline 3,000 to 10,000 mg/L
Very saline 10,000 to 35,000 mg/L
Briny over 35,000 mg/L

**Sand:** (1) A soil particle between 0.05 and 2.0 mm in diameter. (2) Any one of five soil separates, namely: very coarse sand, coarse sand, medium sand, fine sand, and very fine sand. (3) A soil textural class.

**SAR:** See sodium adsorption ratio.

**Silt:** As a soil separate, individual mineral particles that range in diameter from the upper limit of clay (0.002 mm) to the lower limit of very fine sand (0.05 mm). As a soil textural class, soil that is 80% or more silt and less than 12% clay.

**Sodium adsorption ratio (SAR):** The empirical mathematical expression developed as an index of the sodium hazard in soils. The concentrations of sodium, calcium, and magnesium are expressed in meq/L:

$$SAR = \frac{[Na]}{\sqrt{[Ca] + [Mg]}}$$

**Soil separates:** Mineral particles less than 2 mm in equivalent diameter and ranging between specified size limits. The names and sizes (in mm) of separates recognized in the U.S. are as follows:

 Very coarse sand
 2.0 to 1.0 mm

 Coarse sand
 1.0 to 0.5 mm

 Medium sand
 0.5 to 0.25 mm

 Fine sand
 0.25 to 0.10 mm

 Very fine sand
 0.10 to 0.05 mm

 Silt
 0.05 to 0.002 mm

 Clay
 less than 0.002 mm

**Soil solution:** The aqueous liquid phase of the soil and its solutes that consists of ions dissociated from the surface of the soil particles and of other materials.

**Structure, soil:** The arrangement of primary soil particles into compound particles or aggregates. The principal forms of soil structure are as follows: *platy* (laminated), *prismatic* (vertical axis of aggregates longer than horizontal), *columnar* (prisms with rounded tops), *blocky* (angular or subangular), and *granular*. *Structureless* soils are either *single grained* (each grain by itself, as in dune sand) or *massive* (the particles adhering without any regular cleavage, as in many hardpans).

**Texture, soil:** The relative proportions of sand, silt, and clay particles in a mass of soil. The basic textural classes, in order of increasing proportion of fine particles, are *sand*, *loamy sand*, *sandy loam*, *silt loam*, *silt*, *sandy clay loam*, *clay loam*, *silty clay loam*, *sandy clay*, *silty clay*, and *clay*. The sand, loamy sand, and sandy loam classes may be further divided by specifying "coarse," "fine," or "very fine."

Note: definition of the terms included in this glossary were excerpted from API publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities.

# XI. APPENDICES

## **APPENDIX A**

### **Environmental Equipment List**

EC and pH meters

Filter

**Spatulas** 

Measuring wheel

Hand-coring tool

Plastic, stacking sample cups (for mixing soil/distilled water)

Whirl-pak sampling bags – or Ziploc type plastic bags

pH buffer standards

Wash bottles (distilled water)

Hand garden trowel

Box to store smaller equipment

**GPS** 

Vest

Logbook/composition book

Digital camera

Indelible pen (permanent marker or ink pen)

Site evaluation and investigation forms

# APPENDIX B

# **Analytical Equipment and Amendment Suppliers**

Product & Product Information	Approx. <u>Price</u>	<b>Suppliers</b>
EC and pH Meters		
Cary Twin EC Meter #2205	\$294.00	Spectrum
Cary Twin pH Meter #2103	\$249.00	Technologies, Inc.
pH Pro Meter #2100A	\$169.00	23839 W Andrew Rd
		Plainfield, IL 50644
		1-800-323-4340
T214		www.specmeters.com
<u>Filters</u> National Scientific	\$133.00	National Scientific
25 mm Nylon Filters	\$133.00	1790 Satellite Blvd
Part # F2500-50		Bldg 180
Pore size – 5.0 um		Duluth, GA 30097
Qty/box - 50		1-800-332-3331
Qty/00X = 30	<b>W</b> /3	ww.nationalscientific.com
	<u></u>	www.mattonansetentific.com
C-21 C		
Soil Sampler Tube Cole-Parmer	\$ 21.00	Cole-Parmer
10-inch, hand soil sampler	\$ 21.00	625 East Bunker Court
Page 1744		Vernon Hills, IL 60061
#U – 99027-00		1-800-323-4340
110 77027-00		www.coleparmer.com
		www.coreparmer.com
LSS Lab Supplies	\$ 33.40	LSS Lab Supplies
17-inch hand soil sampler		PO Box 1368
Page 802 #4BC - 106078		Janesville, WI 53547
		1-800-356-0783
		www.lss.com
pH Buffer Standards		
Pint size	\$ 9.00	Cole-Parmer,
pH 7.0	Ψ 2.00	National Scientific, or
pH 10.00		LSS
r		
Wash Bottles		
250 ml	\$ 20.00	Any supplier listed
		above

### **Miscellaneous**

Tilling spade
Hand garden trowel—6 inch blade, narrow and sharp
Box to store smaller equipment
Plastic containers for mixing soil and distilled water
Distilled water
Spatulas
Measuring wheel
Humex<sup>TM</sup>
GeoRe

GeoResources, Inc. P.O. Box 1505 Williston, ND 58802 (701) 572-2020 www.georesources.net

# **APPENDIX C**

### **References and Additional Resources**

- Plaster, Ed. S. 1992. Soil Science and Management, 3<sup>rd</sup> Edition. Delmar Publishers.
   Brady, N.C. and Weil, R.R. 2002. The Nature and Properties of Soil, 13<sup>th</sup> Edition. Prentice Hall.
- Bohn, H.L. et al. 2001. Soil Chemistry. 3<sup>rd</sup> Edition. John Wiley and Sons, Inc.
   American Petroleum Institute- Remediation of Salt-Affected Soil At Oil and Gas Production Facilities.

# APPENDIX D

# **Record Keeping Form Example**

Date	Site Name	
Location Information_		
		nty
Volume of Fluid		
	over one percent: yes / no	
Area Impacted (sq. ft.)	)	
Area H. C. penetrated	soil over 10 inches (sq. ft.)	
Immediate Spill Respo	onse	
Type of release		
Environmental Impact	:	
Crop kind	Range land	Surface water
Special Environmenta	l Endangerment	
	Remediation	o <u>n</u>
Date	Soil Work	
Gypsum(lbs)	Humex <sup>TM</sup> (lbs)	Fertilizer(lbs)
Organic Material		
Final Soil Work		
Soil and Weather Con	ditions	
Soil Work History		
Form Completed by:	Date	

### APPENDIX E

### **Soil Properties**

### A. Physical Components of Soil.

Soil has four physical components; inorganic solids, organic matter, air and water. The typical proportions of these components in a healthy soil are:

45% inorganic solids 5% organic matter 25% air 25% water

Depending on the environment, the percentage of air and water in the pore spaces can change in a relatively short time period. In contrast, inorganic solids and organic matter remain somewhat constant but can change over long periods of time.

Although soil appears to be a simple media, it is the most complex ecosystem on our planet. As the world population grows, we are experiencing a high demand on our soils for agriculture use as well as for non-farm use. In addition, our soil quality is deteriorating due to poor agriculture practices.

Soil is a renewable resource but the process is very slow. Due to many factors, agricultural soil is impacted, rearranged, lost, and even destroyed as a functional agricultural media.

Soil fertility is the result of a relationship between physical, chemical, and biological components of soil in an interactive balance. The ratio of one element to another is more important in soil fertility than the level of total nutrients. The key to soil fertility and plant growth is ionic balance among the four physical components in the soil solution.

### 1. Inorganic Solids

The inorganic parts of soil are made up of three components: sand, silt, and clay. These solids occur as a mixture of variously sized particles, known as "soil separates," and contain various types of chemical charges. Soils types are classically differentiated by particle size.

	Particle Size	Particle Texture	Chemical	Approx. surface
	(mm)		Activity	Area (sq ft/g)
Sand	2 - 0.05	Gritty	Inactive	0.05
Silt	0.05 - 0.002	Silky	Inactive	5
Clay	< 0.002	Waxy	Active	5,000

The various amounts of each soil separate (sand, silt, and clay) will determine the properties and fertility of soil. Clays and organic matter are chemically active (are negatively charged) whereas sand and silt are not. Organic matter should also be considered a soil separate even though it is not included in particle size classification. Nevertheless, organic matter in soil constitutes a

major role in soil fertility and plant growth. It is common for fertile soil to contain 5% organic matter.

Soils also contain large-size particles (> 2 mm) like gravel and stones. These larger sized particles are not a major concern unless they occupy large volumes of space in the soil.

The sand and silt particles commonly consist of quartz, mica, and feldspar minerals. These particles are not chemically active and function as a media for plant roots and associated chemical reactions which occur in the water interface of the soil.

Clay particles in soils are negatively charged and chemically reactive. Clays are the focal point of a majority of the chemical reactions in soil chemistry. This is due primarily to the volume of clay as compared to the volume of organic matter in the soil.

A wide variety of clay particles with very different characteristics are found in the soil. The differences in clay type will affect the characteristics of the soil quality.

### 2. Soil Triangle

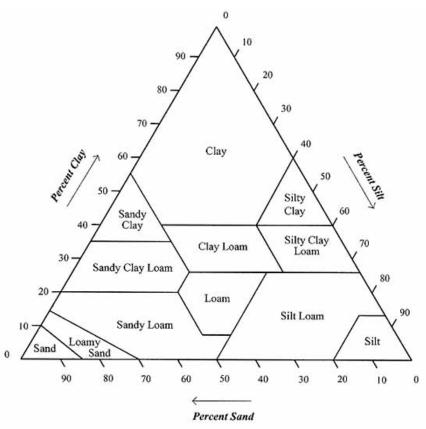


Figure 4 - Textural triangle illustrating the twelve USDA soil classifications.

- Soil with 40% clay it is classified as a clay soil.
- Soil with 50% sand is classified as a sandy soil.
- Soil with equal parts of sand and silt and 20% clay is considered a loam type soil.
- Each soil separate has a broad range.
- Soil texture combinations include: loam, sandy loam, silty loam, and clay loam.

### 3. Soil Clays

There are many different clay types and various charge properties. In this remediation guide, clay content is not broken down by clay type and is considered as "total clay."

It is possible to estimate the total cation (-) charges in the soil by determining cation exchange capacity (CEC). The CEC is related to the clay "activity" in soil but its use in soil remediation is questionable. Moreover, since there are no simple in-the-field methods to determine CEC, analyses must be conducted in a laboratory which can take considerable time to obtain. Nonetheless, CEC data has indirect applicability when developing a remediation strategy: in

most soils, as clay content increases, the CEC will correspondingly increase. Therefore, for the purposes of this guide, amendment volumes are adjusted relative to soil clay content.

### 4. Organic Content of Soil

Mineral soils like those typically found in North Dakota commonly contain 4 to 5% organic matter. Similar to clays, organic matter is chemically active and normally carries a dominant negative charge. Organic matter can exceed 40% of the total CEC of the soil. Proportionately, organic material accounts for only 5% of the soil volume yet contributes at least 40% of the CEC.

Organic matter is the single most important material responsible for the stability and formation of soil aggregation. In turn, soil aggregation is central to soil fertility. A majority of the nutrients are supplied, stored, or in part produced by the complex organic matter. This material also aids the storage of moisture. Organic matter and humus are considered to be the same material.

The source of a majority of the organic matter found in soil comes from the decomposition of plant tissue. A complex group of microorganisms biodegrade plant tissue to form humus. In addition, certain forms of animal life like earthworms, ants, and centipedes also are involved in the formation of organic matter. Humus is highly colloidal and is amorphous in nature.

The large variety of compounds found in humus is due primarily to the various rates of biodegradation of organic compounds. In the process of forming soil humus, all the nutrients and elements are made available for healthy plant growth. Chemical elements in this process are carbon, hydrogen, oxygen, nitrogen, phosphorous, potassium, sulfur, calcium, magnesium, and a variety of trace elements. Various mineralization cycles continue to drive the process.

The formation of humus (organic matter), although an exceedingly complex biochemical process, is reduced to relatively simple terms. Factors which stimulate the production of humus also increase soil fertility.

An increase in salt concentration in soil will reduce biological activity and reduce the production of humus. To reduce this impact, Humex<sup>TM</sup> is added to the soil following a salt water spill event. The Humex<sup>TM</sup> amendment will increase the microbiological activity which will stimulate the production of humus. In addition, the addition of Humex<sup>TM</sup> will help restore the formation of aggregation in the soil. Humex<sup>TM</sup> will also assist the transportation and adsorption of water in the soil.

Humex<sup>TM</sup> can also be used to increase the biodegradation rate of chemicals commonly used for lease weed control.

#### 5. Sand and Silt

Although sand and silt particles are not chemically active, they do play an important role in the total fertility of soil. In the soil triangle classification, when clay content of soil is 20-30% and sand and silt are 30-40%, an "ideal" loam soil is obtained. Organic matter, although not part of the particle classification, should be 5% of the total soil composition.

Sand and silt together form the bulk of the soil media. Pore spaces between the sand and silt particles allow the exchange and infusion of air and water into the soil root area. A pore space of 50% is considered optimum.

In an ideal mixture of sand and silt, pore spaces provide for easy penetration of roots and unimpeded mixing and exchange of air, water, and nutrients in the rhizosphere (plant root zone).

Determination of the relative proportions of silt, sand, and clay in soil can easily be conducted in the field using the classic "ribbon test," whereby a small amount of soil is squeezed between the thumb and forefingers to determine the relative clay content of the soil. Soil that remains intact but curls upon itself is considered to contain greater than 50% clay. Although the soil content of sand and silt is not directly related to determining amendment concentration, small adjustments may reduce the time required to remediate the site.

Sand particles will feel gritty in a water/soil paste mixture. In contrast, a silt component of soil will feel silky and smooth but will not have structure like the clay particles. Clay will have a waxy feel with the structural strength related to clay content.

An "ideal" soil solids mix consists of:

Silt 40%
Sand 30%
Clay 25%
Organics 5% "plus"

### B. Soil Profile

Soil is divided into several horizons depending on the depth from the soil surface. The majority of the remediation will be focused in the top A horizon which is usually 10 inches in depth. The soil profile may also include the top 1 to 2 inches which in prairie, forest, and continuous cropping environments is described as the loose non-organized O horizon. In cropped and cultivated environments, the O horizon is unrecognizable.

In a majority of cases, we are concerned with remediation of the top 6-8 inches of soil (i.e., the root or plow zone). The major impact of a spill occurs in this "top soil" area where a majority of the plant's roots are active. Roots can penetrate below the 10 inch A horizon. However, the top 6-8 inches of soil will contain the majority of salt and/or hydrocarbon in a spill event. This area also contains the majority of the plant roots and a majority of the biochemical soil interaction. Therefore, remediation will focus on removing the contaminants from the A horizon and restoring the soil to its original productivity.

# **SOIL PROFILE**

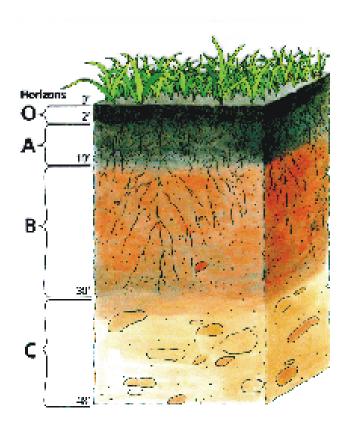


Photo © http://www.mo15.nrcs.usda.gov/.../ images/horizons.gif

Profiles vary from site to site. Remediation involves the top 6 to 8 inches of soil. Soil horizon types and depth influence contamination and thus, the remediation process; however, we will consider this parameter only in spills of significant impact.

### C. Soil Aggregation

One of the most important properties of soil structure is aggregates. The aggregate structures are produced naturally in soil under normal conditions. Aggregates are the bases of soil fertility and plant growth and are formed from a mixture of sand, silt, clay, humus, minerals and bacterial interactivity. The amount of aggregates can be enumerated by visual inspection.

### Soil aggregation:

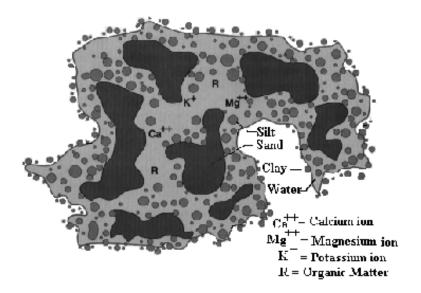
- Provides pore spaces for proper nutrient exchange.
- Allows moisture to enter and be stored in the root zone.
- Promotes gas exchange in the root area.
- Provides a stable media for root development.
- Promotes bacterial activity for mineralization cycles.
- Provides a medium for maximum plant development and nutrient uptake.
- Provides an environment where plants can survive adverse conditions.

Aggregation of soil is destroyed by an introduction of high amounts of sodium ions. The high sodium concentrations cause an imbalance in the cation exchange capacity and promote a state of dispersion. When aggregation is destroyed by sodium, dispersion of soil particles occurs. In addition, osmotic stress on the plant root occurs. The osmotic stress reduces the plants ability to obtain water from the soil.

### Soil dispersion causes:

- Loss of aggregate structure.
- Loss of pore structure.
- Reduction of air and water movement in soil.
- Reduction of biological activity.
- Reduction of nutrient storage and transfer.
- Increased water run off and erosion.

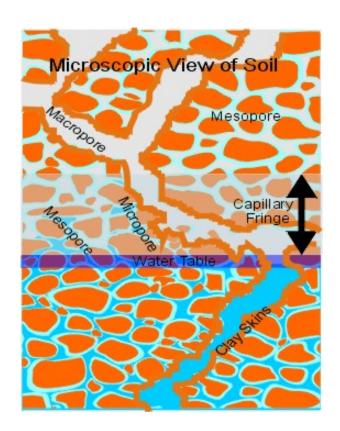
The major consequence of a saltwater spill is the loss of soil aggregation and the inability of soils to properly mobilize soil moisture due to osmotic stress. In short, dispersion destroys soil fertility.



# Parts of the A horizon:

- Solids
- LiquidsGases

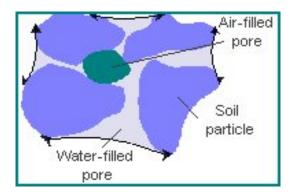
Aggregate/peds



 $\begin{array}{ll} \text{Macropores} & 0.80-5+\text{ mm} \\ \text{Mesopores} & 0.03-0.08\text{ mm} \\ \text{Micropores} & 0.005-0.03\text{ mm} \\ \text{Ultramicropores} & 0.0001-0.005\text{ mm} \end{array}$ 

Cryptopores < 0.0001

Soil aggregates are larger and more stable in native prairie than in cultivated crops.



Factors which hold aggregate in equilibrium:

- Electronic charges
- Microorganism activity in the rhizosphere (bacteria, actinomycetes, mold, yeast)
- Bacterial "glues"
- Organic material humus (clays, iron oxides)
- Balanced water chemistry
- Buffering capacity of soil chemistry

### D. Soil pH

The pH value determines to what degree the soil environment is acidic or alkaline. The pH of a solution is the logarithm of the reciprocal of the hydrogen ion concentration where pH =  $\log 1/H^+$  and  $H_2O$  is ionized as an  $H^+$  cation (acid) and an  $OH^-$  anion (base).

A pH value between 6.5 and 7.5 is considered optimum for the growth of many plants. Although many plants respond to an optimum pH, this value usually covers a range from 0.5 units below to 0.5 units above the optimum level. It should be noted one pH unit is a factor of 10. Therefore, plants have a fairly broad pH tolerance.

The pH of soil influences the absorption and availability of nutrients to plants. There are two general sources of soil nutrients. Some nutrients are absorbed on colloids and some are available to plants as ions in solution. In both cases the various nutrients are present as ions. In most cases the cations (positively charged ions) are absorbed on colloids and the anions (negatively charged ions) are in solution.

Soil is a highly buffered ecosystem. Hydrogen ions in the soil solution are in equilibrium with negative exchange sites on the soil particles. In cation exchange, hydrogen acts as a reserve pool which continuously supplies hydrogen ions to the soil.

In areas of high rainfall, soil tends to be acidic due to the leaching effect on the exchange sites. In arid and semi-arid regions, soils tend to be basic. Basic soils have higher concentrations of calcium, magnesium, and sodium carbonates.

The pH of soil varies significantly in thin soil zones. These variations in pH are due to differences in both macro and micro ecosystems. The microbial population near root surfaces is an example of such an ecosystem. The rhizosphere bacteria population significantly impacts pH this microsystem and thus affects plant growth and the progress of soil remediation. Restoring the rhizosphere bacteria population and activity significantly increases available nutrients to the soil.

Since most soils in North Dakota are basic, the addition of sulfur with fertilizer is an important part of the remediation. As pH approaches 8.7, the addition of sulfur can be justified. To lower the pH of an 8 inch deep loam soil 0.5 pH units, 1,000 lbs of sulfur per acre is required. Sulfur lowers the pH thus increases the solubility of gypsum.

### E. Soil Moisture

The volume and movement of water in the soil is the single most important factor determining plant growth. Depending on the plant, water comprises 50% to 90% of the plant tissue. Photosynthesis and nutrient availability depend on water. Water is the solvent in which all chemical reactions take place.

Similarly, water is the most important factor determining remediation of salt water and hydrocarbon spills. Approximately 12-14 inches of rain are required to remediate 10,000 uS/cm of electrical conductivity per year, depending on soil type.

Gravitational force pulls water down through the soil matrix and is the predominant influence on water movement in soil.

Water can also move by capillary action due to hydrogen bonding and the subsequent magnetic attraction of water molecules to one another. Capillary forces can overcome gravitational forces and move water in a direction other than straight down into the soil. Both gravitational and capillary water movement is influenced by soil particle type and distribution in the soil.

Water around soil particles is controlled by adhesive and cohesive forces. "Adhesion water" is held tightly and does not move. In contrast, "cohesion water" is held more loosely on soil particles and can be utilized by plants. Cohesive forces and capillary forces move water against gravitational forces in the root zone to increase water utilization by plants.

The osmotic potential of water becomes important in a saline soil. At high salt concentrations, a higher osmotic potential decreases the movement of water into plants. Additionally, more energy is required to move water into the root at higher osmotic potentials.

Following a rain event, the soil is saturated as soil pores fill with water. Gravitational forces drain water from the root zone. Depending on the soil and amount of rain, the draining process is completed in 48 to 72 hours. As the soil drains, the soil reaches a "field capacity" state. At this point, air will fill the large pores and each soil particle will have a thick film of moisture

(cohesion water). Plant uptake and evaporation will continue to deplete the cohesion water and shrink the soil-water film. As the film becomes thinner it is more difficult for the root to absorb water. As this process continues and capillary water and additional rain fall does not replenish the root zone, a "wilt point" will develop.

During this process of saturation and drainage, calcium ions can replace the sodium ions and remediation can occur. It is important that water move evenly though the soil as it drains out of the root zone. Therefore, pre-work of the soil to produce a "remediation seed bed" to facilitate water drainage out of the root zone is helpful to the total remediation process. Soil texture will determine the "water retention" capacity of a soil. A loamy soil will remediate at a faster rate than a sandy or heavy clay soil.

### APPENDIX F

### **Soil Chemistry**

### A. Chemical Elements

All matter is made up of elements. There are 107 known elements. These elements make up what is known as the periodic table. The atom is the smallest unit of an element. In turn, atoms are made up of three particles, protons, neutrons, and electrons.

Positively charged particles are protons, neutral particles are called neutrons, and negatively charged particles are called electrons. In the configuration of the atom, protons and neutrons inhabit the nucleus, the center of the atom. Around the nucleus in various orbits are the active electrons. Different configurations of the electrons and nucleus will change atomic properties and behavior. The total weight of all electrons, protons, and neutrons make up the atomic weight of the atom. Atoms combine to form molecules. Molecules combine with other molecules to form compounds.

Soils contain all the natural chemical elements of the periodic table. However, only a few elements make up 95 percent of the earth's mass. The majority of the elements in the periodic table are present only in trace and micro amounts.

In soil, there are 17 elements which impact plant growth. The distinction between essential elements and toxic elements is the type of element and concentration of the element.

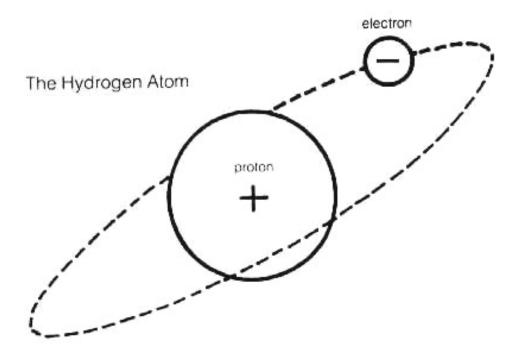
Most of the elements are present as ions in soil solution and flow to roots in a water solution. Plants have a wide range of tolerance to elements and can select the ions required by the plant. However, in cases of salt water spills, the balance of Na<sup>+</sup> (sodium) ions and Cl<sup>-</sup> (chloride) ions are now artificially increased. This imbalance impacts both soil structure and plant physiology.

Chemical reactions in soil are rapid compared to water and air environments. As a general comparison, reaction rates in air can be measured in days and years, in water, hours, and in soil, seconds and minutes.

Soils are colloidal, meaning that they are made up of very small particles (1 to 1000 nm). Each colloidal particle has surface area. It is this surface area on which chemical reactions in soils take place. Not surprisingly then, soils have an astoundingly sizeable surface area for chemical reactions to occur.

Although many chemical reactions are possible in the soil/water interface, only a few elements dominate the impact of salt water spills and thus impact the soil remediation process. Water, sodium chloride, and calcium sulfate are the dominant species we are concerned with in salt water spills and the remediation of the impact. The elements of primary importance are: H<sup>+</sup> and O<sub>2</sub><sup>--</sup> in water, Na<sup>+</sup> and Cl<sup>-</sup> in salt and Ca<sup>++</sup>, S, O<sub>2</sub><sup>--</sup> in gypsum.

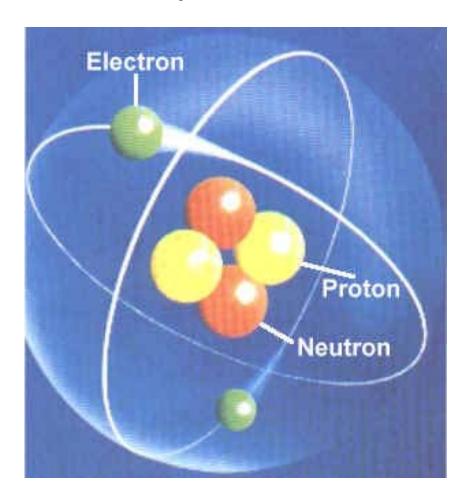
Hydrogen is the simplest element in the periodic table. Hydrogen has one electron and one proton as shown below.



From: http://www.airpower.maxwell.af.mil/airchronicles/aureview/1984/jul-aug/roberds.html

An atom is the smallest unit of an element. Atoms are made of three particles:

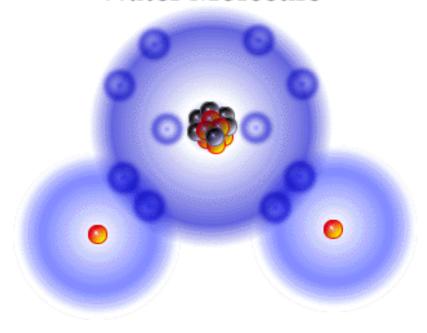
- Electron a negatively charged particle
   Proton a positively charged particle
   Neutron a neutral particle



Atoms combine to form molecules.

- Molecules form compounds.
- State of ionization: Normal compounds (atoms) have equal numbers of electrons and protons. If an imbalance occurs, the molecules (atoms) become ions.  $H_2O = 2H^{2++} + O^{--}$
- $H_2O = protons + anions$

# Water Molecule

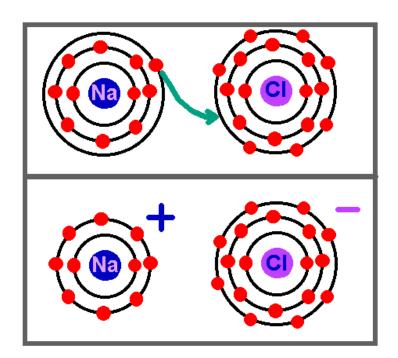


# Sodium chloride

NaCl = Na<sup>+</sup> + Cl<sup>-</sup>
Sodium Chlorine
Na<sup>+</sup> Cl<sup>-</sup>
Cation Anion

11 electrons 17 electrons 11 protons 17 protons

10 electrons 18 electrons 11 protons 17 protons



### Calcium sulfate

$$CaSO_{4} = Ca^{++} + SO_{4}^{--}$$

$$Ca^{++} + SO_{4}^{--}$$

$$Cation + SO_{4}^{--}$$

$$Cation + Anion + SO_{4}^{--}$$

$$20 \text{ electrons} + SO_{4}^{--}$$

$$S = 16 \text{ e$$

Cations/Anions

Cations (positively charged molecules)

Cation exchange capacity (CEC): the total number of cations absorbed by the soil particles.

Sodium (Na<sup>+</sup>) Calcium (Ca<sup>++</sup>) Magnesium (Mg<sup>++</sup>) Potassium (K<sup>+</sup>) Aluminum (Al<sup>+++</sup>) Hydrogen (H<sup>+</sup>) Phosphates (P<sup>+</sup>, H<sub>2</sub>PO<sub>4</sub><sup>++</sup>)

Basic soils: Na<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, K<sup>+</sup>

Sodium has the lowest absorption strength.

Acid soils: Al<sup>+++</sup>, H<sup>+</sup>

Cations -- continually absorbed and replaced on clay particles.

Soil particles are negatively charged and are in balance with positively charged cations. That resistance/repellency creates spaces between soil particles, creating aggregation.

Anions (negatively charged molecules):

Chloride Cl Sulfate SO<sub>4</sub>

Carbonate CO<sub>3</sub> Bicarbonate HCO<sub>3</sub>

Nitrate N<sub>0</sub><sub>3</sub>

Anions are mobile.

Soils have a low anionic exchange capacity.

### B. Dispersion In Soils

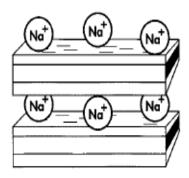
Salt water spills impact soils and plants by dispersing soil particles and causing osmotic stress on plants. Soil dispersion destroys soil structure and osmotic stress reduces the ability of plants to utilize water. The negatively charged ions in soil are primarily from clay micelles and organic material.

- 1. Salt water impact and soil aggregation
- Na<sup>+</sup> ion becomes the dominant cation as compared to Ca<sup>++</sup> and Mg<sup>++</sup> ions.
- The larger Na<sup>+</sup> ions break the soil aggregate bonding causing soil to disperse. Na<sup>+</sup> ion has a weak chemical charge.
- Total salt concentration (EC) increases.
- Soil solution has lost its chemical balance due to the high increase in Na<sup>+</sup> and Cl<sup>-</sup> ions.
- High levels of Cl<sup>-</sup> ions can cause direct toxicity to plants. However, chloride ions are negatively charged so they move rapidly through the soil and out of the root zone.
- Rain on soil with high Na<sup>+</sup> ion concentration will accelerate the dispersion process.
- 2. Salt water impact on osmotic pressure
- As total salt concentration increases the osmotic pressure in the water increases.
- In high osmotic environments, plants must spend more energy to absorb water.
- The soil matrix may have sufficient water but the plants cannot utilize the water, show stress, and wilt.

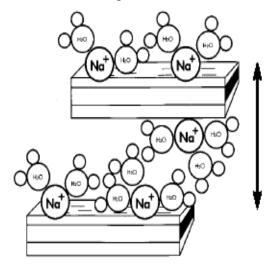
# **DISPERSION**

## Sodic clay

sodic clay (high ESP)



In a sodic soil; sodium, Na<sup>+</sup> is adsorbed onto the surface of the clay. It is a large ion with a weak charge. The positive ions bind the negatively charged clay particles together. sodic clay + water



As water is added to a sodic soil the water is attracted to the sodium. The ions hydrate, forcing the plates apart. The ions' role in binding the clay platelets is overcome, and the clay swells then disperses with water.

# **CLAY BRIDGE STRENGTH**

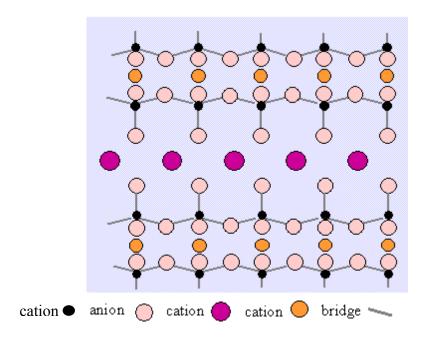


Figure 3:

The sandwich structure of silicate clays.

Layers of silica ions ( ) bridged with two oxygen ions ), form bonds with other cations ( and ). The strength of the bond differs with the cation. Weak bonds such as those formed with sodium ions cause clay particles to break up in water, clogging soil pores and increasing the mechanical resistance to root growth.

### C. Acidity and Alkalinity of Soils

### 1. pH/acidity/alkalinity

In the soil remediation process, acidity and alkalinity are measured by determining the pH of the soil solution. Although the pH is not a true measurement of acid/base buffered reaction in soil, it does reflect the range of acidity vs. alkalinity.

A pH meter measures the hydrogen ions in solution. The higher the hydrogen ion concentration, the more acidic the soil and the lower the pH number. As discussed earlier, pH is the logarithm of the hydrogen ion concentration.

The majority of North Dakota soils are basic or alkaline. This is due to the high base saturation of the soil. The calcareous nature of the soil promotes the hydrolysis of the calcium carbonate resulting in a high (basic) pH. The actual pH of a soil with a base saturation below 100 percent depends on the balance between hydroxyl ions and hydrogen ion reaction. If the sodium saturation exceeds 15 percent, the hydrolysis of sodium produces lye. This reaction will increase the pH. High sodium soils are called sodic soils.

The pH of soil will affect the availability of plant nutrients. In the remediation process, pH is not considered a remediation issue until it reaches 8.7. At a pH of 8.7, the solubility of gypsum is significantly reduced and will increase remediation time.

### 2. Sources of alkalinity

- Predominant cations in soil are Ca<sup>++</sup>, Mg<sup>++</sup>, K<sup>+</sup>, and Na<sup>+</sup>.
- The hydroxyl (OH) ions are principally carbonates (CO<sub>3</sub>) and bicarbonates (HCO).
- Anions originate from the dissolution of such minerals as calcite (CaCO<sub>3</sub>).

$$CaCO_3 \leftrightarrow Ca^{++} + CO_3^{--}$$
  
 $CO_3^- + H_2O \leftrightarrow HCO_3^- + OH^-$ 

• In regions of low precipitation (18-20 inches), rainfall is not sufficient to leach away cations formed by mineral weathering.

### 3. Source of acidity

- Production of H<sup>+</sup> predominantly from soluble Al<sup>+++</sup> and Fe<sup>+++</sup>.
- Carbon dioxide produces acids in the root zone from respiration by roots and organic acids from microbial activity.
- Rainfall generally slightly acidic.

### D. Amendments in Remediation

### **Gypsum**

Gypsum is the main remediation amendment. Gypsum is  $CaSO_4^+ + 2~H_2O$  and is a widely distributed mineral in the earth's crust. It has limited solubility in water at 0.24 g/100 ml of water. Calcium ( $Ca^{++}$ ) in gypsum replaces  $Na^+$  ions on the micelle clays and re-establishes aggregation in the soil.

The initial stages of remediation are the establishment of a soil structure – aggregation. Gypsum is a naturally occurring mineral. Other sources of calcium can be used. Calcite limestone is predominately CaCO<sub>3</sub>, dolomitic limestone is CaMgCO<sub>3</sub> and MgCO<sub>3</sub>, burned lime is CaO, and hydrated lime Ca(OH)<sub>2</sub>; all can supply Ca<sup>++</sup> ions for remediation. Never-the-less, gypsum is the

best source of calcium and the easiest product to handle for soil remediation. It should be noted that burned lime and hydrated lime are difficult to use and their use is not recommended.

### **Leonardite** (Humex<sup>TM</sup>)

Leonardite is a naturally occurring mineral. Humex<sup>TM</sup> is a trade name of the material available commercially. Humex<sup>TM</sup> is leonardite which is mined and ground to a specific particle size.

Leonardite contains humus, humic acids, fulvic acids, and trace minerals. As an amendment, it aides Na<sup>+</sup> ion exchange, improves soil structure, and is an instant soil builder. Leonardite also increases microorganism activity and increases biodegradation of hydrocarbons. Leonardite is also used to reduce and increase biodegradation of weed killer chemical.

#### Fertilizer

The remediation process uses fertilizer to increase nutrients in the top 6 inches of soil. Fertilizer will increase the number of bacteria and thus improve soil physical condition and nutrient content. Fertilizer also increases rate of hydrocarbons biodegradation.

Use 10/20/10/10 fertilizer or equivalent. The 10/20/10/10 complex is nitrogen, phosphate, potassium, and sulfur.

### Sulfur

Sulfur is primarily used to reduce and control high pH (alkalinity) in soil. Sulfur is also considered an essential nutrient in plant growth.

It takes 2,200 lbs/acre of sulfur to reduce pH by one unit (one pH unit is a ten-fold difference). The 2,200 lbs/acre is equal to 50 lbs of sulfur per 1000 sq ft in 8 inches of loamy soil.

At a soil pH greater than 8.6, increase sulfur by 25 lbs/1000 sq ft (1,100 lbs/acre).

### **Manure amendments**

- Add 3 inches of manure and work material into top 4 inches of soil. The manure should be 8 to 10 years old, if possible.
- Three inches of manure is equal to approximately 6 tons per acre.
- Need landowners consent to use manure.
- In most cases the manure has to come from the land owner's property.
- Manure can carry numerous weed seed species. The number of live weed seeds is reduced by the aging process which is the reason to use manure that is 8 to 10 years old.
- Manure has a high nitrate content. Do not use manure near ponds, streams, water supplies, and residences.
- Note: manure will replace 60% of the Humex<sup>TM</sup>, 40% of the gypsum, and all the fertilizer. Need to work soil two times in the second year and once in the third year to stimulate biodegradation.

AZ1413 Revised 08/12

# Using Gypsum and Other Calcium Amendments in Southwestern Soils

Dr. James Walworth

Soil aggregate formation and stability, the primary features of soil structure, are two of the most important manageable soil physical properties. Water, air, and roots primarily move between soil aggregates, which are clumps of soil particles cemented together. The pores between aggregates are fairly large, whereas the pores between particles within aggregates are often too small for effective water movement or root penetration, and sometimes even too small for bacteria to enter. In all but the sandiest soils, good aggregate structure is required for adequate root penetration, water infiltration, air exchange, and soil drainage.

Calcium (Ca) can help stabilize aggregate structure of some soils; using Ca in other soils will not improve soil physical or chemical properties. Therefore, it is helpful to understand how Ca interacts with soil particles.

The most commonly used Ca sources include gypsum, agricultural lime, and a few other Ca salts. In some soils, existing Ca minerals can be dissolved, releasing the Ca they contain. It is important to be familiar with the properties of these various Ca materials, and to understand the chemical processes that occur when amendments are applied to soil.

# Why is calcium important?

Negatively charged soil clay particles can be bound together into clumps or aggregates by positively charged molecules (cations). The formation of stable soil aggregates, a process called flocculation, encourages water infiltration and drainage and prevents surface soil crusting. Flocculation is promoted by high levels of salinity (which may not be conducive to plant growth) and by the presence of cations that are strong flocculators. The dominant soil cations in medium to high pH soils are the monovalent cations (one positive charge per molecule) sodium (Na $^+$ ) and potassium (K $^+$ ), and the divalent cations (two charges per molecule) magnesium (Mg $^{2+}$ ) and calcium (Ca $^{2+}$ ). In highly acidic soils the trivalent aluminum cation (Al $^{+3}$ ) may be present.

The ability of the dominant soil cations to flocculate soil clays, a function of their charge and size, is shown in Table 1. In this table the flocculating power of  $Na^+$  is assigned a value of 1, and the other cations assigned values relative to  $Na^+$ . We can see that  $K^+$  is a stronger flocculator than  $Na^+$ , but that  $Mg^{2+}$  and  $Ca^{2+}$  are much more powerful flocculators than either of the monovalent cations. Calcium is clearly the cation of choice for flocculating soil clays.

We generally consider  $Na^+$  to be the major 'weak' flocculator, and  $Ca^{2+}$  and  $Mg^{2+}$  to be the most common 'strong' flocculators. We can get a rough idea of how stable a soil's structure is by looking at the relative amounts of these weak and strong flocculators. This can be done by calculating the Sodium Adsorption Ratio (SAR), where cation concentrations are in millimoles per liter (mmol/L) or millimoles per kilogram (mmol/kg).

Table 1. Relative flocculating power of major soil cations (Rengasamy and Sumner, 1998).

lon	Chemical Symbol	Relative Flocculating Power
Sodium	Na+	1.0
Potassium	K+	1.7
Magnesium	Mg <sup>2+</sup>	27.0
Calcium	Ca <sup>2+</sup>	43.0

$$SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}}$$

An alternative equation for expressing the impact of Na<sup>+</sup> on aggregate stability is Exchangeable Sodium Percentage (ESP) with units of centimoles of charge per kilogram (cmolc/kg):

$$ESP = \frac{[Na^+]}{cation\ exchange\ capacity}$$

In addition to the relative proportions of flocculating cations, it is also important to know the total concentration of soluble salts in the soil. Cations are always accompanied by negatively charged ions (anions), and together they are called salts. Salts dissolved in water conduct electricity, so we can measure the electrical conductivity or EC of a soil-water mixture to determine the amount of salt.

Together, SAR and EC largely control soil aggregate stability. Figure 1 illustrates the effect of irrigation water quality on aggregate stability. If a soil has a combination of high SAR and low EC, the aggregates will tend to disperse. If it has a high EC and/or low SAR, the soil particles will be aggregated.

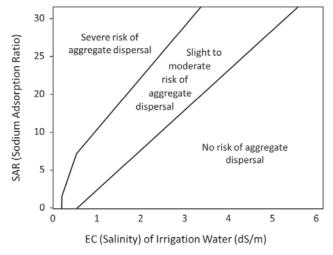


Figure 1. Soil and irrigation water electrical conductivity (EC) and Sodium Adsorption Ratio (SAR) determine aggregate stability (Ayers and Westcott, 1985)

In soils without adequate soluble  $Ca^{2+}$ , increasing the  $Ca^{2+}$  in solution will help to flocculate clay particles. Calcium acts as 'glue' that holds soil particles together into aggregates and stabilizes soil structure. There are two methods that can be used to increase soluble Ca. One is to solubilize Ca already present in the soil; the other is to add a supplemental Ca source.

# How can you solublize Ca already present in the soil?

Let's look at the first option, solubilizing existing soil Ca. This strategy works only if there is an excess of calcium carbonate (CaCO<sub>3</sub>) minerals in the soil. Soils with excess or solid-phase

 $CaCO_3$  are referred to as calcareous soils. They can be identified through a soil analysis. Look for 'free lime' on the soil test. It will usually be reported in general categories such as 'high', 'medium' or 'low'. You can test for the presence of carbonates yourself by putting a drop of dilute acid on them and observing whether or not they effervesce (Figure 2) as the  $CaCO_3$  reacts with the acid (sulfuric acid in the equation below) to produce carbon dioxide  $(CO_3)$  bubbles:

$$H_2SO_4 + CaCO_3 \longrightarrow CO_2$$
(gas)  $+H_2O + Ca^{2+} + SO_4^{2-}$ 

In calcareous soils, acid can be applied to dissolve soil CaCO $_3$ . The products of the reaction of CaCO $_3$  and sulfuric acid are CO $_2$ v water (H $_2$ O), sulfate (SO $_4$ <sup>2-</sup>), and Ca<sup>2+</sup>. The Ca<sup>2+</sup> released from the soil CaCO $_3$  can now act as a flocculant.

Any acid can dissolve soil CaCO<sub>3</sub> and release the bound Ca. Sulfuric acid is most common because it is relatively inexpensive and adds less salt to the soil than hydrochloric acid (HCl). Sulfurous acid (H<sub>2</sub>SO<sub>3</sub>) can be produced by combustion of elemental sulfur in a 'sulfur burner', which is a popular alternative to sulfuric acid. Additionally, acid-forming materials such as elemental sulfur can be used. Elemental sulfur is converted to sulfuric acid by sulfur oxidizing bacteria, producing the same effect as sulfuric acid. Sulfur conversion is a biological process, however, and requires several weeks to months to take place (depending on soil conditions), unlike acids, which react instantly.



Figure 2. Calcareous soil effervescing when acid is applied.

Acids and acid-forming materials will only be effective in calcareous soils! The soil should effervesce when acid is applied, or have 'medium' to 'high' or 'very high' free lime soil test levels.

### Calcium additives

Now let's look at Ca additives. There exist several Ca bearing salts that can be used to add Ca<sup>2+</sup> to soil but in order to be effective they must be soluble. A salt is a compound made up of a cation and an anion. Calcium salts, of course, contain Ca<sup>2+</sup> as their cation.

The anion is sulfate ( $SO_4^{-2}$ ) for calcium sulfates, carbonate ( $CO_3^{-2}$ ) for calcium carbonate, chloride (CI) for calcium chloride, and nitrate ( $NO_3^{-1}$ ) for calcium nitrate.

# Gypsum and calcium sulfate anhydrite

The most widely used Ca soil additive is gypsum. Gypsum is one of the family of calcium sulfates. The chemical formula for gypsum is  $CaSO_42H_2O$ . This means that each gypsum molecule contains one  $Ca^{2+}$  cation, one  $SO_4^{2-}$  anion, and two waters. There are other calcium sulfates, such as calcium sulfate anhydrite ( $CaSO_4$ ). Chemically, these two salts are closely related, the difference being that calcium sulfate anhydrite does not contain water. Consequently, calcium sulfate anhydrite contains more Ca on a weight basis than gypsum. Calcium sulfate anhydrite contains 29.4% Ca, whereas gypsum contains 23.2% Ca.

Both of these Ca salts are mined, and then ground into a powder for use as soil additives. Additionally, by-product gypsum materials, waste products of phosphate fertilizer production (phosphogypsum) or from power plant stack scrubbers (flue gas desulfurization gypsum), are also used.

Gypsum is a good choice for Ca addition because it is inexpensive, non-toxic, and safe to handle, and it is relatively soluble. We are interested both in solubility (how much of the salt will dissolve in the soil water) and the rate of dissolution (how fast the salt dissolves in water). Mined gypsum is wellcrystallized, having formed over millions of years. Waste gypsum, on the other hand, is formed rapidly during industrial processes, and is less crystallized. Although they have the same chemical formula, the waste gypsum materials dissolve more rapidly than mined gypsum. Sometimes powdered gypsum is prilled in order to reduce dust and to improve handling properties, and this slows its rate of dissolution. A study that compared dissolution rates of gypsum sources found that flue gas gypsum dissolved 3.6 times faster than mined gypsum, whereas phosphogypsum dissolved 2.2 times faster than mined gypsum. The rate of dissolution is particularly important for treatment of soil crusting, which is caused by dispersion of clay particles at the soil surface. In this situation, rapid dissolution is critical to maintain a high level of dissolved Ca2+ in the surface soil as raindrops or irrigation water leach cations from the uppermost layer of soil. However, for general treatment of soil structure, the rate of dissolution is less important than the overall solubility.

Calcium sulfate anhydrite can also be used as a Ca supplement. The solubilities of gypsum and calcium sulfate anhydrite are similar, however the dissolution rates differ. Published reports indicate that the dissolution rate of calcium sulfate anhydrite is slower than that of gypsum – anywhere from 5% to 72% that of mined gypsum. In addition to the chemical composition, the dissolution rates of both gypsum and calcium sulfate anhydrite are dependent on type and degree of crystallization, particle size, presence of impurities, and method of manufacture for non-mined salts.

### Lime

Calcium carbonate or limestone is another mined Ca salt. It's often referred to as lime or agricultural lime, although agricultural lime may be a combination of calcium and magnesium carbonates if it is made from dolomitic rather than calcitic limestone deposits. The main use of lime is to raise soil pH (to reduce acidity). In the same manner that CaCO, neutralizes sulfuric acid in the equation above, it also neutralizes acidity in low pH soils. Unlike gypsum and calcium sulfate anhydrite, lime solubility is dependent on soil pH. Its solubility increases in acid soils and decreases as soil pH increases. When soil pH is above approximately 8.2, lime becomes very insoluble. This is why most soils with a pH above this threshold are also calcareous, meaning that they contain solid mineral CaCO<sub>3</sub>. In acidic soils, supplemental CaCO, will dissolve, but in alkaline soils it will not; adding CaCO<sub>3</sub> to calcareous soils accomplishes nothing in terms of increasing soluble Ca levels.

### Calcium chloride and calcium nitrate

Calcium salts that contain  $Ca^{2+}$  and a monovalent anion such as chloride ( $CaCl_2$ ) or nitrate ( $Ca[NO_3^{-1}]_2$ ) are very highly soluble. They are not usually used as Ca amendments because of their expense and their high salt content. Applying enough of these salts to promote soil aggregation would generally increase soil salinity to unacceptable levels.

# **Summary of calcium supplements**

Table 2 provides a concise listing of the circumstances where each of the soil additives is likely to be effective or ineffective. Regardless of source, these soil amendments will only improve soil physical properties in soils with poor structure.

Table 2. Summar	v of conditions	appropriate	for various	soil additives.

	Soil pH		Comments	
Material	<7.0	>7.0	Comments	
Acids	NO	YES*	Only effective in calcareous soils (*calcareous soils usually have pH>8.0)	
Gypsum	YES	YES	Will not change soil pH	
Lime	YES	NO	Raises soil pH; not soluble in higher pH soils	
CaSO <sub>4</sub>	YES	YES	Dissolves more slowly than gypsum; will not prevent surface crusting	
CaCl <sub>2</sub>	YES	YES	Can raise soil salinity to unacceptable levels	
Ca(NO <sub>3</sub> ) <sub>2</sub>	YES	YES	Can raise soil salinity to unacceptable levels if used as a Ca source	

# Do calcium additives such as gypsum supply calcium for plant use?

Calcium is a critical component of cell walls and is therefore an essential plant nutrient. It is needed for cell division and growth and for redistribution of carbohydrates within the plant. Calcium deficiency related to lack of available soil Ca is rarely encountered in moderate to high pH soils, and is usually limited to very acidic or sandy soils. Calcium supply and translocation within plants is dependent on an adequate and continuous supply of water and Ca deficiencies are usually the result of drought stress rather than low soil Ca levels. However, if the supply of available soil Ca is inadequate (exchangeable Ca less than 250 to 500 mg/kg, Jones, 2003; Simmons and Kelling, 1987), supplemental Ca can improve plant nutrition. In this case, any soluble Ca material can be used to alleviate Ca deficiency. Lime (in acidic soils only) and gypsum are the most widely used soilapplied Ca fertilizers, whereas CaCl, and Ca(NO<sub>3</sub>-)<sub>2</sub> are often used for foliar application.

# How much gypsum do I need to apply?

The amount of gypsum that should be applied is best determined by a soil analysis. Soil analyses should be conducted to determine soil sodium status, either as "sodium adsorption ratio" (SAR) or as "exchangeable sodium percentage" (ESP). Either provides a good indication of the need for gypsum and the two measures are roughly equivalent. Approximate amounts of gypsum to add, based on soil analyses, are shown in Tables 3 and 4. These values were calculated based on cation exchange values of 15 cmol<sub>c</sub>/kg coarse soil, 25 cmol<sub>c</sub>/kg medium-textured soil, and 35 cmol<sub>c</sub>/kg of fine-textured soil, bulk density 3.33 g/cm³, soil depth 6 inches, and assume replacement of all the exchangeable Na. Application rates may need to be adjusted for actual soil conditions.

### **Summary**

In soils with weak structure resulting from an imbalance between Na<sup>+</sup> and Ca<sup>2+</sup>, increasing soluble Ca<sup>2+</sup> can improve aggregation, water infiltration, soil drainage, and root penetration. Acid or acid-forming amendments are acceptable additives for increasing soluble Ca<sup>2+</sup> in calcareous soils only. In all soils, regardless of pH, gypsum is a good Ca<sup>2+</sup> additive when Ca<sup>2+</sup> is needed. Calcium sulfate anhydrite will also supply Ca<sup>2+</sup>, but it will dissolve more slowly than gypsum. With either gypsum or calcium sulfate anhydrite it is important to know the composition of the material you select, which can vary considerably depending on source. Soil analysis can help determine how much of these materials to apply to your soil.

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Table 3. Gypsum requirements in tons per acre as influenced by soil texture and exchangeable sodium percentage.

	Exchangeable Sodium Percentage					
Soil Texture	10	15	20	30	40	50
	Gypsum (tons per acre)					
Coarse	1.1	1.7	2.3	3.4	4.6	5.7
Medium	1.9	2.9	3.8	5.7	7.7	9.6
Fine	2.7	4.0	5.4	8.0	10.7	9.6

Table 4. Gypsum requirements in pounds per one thousand square feet as influenced by soil texture and exchangeable sodium percentage.

	Exchangeable Sodium Percentage					
Soil Texture	10	15	20	30	40	50
	Gypsum (lbs per 1000 ft <sup>2</sup> )					
Coarse	55	80	105	160	210	265
Medium	90	130	175	265	350	440
Fine	125	185	245	370	490	615



# THE UNIVERSITY OF ARIZONA COLLEGE OF AGRICULTURE AND LIFE SCIENCES TUCSON, ARIZONA 85721

### DR. JAMES WALWORTH

STATE SOIL SPECIALIST, DEPARTMENT OF SOIL, WATER AND ENVIRONMENTAL SCIENCE

#### CONTACT:

JAMES WALWORTH walworth@cals.arizona.edu

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