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 Department

Oil Conservation Division
1220 South St. Francis Dr.
Santa Fe, NM 87505

Form C-141
Revised August 24, 2018
Submit to appropriate OCD District office

Incident ID	NRM2010059368
District RP	
Facility ID	
Application ID	

Release Notification

Responsible Party

Responsible Party: Catena Resources Operating, LLC	OGRID: 328449
Contact Name: Anthony Riggan, P.E.	Contact Telephone: 210-428-6144
Contact email: ariggan@catenares.com	Incident # *(assigned by OCD)* NRM2010059368
Contact mailing address: 18402 Hwy 281, Suite 258, San Antonio, TX 78259	

Location of Release Source

Latitude 32.72116 Longitude -103.43916
(NAD 83 in decimal degrees to 5 decimal places)

Site Name: South Vacuum #275	Site Type: Oil Well
Date Release Discovered: 01/22/2020	API# *(if applicable)* 30-025-37299

Unit Letter	Section	Township	Range	County
H	27	18S	35E	Lea

Surface Owner: ☒ State ☐ Federal ☐ Tribal ☐ Private (*Name:* ______________________)

Nature and Volume of Release

Material(s) Released (Select all that apply and attach calculations or specific justification for the volumes provided below)

☐ Crude Oil	Volume Released (bbls)	Volume Recovered (bbls)
☒ Produced Water	Volume Released (bbls) 32.41 bbls	Volume Recovered (bbls) 10 bbls
	Is the concentration of dissolved chloride in the produced water >10,000 mg/l?	☒ Yes ☐ No
☐ Condensate	Volume Released (bbls)	Volume Recovered (bbls)
☐ Natural Gas	Volume Released (Mcf)	Volume Recovered (Mcf)
☐	Volume/Weight Released (provide units)	Volume/Weight Recovered (provide units)

Cause of Release:

Release is believed to be result of outside, unauthorized party equalizing an in-service tank with an out-of-service water tank onsite. The out-of-service tank had previously had all of its manways removed, so when the produced water was illegally transferred to this tank, the produced water was automatically released from an open manway.

General Information

NMOCD District:	District 1	Incident #	NRM2010059368
Landowner:	State		
Client:	Catena Resources Operating, LLC	Site Location:	South Vacuum #275
Date:	June 22, 2020	Project #:	20E-00893-001
Client Contact:	Anthony Riggan, P.E.	Phone #:	(210) 428-6144
Vertex PM:	Natalie Gordon	Phone #:	(505) 506-0040

Objective

The objective of this environmental remediation work plan is to identify areas of exceedance for constituents of concern found during spill assessment and site characterization activities and propose appropriate remediation techniques to address the open release at South Vacuum #275 (hereafter referred to as "South Vacuum"). This incident was discovered on March 30, 2020, and is believed to be the result of an outside, unauthorized party equalizing an in-service tank with an out-of-service water tank onsite. The out-of-service tank had previously had all its manways removed, so when the produced water was illegally transferred to this tank, the produced water was automatically released from an open manway. Approximately 32 barrels (bbls) of produced water are believed to have been released onsite. The produced water ran off-pad into an adjacent field between two access roads and crossed the easternmost road to an area of undisturbed pasture. The location and boundaries of this release are identified on Figure 1 (Attachment 1). Areas of concern identified and delineated include the spill footprint as mapped on April 24, 2020.

Initial site research and characterization has been completed and a closure criteria determination worksheet is included in Attachment 2. The release at South Vacuum is not subject to the requirements of Paragraph (4) of Subsection C of 19.15.29.12 *New Mexico Administrative Code* (NMAC) and the closure criteria for the site are determined to be associated with the following constituent concentration limits.

Table 1. Closure Criteria for Soils Impacted by a Release

Minimum depth below any point within the horizontal boundary of the release to groundwater less than 10,000 mg/L TDS[1]	Constituent	Limit
50 < 100 feet	Chloride	10,000 mg/kg
	TPH[2] (GRO + DRO + MRO)	2,500 mg/kg
	GRO + DRO	1,000 mg/kg
	BTEX[3]	50 mg/kg
	Benzene	10 mg/kg

[1] Total Dissolved Solids (TDS)

[2] Total petroleum hydrocarbons (TPH) = gasoline range organics (GRO) + diesel range organics (DRO) + motor oil range organics (MRO)

[3] Benzene, toluene, ethyl benzene and xylenes (BTEX)

In addition to the Closure Criteria established in Table 1, further remediation will be required for off-pad portions of the release in order to meet restoration and reclamation requirements associated with releases into undisturbed areas, as outlined in Paragraph (1) of Subsection D of 19.15.29.13 NMAC. This regulation requires a minimum of four feet of non-waste containing, uncontaminated, earthen material with chloride concentrations of less than 600 mg/kg, and levels of other contaminants that meet the most protective concentrations contained in 19.15.29.12 NMAC as shown in Table 2.

Table 2. Reclamation Criteria for Soils Impacted by a Release

Minimum depth below any point within the horizontal boundary of the release to groundwater less than 10,000 mg/L TDS	Constituent	Limit
<50 feet	Chloride	600 mg/kg
	TPH (GRO + DRO + MRO)	100 mg/kg
	BTEX	50 mg/kg
	Benzene	10 mg/kg

Site Assessment/Characterization

The South Vacuum release characterization was completed on April 24, 2020. A total of sixteen sample points were established across the release area (Attachment 1) and soil samples were collected from these locations at depths of up to approximately 1.5 feet below ground surface (bgs). Each soil sample was field screened, using an electrical conductivity (EC) meter to estimate the level of chloride in the soil. The results were then used to determine the horizontal extent of the release. Typically, this same method is used to determine the vertical extent of the release; however, at South Vacuum, there is a layer of rock refusal at approximately 1-1.5 feet bgs that prevented soil sampling at deeper depths. Based on field screening and lab data from soil samples collected at this rock layer, chloride appears to have penetrated to that layer and remained there. Additional sampling of the rock itself is advised to demonstrate that contaminants have not permeated past the layer of refusal and can be done at the time of remediation fieldwork.

The New Mexico Oil Conservation Division (NM OCD) requires full release delineation to the extent possible and has provided guidance specific to this situation, whereby remediation to the rock layer is required and full documentation should be conducted to demonstrate that everything possible was done to clean up contaminants. The NM OCD response regarding this remediation process is included as Attachment 3.

Data from the field screening process have been compared to the above-noted closure and reclamation criteria to establish the appropriate level of remediation required. Field screening results are presented in Table 3 (Attachment 4) and exceedances are identified in the table as bold with a grey background. Because this was a produced water release, the presence of hydrocarbons are considered to be negligible.

Proposed Remedial Activities

Vertex proposes areas identified with contaminant concentrations approaching, or above, closure criteria (on-pad) and reclamation criteria (off-pad) be remediated through treatment in-situ with the chloride treatment product, SA-1000. This recommendation is based on the size of the contaminated footprint of approximately 17,417 square feet and represents significant environmental benefits and cost savings over mechanical excavation. Please see SA-1000 in-situ treatment information for details (Attachment 5). In-situ treatment will involve the mechanical turning (disturbance) and wetting (treatment) of contaminated soil in one-foot depth lifts to varying depths depending on the depth of contamination as delineated during initial characterization activities, generally to 1.5 feet bgs or rock refusal.

An alternative remediation option is excavation and removal of contaminated soil with the use of mechanical equipment, to a depth of approximately 1.5 feet bgs or to rock refusal. Excavation would be guided by an onsite Vertex environmental technician, who would be conducting field screening during the excavation activities. Approximately 980 cubic yards of contaminated soil are projected to be removed if using the excavation option. Contaminated soils should be stored on a heavy-duty liner prior to disposal at an approved facility.

Once the requisite time has elapsed following in-situ treatment (approximately 30-45 days) or, if using the excavation remediation option, once the environmental technician confirms removal of contaminated soil to below applicable closure and reclamation criteria as shown in Tables 1 and 2, confirmatory samples will be conducted. Five-point composite confirmatory samples will be collected from various depths, to depth of remediation, within the treated footprint, or from the base and sidewalls of the excavation, in accordance with the sampling plan detailed in Attachment 6. This sampling plan is based on a non-parametric statistical sampling design using the Hahn and Meeker method through the Visual Sample Plan (VSP) program that meets the Environmental Protection Agency's data quality assessment standards for composite sampling.

Confirmatory samples will be placed into laboratory-provided containers, preserved on ice and submitted to a National Environmental Laboratory Accreditation Program-approved laboratory for chemical analysis. Laboratory analyses will include Method 300.0 for chlorides, Method 8021B for volatile organics, including benzene and BTEX, and EPA Method 8015 for TPH, including MRO, DRO and GRO.

A GeoExplorer 7000 Series Trimble global positioning system (GPS) unit, or equivalent, will be used to map the approximate center of each of the five-point composite samples.

In the event that dig and haul is the chosen remediation method, excavations will be backfilled with clean soil sourced locally. Because the native soil at South Vacuum is not currently four feet deep, the depth of clean soil meeting Table 2 criteria will likely be limited to no more than two feet, as required to reconstruct existing grade, and pending NM OCD and New Mexico State Land Office (SLO) approval. Both remediation options will likely require re-seeding of the off-pad portions of the release with a BLM-approved seed mix at the appropriate time of year to take advantage of seasonal rains, in order to aid in the reestablishment of vegetation over the impacted area.

No reclamation activities are planned for any portion of the release on the active wellpad.

Timeline for Completion

Remediation activities, as outlined in this workplan, are projected to be completed within 90 days of NM OCD approval of the sampling plan.

If there are any questions regarding this report, please contact Natalie Gordon at 505-506-0040.

Sincerely,

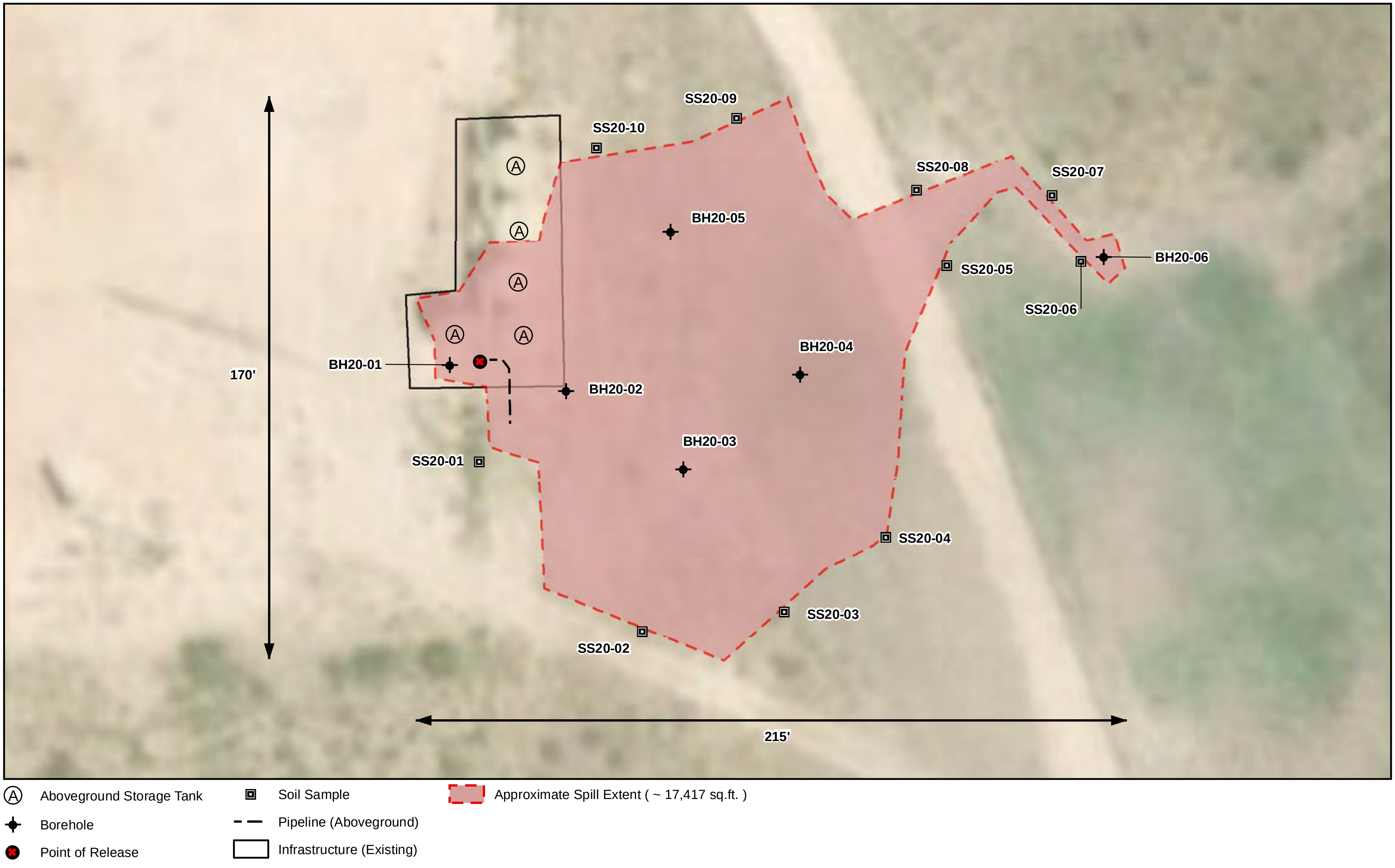
Natalie Gordon

Natalie Gordon
PROJECT MANAGER

Attachments

Attachment 1: Figure 1 – Release Area and Field Screen Sample Points
Attachment 2: Closure Criteria Determination Worksheet
Attachment 3: NM OCD Guidance on Remediation of Soils on Solid Rock
Attachment 4: Table 3 – Release Characterization Sampling – Field Screen Data
Attachment 5: SA-1000 Treatment Product Information
Attachment 6: Sampling Plan

ATTACHMENT 1



VERTEX

20 10 0 20 ft

Map Center:
Lat/Long: 32.720955, -103.438417

WGS 1984 UTM Zone 13N
Date: Apr 24/20

N

Site Schematic and Initial Release Characterization
South Vacuum #275

FIGURE:
1

ATENA RESOURCES

Note: Background image from ESRI 2017.

VERSATILITY. EXPERTISE.

Document Path: G:\1-Projects_US PROJECTS\Catena Resources Management\Figure 1 Initial Characterization South Vacuum #275.mxd

ATTACHMENT 2

Site Name: South Vacuum #275			
Spill Coordinates: 32.72116, -103.43916		**X: 646271.66**	**Y: 3621452.54**
Site Specific Conditions		**Value**	**Unit**
1	Depth to Groundwater	**60**	feet
2	Within 300 feet of any continuously flowing watercourse or any other significant watercourse	3,681	feet
3	Within 200 feet of any lakebed, sinkhole or playa lake (measured from the ordinary high-water mark)	1,105	feet
4	Within 300 feet from an occupied residence, school, hospital, institution or church		feet
5	i) Within 500 feet of a spring or a private, domestic fresh water well used by less than five households for domestic or stock watering purposes, **or**	1,100	feet
	ii) Within 1000 feet of any fresh water well or spring	1,100	feet
6	Within incorporated municipal boundaries or within a defined municipal fresh water field covered under a municipal ordinance adopted pursuant to Section 3-27-3 NMSA 1978 as amended, unless the municipality specifically approves	No	(Y/N)
7	Within 300 feet of a wetland	1,105	feet
8	Within the area overlying a subsurface mine	No	(Y/N)
9	Within an unstable area (Karst Map)	Low	Critical High Medium Low
10	Within a 100-year Floodplain	>100	year
11	Soil Type	Kimbrough-Lea Complex (border of Kimbrough gravelly loam)	
12	Ecological Classification	Very Shallow	
13	Geology	To - Ogallala Formation - alluvial and eolian deposits and petrocalcic soils of the southern High Plains	
	NMAC 19.15.29.12 E (Table 1) Closure Criteria	51-100'	<50' 51-100' >100'

ATTACHMENT 3

Natalie Gordon

From: Dhugal Hanton <vertexresourcegroupusa@gmail.com>
Sent: Tuesday, May 12, 2020 4:30 PM
To: Natalie Gordon
Subject: Fwd: [EXT] Release characterization/delineation question

---------- Forwarded message ---------
From: **Hamlet, Robert, EMNRD** <Robert.Hamlet@state.nm.us>
Date: Tue, May 12, 2020 at 4:11 PM
Subject: RE: [EXT] Release characterization/delineation question
To: Dhugal Hanton <vertexresourcegroupusa@gmail.com>, Venegas, Victoria, EMNRD <Victoria.Venegas@state.nm.us>, Bratcher, Mike, EMNRD <mike.bratcher@state.nm.us>, rmann@slo.state.nm.us <rmann@slo.state.nm.us>

Dhugal,

Rock Refusal (Remediation Process)

If rock refusal interferes with the remediation process, use a back-hoe/track-hoe to remove the rock. If the rock is immovable and target depth cannot be reached, use a hydrovac to clean the contaminated soil off of the rock surface and outline specific locations and steps taken on the Closure Report.

The OCD likes to see samples taken from the rock to see if the liquids have permeated the rock. This might consist of a 12-18" hole drilled with a rotary drill. If the drill sample doesn't show contaminants, spray the rock with Microblaze or other surfactants that will digest the organics (Get Approval by State/Federal Agency). At that point you've shown the OCD that you've done everything possible to clean up the contaminants.

Hopefully this helps.

Robert J Hamlet

State of New Mexico

Energy, Minerals, and Natural Resources

Oil Conservation Division

811 S. First St., Artesia NM 88210

(575) 748-1283

Robert.Hamlet@state.nm.us

From: Dhugal Hanton <vertexresourcegroupusa@gmail.com>
Sent: Tuesday, May 12, 2020 2:27 PM
To: Venegas, Victoria, EMNRD <Victoria.Venegas@state.nm.us>; Hamlet, Robert, EMNRD <Robert.Hamlet@state.nm.us>; Bratcher, Mike, EMNRD <mike.bratcher@state.nm.us>; rmann@slo.state.nm.us
Subject: [EXT] Release characterization/delineation question

Hello District 2 and SLO reps,

I have a question regarding delineating a release vertically. When we try to vertically delineate a produced water release and hit a solid hardpan/refusal at approximately 1-2 feet below ground surface, are we supposed to try to drill or break through that rock layer? The soil collected and field screened/analyzed from immediately atop the refusal layer still shows chloride levels of greater than 10,000 mg/Kg so within closure criteria for the area, but NOT within reclamation standards of 600 mg/Kg for the off-pad portion.

Breaking through the solid layer opens a conduit for contamination to move deeper into the soil so it seems like a less-than-great idea. However, fully delineating the release is a necessity.

Please advise the OCD preferred method for handling this type of situation.

Thank you,

Natalie

Natalie Gordon
Project Manager

Vertex Resource Group Ltd.
213 S. Mesa Street
Carlsbad, NM 88220

P 575.725.5001 ext 709
C 505.506.0040
F

www.vertex.ca

ATTACHMENT 4

Client Name: Catena Resources Operating, LLC
Site Name: South Vacuum #275
NM OCD Incident Tracking Number: NRM2010059368
Project #: 20E-00893-001
Lab Report: 2004611

Table 3. Characterization Field Screen and Sampling Laboratory Data - Depth to Groundwater 50 >100 ft

Sample Description			Field Screening			Petroleum Hydrocarbons							Inorganic
						Volatile		Extractable					
Sample ID	Depth (ft)	Sample Date	Volatile Organic Compounds (PID) (ppm)	Extractable Organic Compounds (Petro Flag) (ppm)	Inorganics (Quantab - High/Low) (+/-)	Benzene (mg/kg)	BTEX (Total) (mg/kg)	Gasoline Range Organics (GRO) (mg/kg)	Diesel Range Organics (DRO) (mg/kg)	Motor Oil Range Organics (MRO) (mg/kg)	(GRO + DRO) (mg/kg)	Total Petroleum Hydrocarbons (TPH) (mg/kg)	Chloride (mg/kg)
BH20-01	0	April 8, 2020	-	-	**19,214**	-	-	-	-	-	-	-	-
BH20-01	0.5	April 8, 2020	-	-	**9,265**	-	-	-	-	-	-	-	-
BH20-01	1	April 8, 2020	-	-	**3,265**	-	-	-	-	-	-	-	-
BH20-01	1.25	April 8, 2020	-	-	**5,271**	<0.024	<0.216	<4.8	<9.4	<47	<14.2	<61.2	**5,900**
BH20-02	0	April 8, 2020	-	-	**28,650**	<0.012	<1.04	<23	62	<49	62	62	**52,000**
BH20-02	0.5	April 8, 2020	-	-	**16,415**	-	-	-	-	-	-	-	-
BH20-02	1	April 8, 2020	-	-	**19,974**	-	-	-	-	-	-	-	-
BH20-03	0	April 8, 2020	-	-	**28,563**	-	-	-	-	-	-	-	-
BH20-03	0.5	April 8, 2020	-	-	**25,189**	-	-	-	-	-	-	-	-
BH20-03	1	April 8, 2020	-	-	**11,388**	-	-	-	-	-	-	-	-
BH20-04	0	April 8, 2020	-	-	**28,529**	-	-	-	-	-	-	-	-
BH20-04	0.5	April 8, 2020	-	-	**14,894**	-	-	-	-	-	-	-	-
BH20-04	1	April 8, 2020	-	-	**17,717**	-	-	-	-	-	-	-	-
BH20-05	0	April 8, 2020	-	-	**28,758**	-	-	-	-	-	-	-	-
BH20-05	0.5	April 8, 2020	-	-	**19,010**	-	-	-	-	-	-	-	-
BH20-05	1	April 8, 2020	-	-		-	-	-	-	-	-	-	-
BH20-06	0	April 8, 2020	-	-	**2,692**	-	-	-	-	-	-	-	-
BH20-06	0.5	April 8, 2020	-	-	**762**	-	-	-	-	-	-	-	-
BH20-06	1	April 8, 2020	-	-	340	<0.025	<0.222	<4.9	<9.7	<49	<14.6	<63.6	380
SS20-01	0	April 8, 2020	-	-	<0	<0.023	<0.208	<4.6	<9.6	<48	<14.2	<60.2	150
SS20-01	0.5	April 8, 2020	-	-	<0	-	-	-	-	-	-	-	-
SS20-02	0	April 8, 2020	-	-	174	<0.025	<0.221	<4.9	<9.8	<49	<14.7	<63.7	340
SS20-02	0.5	April 8, 2020	-	-	145	-	-	-	-	-	-	-	-
SS20-03	0	April 8, 2020	-	-	<0	-	-	-	-	-	-	-	-
SS20-03	0.5	April 8, 2020	-	-	<0	-	-	-	-	-	-	-	-
SS20-04	0	April 8, 2020	-	-	<0	<0.024	<0.217	<4.8	<9.4	<47	<14.2	<61.2	190
SS20-04	0.5	April 8, 2020	-	-	223	-	-	-	-	-	-	-	-
SS20-05	0	April 8, 2020	-	-	<0	-	-	-	-	-	-	-	-
SS20-05	0.5	April 8, 2020	-	-	<0	-	-	-	-	-	-	-	-
SS20-06	0	April 8, 2020	-	-	280	-	-	-	-	-	-	-	-
SS20-06	0.5	April 8, 2020	-	-	384	-	-	-	-	-	-	-	-
SS20-07	0	April 8, 2020	-	-	<0	-	-	-	-	-	-	-	-
SS20-07	0.5	April 8, 2020	-	-	514	-	-	-	-	-	-	-	-
SS20-08	0	April 8, 2020	-	-	289	-	-	-	-	-	-	-	-
SS20-08	0.5	April 8, 2020	-	-	223	-	-	-	-	-	-	-	-
SS20-09	0	April 8, 2020	-	-	329	-	-	-	-	-	-	-	-
SS20-09	0.5	April 8, 2020	-	-	595	-	-	-	-	-	-	-	-
SS20-10	0	April 8, 2020	-	-	<0	<0.024	<0.216	<4.8	39	70	39	109	130
SS20-10	0.5	April 8, 2020	-	-	48	-	-	-	-	-	-	-	-

"-" indicates not sampled/analyzed

Bold and shaded indicates exceedance outside of applied action level

ATTACHMENT 5

The Next Generation Treatment

SODIUM & HEAVY METALS IN SOIL AND WASTEWATER

TIDWELL
INDUSTRIES

Tidwell Industries is proud to introduce a revolutionary shift in the management and remediation of high sodium and metal contaminated soils and wastewater streams. SA-1000™ is the newest treatment that combines two, next generation, organic bio-polymers. This uniquely blended product possess the following properties and functions; optimal molecular mass, active functional groups, hydrophilic and hydrophobic sites, positively and negatively charged sites, non-ionic sites, and specific interactions between molecules themselves and organic/mineral compounds. The combination of these diverse properties and functions provide a product that utilizes multiple functions and mechanisms to detoxify, neutralize, bind, and convert a myriad of toxic metals to benign residual metals.

SA-1000™

SA-1000™ is a convenient, cost effective, liquid treatment product derived from and naturally occurring organic substrate. Our proprietary and patented manufacturing process unleashes unparalleled performance that address most of the potential effects that excess sodium and heavy metals will have in all soil and wastewater applications.

Product Benefits:

- SA-1000™ adsorbs and coordinates sodium cations and chlorine anions which allow excessive amounts of salt to become more mobile in terms of sodium cations and chloride anions that have a natural ability to flush through the soil or precipitate out of water. Any sodium residue creates a new mineral formation resulting in sodium, chlorine, cation and anion conversion into physically and mechanically bound status, thus eliminating salt toxicity resulting in desalination and salt toxicity reduction/ elimination.
- SA-1000™ will naturally stimulate toxic organic and mineral pollutants decomposition into neutral compounds such as converting Chromium VI to Chromium III.
- SA-1000™, with an abundance of hydroxyl and phenolic groups, provides these functional groups that are key to the metal complexation resulting in the binding of various metals.
- SA-1000™ is immediately soluble and active compared to gypsum applications. See results within a couple weeks.
- In soil, SA-1000™ creates fresh soil organic matter that results in increased CEC, better water holding capacity, and soil porosity/structure that results in healthy, active soil for re-use.
- SA-1000™ is a chemically, biologically and geologically active material.
- Cost effective low dose rates for either injection or mechanical applications.

For additional information and specific application rates for your project, contact an authorized Tidwell Industries representative.

SA-1000 PERFORMANCE CASE STUDY

The remediation and management of waste tailings from the metals refinery industry is a growing challenge with increased regulations towards heavy metals, salts, and other related contaminants. In an effort to demonstrate the real world performance of SA-1000 and the direct impact it has on metals and salts, Tidwell Industries received a sample of stainless steel slag directly from a refinery to treat.

TRIAL OUTLINE:

The slag sample was crushed and screened to a homogenous material with all large clumps removed. An equal amount of processed slag was added to two clean plastic dishes. One dish was treated with SA-1000 (Right Photo Below), wheat seed was added to each dish and mixed into the slag, and each dish watered. Each dish received equal amounts of water daily to aid in normal seed germination for five days.

The photo below shows plant germination after 5 days. After 10 days, the treated sample continued to grow while the untreated dish with limited initial germination all died. The trial was abandoned after 30 days with the treated sample plants remained healthy for the entire time.

SUMMARY:

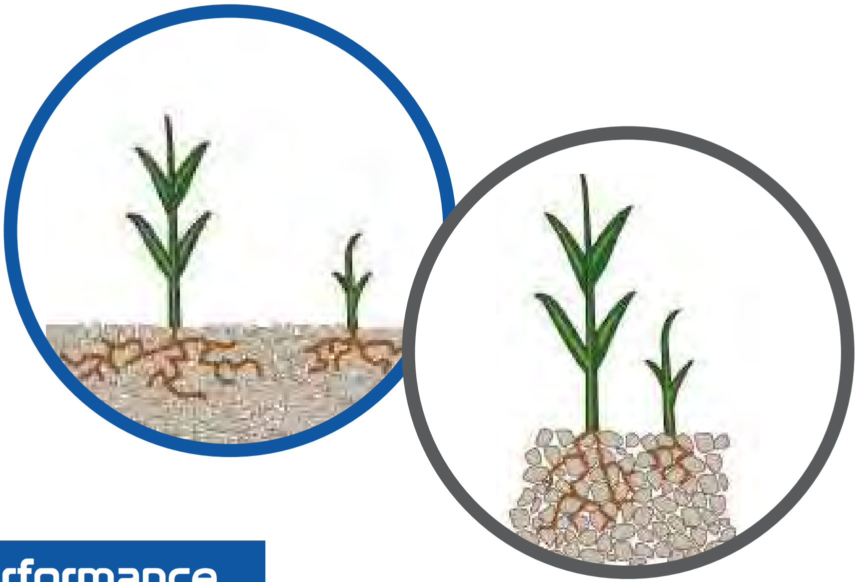
This study has demonstrated the performance of SA-1000 and its ability to reduce/eliminate salt and metals toxicity while providing a valuable organic structure which will sustain growth. Additionally, this study has laid the foundation for a large scale pilot study for the treatment of refinery tailings. The new pilot study will include pre and post material metals and sodium testing and replicate the ability of the tailings to support various plants from seed.

Tidwell Industries is seeking additional tailing remediation locations as well as salt and/or metal contaminated soil sites for additional performance pilot studies. Contact Steve Tidwell at steve@tidwellind.com or Call (361) 200 - 0011.

HOW SA-1000 WORKS

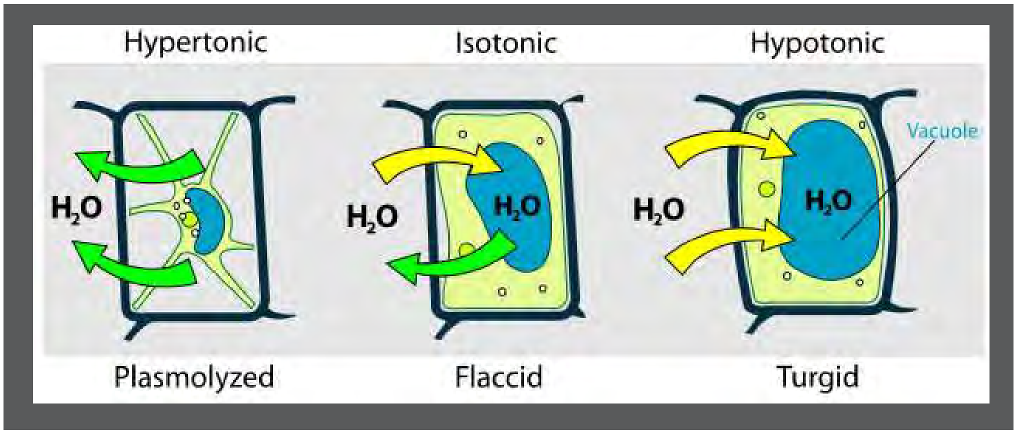
THE EFFECTS OF SODIUM & CHLORIDES ON SOIL

Sodium & Chlorides Impact Soil Structure, Increase Compaction, Limit Moisture Movement, Reduce Nutrient Availability, & Reduce Beneficial Bacteria



Things That Impact Product Performance

- Soil Structure
- Total Contaminant Loading
- Moisture
- Application Process
- Rate of Application Versus Results Required
- Additional Chemical Treatments
- Expectations or Regulatory Requirements
- Testing Methods

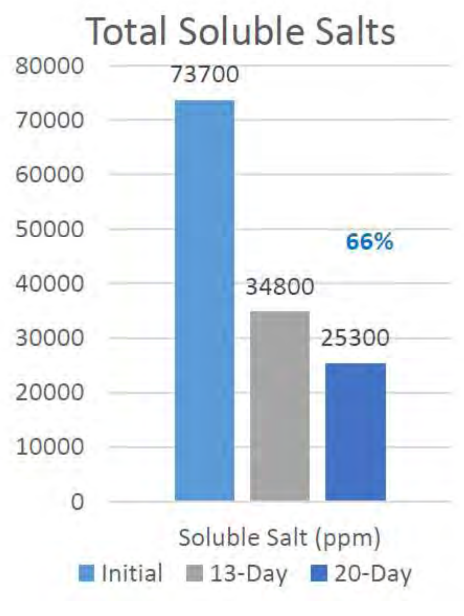


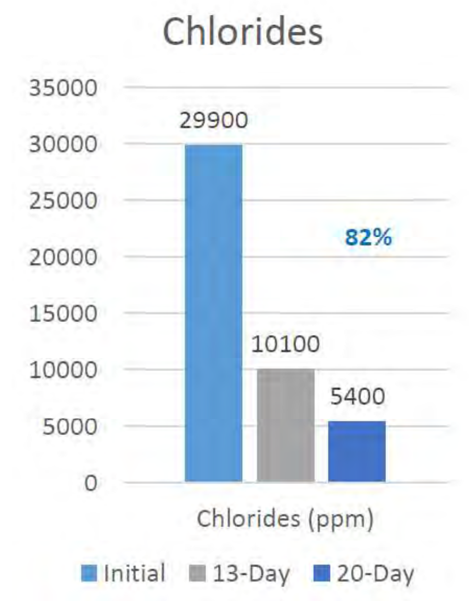
Produced Water Spill Clean-Up -1

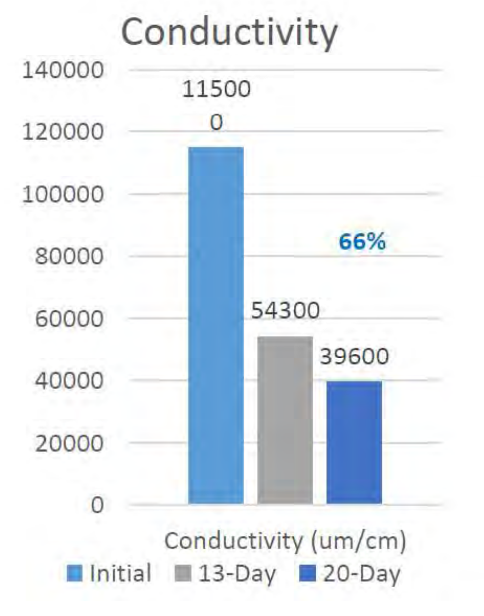
LOCATION: WESTERN OKLAHOMA – DISPOSAL STATION
CONTAMINANT: PRODUCED WATER (BRINE)
IMPACT AREA: MEDIUM SPILL AREA

Application Day

13 Days After Application





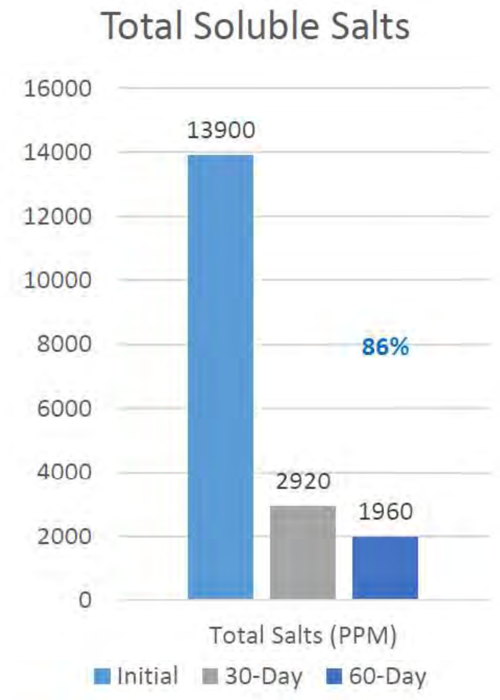


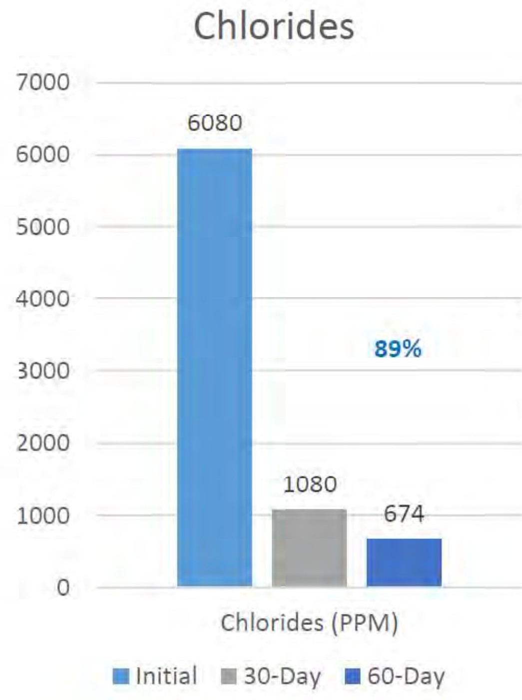
Produced Water Spill Clean-Up -2

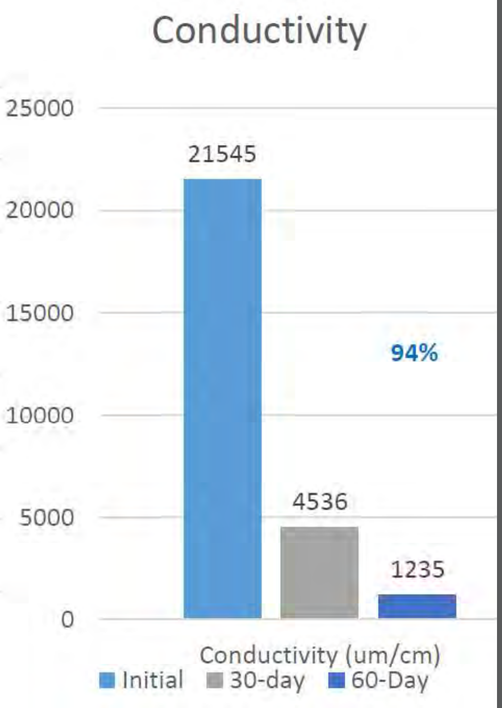
LOCATION: CENTRAL OKLAHOMA –STORAGE TANK LEAK

CONTAMINANT: PRODUCED WATER (BRINE)

IMPACT AREA: 1.58 ACRES BY 18” DEEP





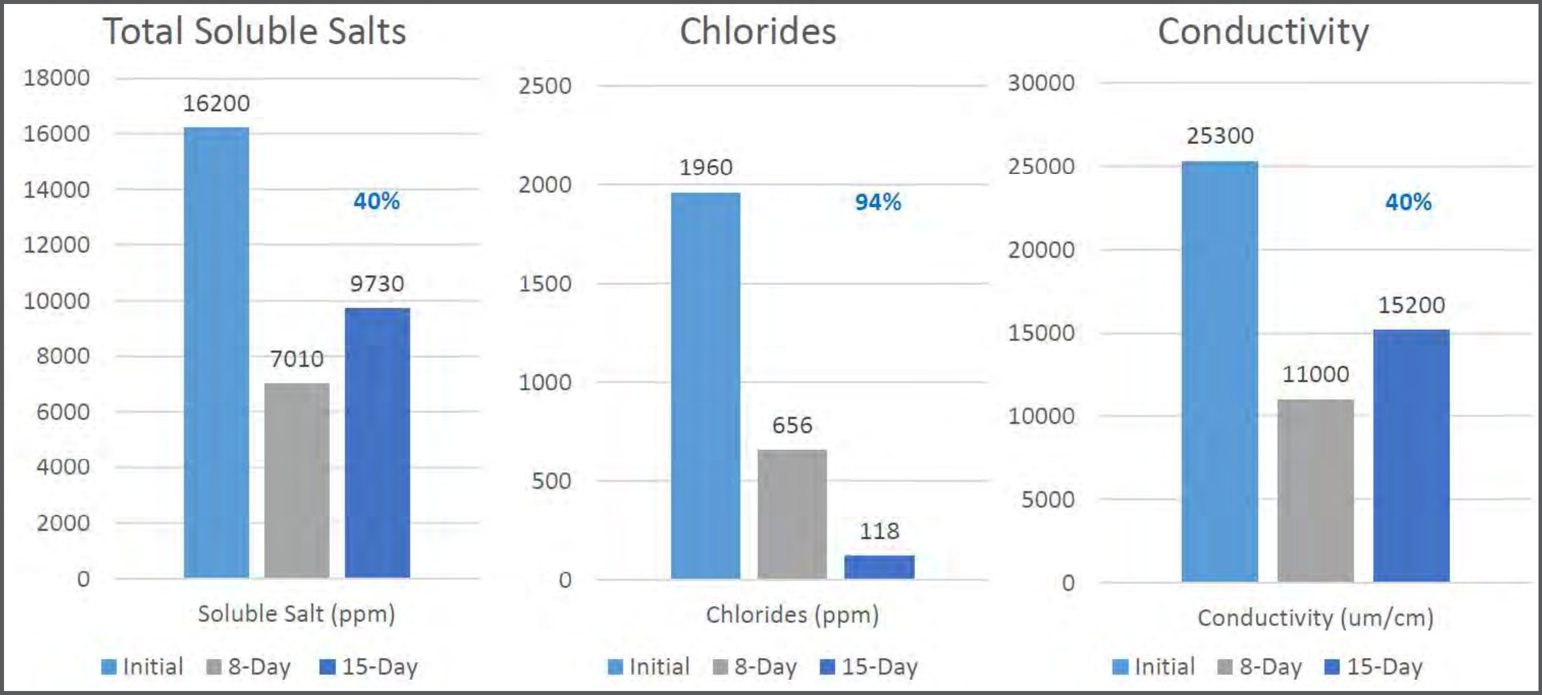


Produced Water Spill Clean-Up -3

LOCATION: WESTERN OKLAHOMA – DISPOSAL STATION
CONTAMINANT: PRODUCED WATER (BRINE)
IMPACT AREA: SMALL SPILL AREA

Application Day

13 Days After Application



REVERSING THE EFFECTS OF SODIUM & BICARBONATES

July 13, 2015

August 13, 2015

September 12, 2015

This is the result of years of effluent water use and the effects it has on traditional sand based greens.

SALTS & CHLORIDES REMEDIATION

The remediation of salts and chlorides is not a process of consumption but rather a process of binding, buffering, immobilization, detoxification, filtering, or conversion into a non-toxic soil mineral. This is accomplished in a variety of both cationic and anionic processes and reactions. The following information will provide some additional information that will assist in how some of these processes occur and a foundation on what these potential contaminants do in soil.

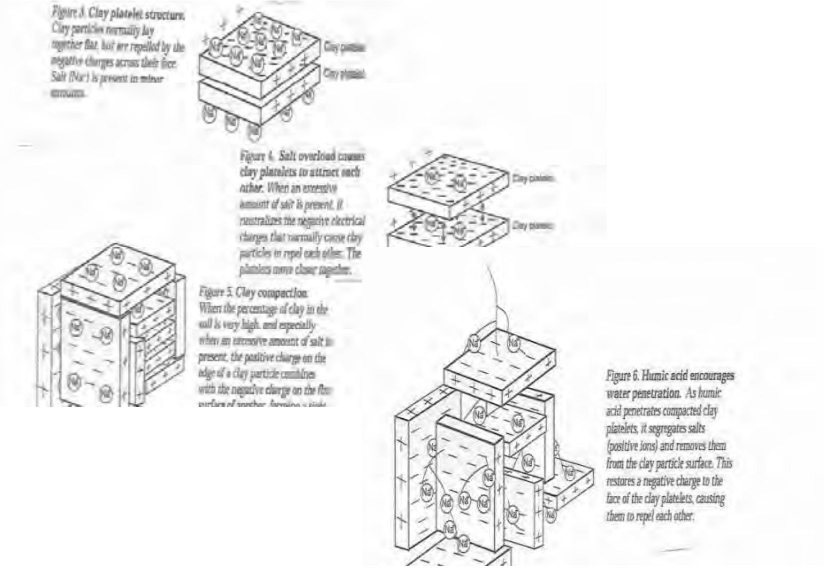


Figure 3. ***Clay platelet structure.*** *Clay particles normally lay together flat, but are repelled by the negative charges across their face. Salt (Na⁺) is present in minor amounts.*

Figure 4. ***Salt overload causes clay platelets to attract each other.*** *When an excessive amount of salt is present, it neutralizes the negative electrical charges that normally cause clay particles to repel each other. The platelets move closer together.*

Figure 5. ***Clay compaction.*** *When the percentage of clay in the soil is very high, and especially when an excessive amount of salt is present, the positive charge on the edge of a clay particle combines with the negative charge on the fla*

Figure 6. ***Humic acid encourages water penetration.*** *As humic acid penetrates compacted clay platelets, it segregates salts (positive ions) and removes them from the clay particle surface. This restores a negative charge to the face of the clay platelets, causing them to repel each other.*

Impact of Salt/Chloride 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.

Impact of sodium on soil & plants.

The Na+ ion of sodium chloride causes the dispersion of the soil. Due to the large number of Na+ ions available, the Na+ ions are able to exchange with a sufficient number of the Ca++ and Mg++ ions. The Na+ 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+ 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.

Impact of chloride on soil & plants

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

The Cl– 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.

The term “chloride” does not refer to any specific compound but is a category of substances that are either present in the soil or groundwater or are added to drilling muds or hydro-fracturing fluids to facilitate development of a gas/oil well. The most common chlorides of interest include sodium chloride, calcium chloride, magnesium chloride, ammonium chloride, potassium chloride, and barium chloride. Therefore the remediation of “Chlorides” may encompass a variety of compounds that can respond differently to treatments due to a variety of variables and conditions. It is also known that within any remediation of salts and chlorides that a variety of charges and reactions are required due to the fact that Cations migrate to negative charges and anions migrate to positive charges. Therefore, multiple charges of treatment products will be required to react appropriately with the different charges of the various components in the soil and water.

PROPER SITE CHARACTERIZATION AND ANALYTICAL DATA FOR MAXIMUM PERFORMANCE RESULTS:

Basic sodium and chloride testing will ONLY provide one small piece of the puzzle………what is the level of loading! Understanding the makeup and use of the site, soil structure, and analytics that detail the impact of the sodium/chloride to the specific site are all critical to development of an effective remediation process that can yield maximum results in the shortest period of time. Without a complete site picture, the remediation process will, in most cases, will not perform to the required expectations resulting in retreatment, additional time, and additional expense that can be avoided with proper testing and investigation of the site.

Required site testing:

(the best method for overall site analysis is composite soil sampling)

- pH
- Bicarbonate Alkalinity
- Carbonate Alkalinity
- Electrical Conductivity (EC)
- Total Soluble Salts (TSS)
- Calcium
- Potassium
- Magnesium
- Sodium
- Chloride (Anions)
- Nitrate as N (Anions)
- Sulfate as SO4 (Anions)
- Cation Exchange Capacity (CEC)
- Exchangeable Sodium Percentage (ESP)
- Sodium Absorption Ration (SAR)
- Soil Texture Analysis (Sand, Silt, Clay)

Required site specific information:

- General topography of site
- Site accessibility
- Principal site use (Pasture, Agricultural, Stabilization)
- Regulatory Standard
- Surface/Groundwater impact or influence (location of creeks, rivers, ponds and depth to groundwater if known)
- Age/Volume of Spill
- Makeup of the water spilled (Produced Water, Frack Water, Hydrocarbon present, Metals, other potential remediation concerns presented by spill, MAY REQUIRE ADDITIONAL TESTING DATA)
- Depth of contamination (Soil Texture Testing at incremental depths may be required)
- Depth to groundwater, type & potential water uses

Frequent work within a general geographic area may limit the amount of information required for all sites through experience though it is not uncommon for soil structure to vary significantly from location to location. Due to the relatively low cost for all tests, establishing a consistent testing regime will insure consistent results and a portfolio of proven reference data for replicatable results and success.

SA-1000 TECHNICAL MECHANISMS
(SALTS/CHLORIDES)

- The bio-polymers that makeup SA-1000 are chemically, biologically and geologically active material. In other terms, PEB is a nonspecific material that provides a positive impact to many, if not all, soil compounds (organic and mineral matter, soil bacteria, plant, etc.); organic pollutant (oil hydrocarbon and others); mineral toxicant (heavy metals, salts, etc.); soil function and properties (water holding capacity, porosity and density, CEC, EC, etc.) as well as plant growth / development processes. These are caused by PEB which is a poly fractional organic-mineral composition and colloidal origin (PEB contains molecules with different molecular mass); biopolymer or polyelectrolyte nature (PEB molecules are biologically synthesized molecules – biopolymer, while at the same time these polymers - molecules are electrolyte – or rather a polyelectrolyte); volumetric structure (three dimensional molecules with ability to conformational changes – ability to change their shapes) , its functional groups and a number of local positively and negatively charged active centers – negatively charged centers located primarily on the outer/external edges and positively charged centers located primarily in the inner/internal sites of these molecules. This unique molecular structure allows SA-1000 to be effective on both sodium cations and chloride anions.

- It is well known that soil particles bear negative electrical charges and this results in cations (positively charged ions) absorption on their surfaces. Note: Soil particles form a soil “skeleton” that means they are not available for moving through soil profile (in most cases). These cations form thin or thick hydrated layer around each soil particle. This electrically charged layer is called a “Double Electrical Layer”. This property primarily causes soil Cation Exchange Capacity (CEC). There is primarily hydrogen, calcium, magnesium, sodium; potassium and some other cations are present in this layer. Depending on makeup of the soil, the type of cations that dominates various soils could vary significantly. According to modern agro chemistry the best cation is calcium. If sodium cations dominate in this layer and the layer is thick, the sodium cations can move into soil pore solution due to diffusion, in this case, soil gets toxic for plant and soil bacteria (due to several mechanisms including high osmotic pressure). However, most sodium cations are strongly bound with soil particles and even soil washing with plenty of water does not remove any significant amount of sodium. That is why sodium removal is possible through ions exchange mechanisms: usually calcium (calcium sulfate – bio-available calcium) is used to replace sodium by calcium and sodium is available for removal from soil due to rainfall, natural diffusion processes, etc. If soil has high CEC (for example, black soil; clay; clay loam), soil can accumulate high levels of sodium without detectable sodium toxicity to plants because sodium cations are strongly bound and sit in “double electric layer”. Soil with low CEC cannot absorb high levels of sodium that is why in “light” soil (sandy soil; sandy clay; etc.) even a small amount of sodium results in great toxicity for plant/soil bacteria. Tidewell PEB’s increase CEC because activated bio-polymers have many active functional groups which have increased ions exchange capacity. The greater CEC, the greater the amount of sodium is absorbed and the lower its toxicity. Our PEB is the real molecular solution with dominated mass around 27,000 Daltons up to 100,000 Daltons. Therefore, with a sodium cation mass being 23 D (chlorine ion 36 D) a single PEB molecule is greater/heavier than a sodium ion by 1,174 times. The greater/heavier the molecules, the less mobile they are. Once sodium ions are absorbed by the PEB molecule, it makes sodium ions less mobile and respectively less toxic. It is possible to say roughly, that each PEB molecule works like a soil “particle” which forms a “Double electrical layer” with sodium resulting in reduced sodium mobility/toxicity.

- Our PEB molecules are volumetric: meaning three dimensions. Sodium ions can travel inside volumetric molecules and interact with their negatively charged sites. This can be described in terms of “sodium coordination”.

  Note: It can be explained in very simple terms. - For example, the Moon is coordinated by the Earth (due to gravity) and this doesn’t allow the Moon travel freely. But if the Moon gets extra energy, it can leave the Earth because there are no other forces or bonds which keep them together.

- In the soil or waste water PEB molecules absorb and coordinate sodium cations on negatively charged external surfaces and chlorides anions on the positively charged centers. Due to "diffusion" by water, chlorides ions have a significantly greater concentration on the inside portion of the molecule, while the sodium ions are captured in greater concentration on the outside of the PEB molecules rather than in the surrounding water. In soil this results in lowering sodium and chlorides concentration in soil pore solution and greater concentration around solid phase. The lower sodium and chlorides content in soil pore solution, the less salt toxicity to the plants. Though this process of absorption and coordination still binds sodium and chlorides ions, they still remain mobile and soluble without the inhibiting effects to the soil, water, and the environment trying to survive in it.

  Note: PEB molecules interaction with calcium, magnesium and two others with greater valent cations resulting in PEB molecules coagulation and precipitation. Calcium, magnesium, etc. make conformational changes or in other terms change PEB molecules shapes to more spherical which include sodium and chloride inside such spheres. This is the sodium and chlorides occlusion that results in less mobility/toxicity of these ions.

- Solid phase formation in soil or sediment formation in waste water due to PEB coagulation by calcium, magnesium, etc. significantly changes the mechanisms of sodium and chlorides diffusion in solid-liquid media. Sodium and chlorides distribution between liquid phase (water) and solid phase (coagulated PEB in soil and sediment in waste water) results in greater sodium and chlorides content in solid phase. This difference can be detected by sodium and chlorides content determination in liquid phase before and after PEB application. Liquid phase electro conductivity can be read also before and after PEB application. Electro conductivity reduction is more than expected.

  Note: without solid phase or sediment formation a PEB application could result in electro conductivity increase due to its electrolytic nature. Sodium and chlorides diffusion in solid phase and sediment is still great because they are not strongly bound; they are just absorbed and coordinated. This diffusion allows sodium and chlorides leaving the top soil into deeper layers. This results in top soil desalination. If this sediment in waste water is located on the surface of native ground (loam, sandy loam, etc.) it can result in sodium and chlorides diffusion to deeper layers and salt content reduction in waste water.

  Note: PEB molecules which were coagulated to sediment are not mobile. They can catch sodium in the same manner as it does cationic resins in case of sodium prevalent content over calcium, magnesium, etc. In this case sodium replaces calcium, magnesium, etc. and calcium chloride, magnesium chlorides content can increase while lowering sodium chloride concentration in water.

- As previously stated, PEB is a biologically active product which catalyzes the processes of new soil organic matter formation due to fresh organic matter and organic residue humification into colloidal PEB and primarily to Humus. Freshly formed colloidal PEB is negatively charged in wet soil having a high CEC that results in sodium ions absorption and protons H+ release. Protons replace sodium and form H+ Cl- . So, original NaCl turns to H+ Cl- . Protons and chlorides are very mobile which results in rapid filtering and movement from the soil top layer. Freshly formed colloidal PEB can absorb and keep protons and chlorides "mechanically" bound thus reducing or eliminating chlorides toxicity.

  Note: PEB also acts as a biologically active product in soil. First of all, PEB stimulates autotroph group of bacteria which use mineral compounds such as ammonia/ammonium; sulfur; iron, etc. as energy source. This group of bacteria can utilize carbon dioxide as carbon source. But carbon dioxide is a gas and not available for this bacteria. Carbon dioxide dissolution in soil pore solution or waste water results in bicarbonate formation. Bicarbonate in soil or waste water is rapidly available for autotroph and they turn bicarbonate into bacterial organic matter. If soil is contaminated, for example by sodium bicarbonates, bicarbonates consumption by bacteria results in free sodium ions release and their absorption by soil negatively charged particles – CEC or leaching from soil in form of sodium hydroxide (NaOH). So, PEB is most effective for soil which is contaminated by bicarbonates – sodium bicarbonate, magnesium bicarbonate, etc.

- PEB acts as effective bio stimulator for plant and soil native microbiology. PEB can be applied by mixing into the soil or as foliar spray. PEB molecules regulate soil and plant's cells osmotic pressure. It is known, that the higher salt content in water, the greater the osmosis pressure and greater the salt toxicity will be to the plants. High osmosis pressure makes water unavailable for plant resulting in their drying and death. PEB molecules reduce osmosis pressure making water available for plant.

- As we also stated, PEB is geologically active product. It means that PEB catalyzes the process of new soil mineral formation acting as a "matrix" which collects dissolved cations (primarily magnesium, calcium) and anions (primarily hydroxyl groups, silicates) into new clayey minerals. Sodium and chlorides are "mechanically" occluded between mineral's crystals and lose their mobility and toxicity to plants. These processes in soil a reasonable period of time and result are detectable in several weeks: sodium and chlorides reduction while soil clay mineral content may increase.

FAQ – BIO-REGEN SA-1000 FOR SALT REMEDIATION

What is SA-1000?

Tidwell Industries SA-1000 is a new management tool for remediation of high sodium and metal contaminated soils and wastewater streams. SA-1000 is an advanced treatment product combing two, next generation, Polyelectrolyte Enhanced Organic Bio-Polymers (PEB) with bio-available calcium. This uniquely blended product possess the following properties and functions; optimal molecular mass, active functional groups, hydrophilic and hydrophobic sites, positively and negatively charged sites, non-ionic sites, and specific interactions between molecules themselves and organic/mineral compounds. The combination of these diverse properties and functions provide a product that utilizes multiple functions and mechanisms to detoxify, neutralize and bind, salts and chlorides with the added ability to convert a myriad of toxic metals to benign residual metals.

What is Tidwell's Polyelectrolyte Enhanced Biopolymer (PEB)?

The foundation of SA-1000 is an advanced blend of two Polyelectrolyte Enhanced Biopolymer (PEB) that are derived from very stable, organic compounds found in brown and oxidized black coal. Our proprietary processing technology purifies and unleashes the vast potential of these massive molecular formulas.

PEB is a highly reactive long-chain molecule providing a purified carbon source available with various concentrations of fulvic acids, highly reaction functional groups, high CEC potential, and low ash and ballast. SA-1000 contains a combination of negatively charged molecules for reactions with positively charged Na and a new generation of non-ionic molecules for negatively charged chlorides. This unique combination with the addition of calcium creates a complete remediation tool for salts, chlorides and metals. PEB is an all-natural, highly soluble, liquid concentrate that is safe and easy to use for both soil and aqueous application

Why is the PEB important to the salt remediation process?

PEB naturally binds, adsorbs, and coordinates sodium cations and chlorine anions which allow excessive amounts of salts/chlorides to become more mobile in terms of sodium cations and chloride anions, which eliminates the salt's/chlorides ability to bind to soil particles, especially clay. This reaction allows sodium/chlorides to be safely leached and naturally filtered through the soil profile. Any sodium/chloride residue creates a new mineral formation resulting in sodium, chloride, cation and anion conversion into physically and mechanically bound status, thus eliminating salt toxicity resulting in desalination and salt toxicity reduction/elimination. This process also improves the growing profile by reversing negative osmotic pressure, reducing electrical conductivity, increasing soluble organic matter allowing proper nutrient and moisture retention, percolation, and uptake, therefore allowing new plants to establish and regenerate soil back to a healthy and productive state. In aqueous solutions, the reactions are similar, resulting in the precipitation of most of the sodium, chlorides and metals with the remaining soluble forms being neutralized into non-toxic forms.

How does SA-1000 work?

SA-1000 possesses several beneficial characteristics that buffers the treatment environment, creates a foundation for maximum biological, geological and chemical reactions, is both hydrophobic and hydrophilic, and is designed to work effectively in both soil and aqueous environments. Through these various reactions with contaminants, SA-1000 attracts various contaminants, reverses their negative impact in their environment and reduces/or eliminates the harmful impact through the following processes:

- SA-1000 adsorbs and coordinates sodium cations and chlorine anions which allow excessive amounts of salt to become more mobile in terms of sodium cations and chloride anions that have a natural ability to safely filter through the soil or precipitate out of water. Any sodium residue creates a new mineral formation resulting in sodium, chlorine, cation and anion conversion into physically and mechanically bound status, thus eliminating salt toxicity resulting in desalination and salt toxicity reduction/elimination.
- SA-1000 with bio-available calcium is immediately soluble and active compared to gypsum applications. See results within a couple weeks.
- In soil, SA-1000 creates fresh soil organic matter that results in increased CEC, reduced Electrical Conductivity (EC), better water holding capacity through osmotic pressure reduction, and soil porosity/structure that results in healthy, active soil for re-use.
- SA-1000 will naturally stimulate toxic organic and mineral pollutants decomposition into neutral soil mineral compounds such as converting Chromium VI to Chromium III which is accomplished by an abundance of hydroxyl and phenol groups. These functional groups are key to the metal complexation resulting in the binding of various metals which protects the environment.

How does SA-1000 improve the soil condition?

When frack/production water or drilling muds are accidentally released onto healthy soils, the results on vegetation are immediate, with devastating results. The impact of the sodium increases compaction through interactions with clay particles, reduces the ability for moisture to naturally penetrate the soils, dramatically increases Electrical Conductivity (EC), and limits natural nutrient conversion and availability to plants resulting in certain death.

Treatment of soils with SA-1000 creates fresh soil organic matter that results in healthy, active soil for re-use. SA-1000 will increase CEC while reducing electrical conductivity, improve water holding capacity by reducing the osmotic pressure, and soil porosity/ structure by releasing the sodium for the clay and reversing the charge of the clay particles forcing them apart. SA-1000 helps safely regenerate soil affected by salts/chlorides/metals and promotes improved soil structure for healthy, productive use of the site.

How quickly will SA-1000 work and when can you expect desired results?

In most of our project sites, the application of SA-1000 resulted in a reduction in excess of 75% of Total Soluble Salts and over 80% reduction in chlorides within 30 days after application. While results may vary from one project site to the next, it is important to evaluate results after a minimum of six months. At such time SA-1000 full impact would be realized in terms of improving the soil structure.

In most cases, the speed in which the product will work is impacted by a variety of variables. The most important factor is accurate soil analysis the clearly defines the level of contamination and soil structure/type. This information will insure proper application dosage of the treatment for the desired results. Other critical factors include soil moisture after application (Limited or no rainfall will slow analytical results), proper dosing rate and application, and the establishment of accurate expectations. A reasonable expectation is to see significant results in 30 days if the recommended dosage is used.

Once SA-1000 is applied is it safe to apply seed and any other required nutrients?

Yes, the impact of SA-1000 is almost immediate in terms of detoxifying and buffering the soil structure. If desired, you may apply seed & required nutrients to the treated soil immediately after the application of SA-1000. With the proper moisture level & rain fall, germination may be seen in as little as 2 weeks

Why is the PEB important to the salt remediation process?

PEB naturally binds, adsorbs, and coordinates sodium cations and chlorine anions which allow excessive amounts of salts/chlorides to become more mobile in terms of sodium cations and chloride anions, which eliminates the salt's/chlorides ability to bind to soil particles, especially clay. This reaction allows sodium/chlorides to be safely leached and naturally filtered through the soil profile. Any sodium/chloride residue creates a new mineral formation resulting in sodium, chloride, cation and anion conversion into physically and mechanically bound status, thus eliminating salt toxicity resulting in desalination and salt toxicity reduction/elimination. This process also improves the growing profile by reversing negative osmotic pressure, reducing electrical conductivity, increasing soluble organic matter allowing proper nutrient and moisture retention, percolation, and uptake, therefore allowing new plants to establish and regenerate soil back to a healthy and productive state. In aqueous solutions, the reactions are similar, resulting in the precipitation of most of the sodium, chlorides and metals with the remaining soluble forms being neutralized into non-toxic forms.

TIDWELL
INDUSTRIES

Tidwell Industries is a complete solution for oil-spill cleanup. Our ground-breaking patented technology is redefining oil cleanup methods. We make the entire process quick and easy so that we do not disrupt your ability to use the location. All of our products are non-toxic products, easily applied, and rapidly absorbs spills from water, soil, and all hard surfaces.

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ATTACHMENT 6

Sampling to Compute a Nonparametric (Distribution-Free) One-Sided Upper Tolerance Limit to Test that a Large Portion of Room Surfaces Does Not Contain Contamination

Summary

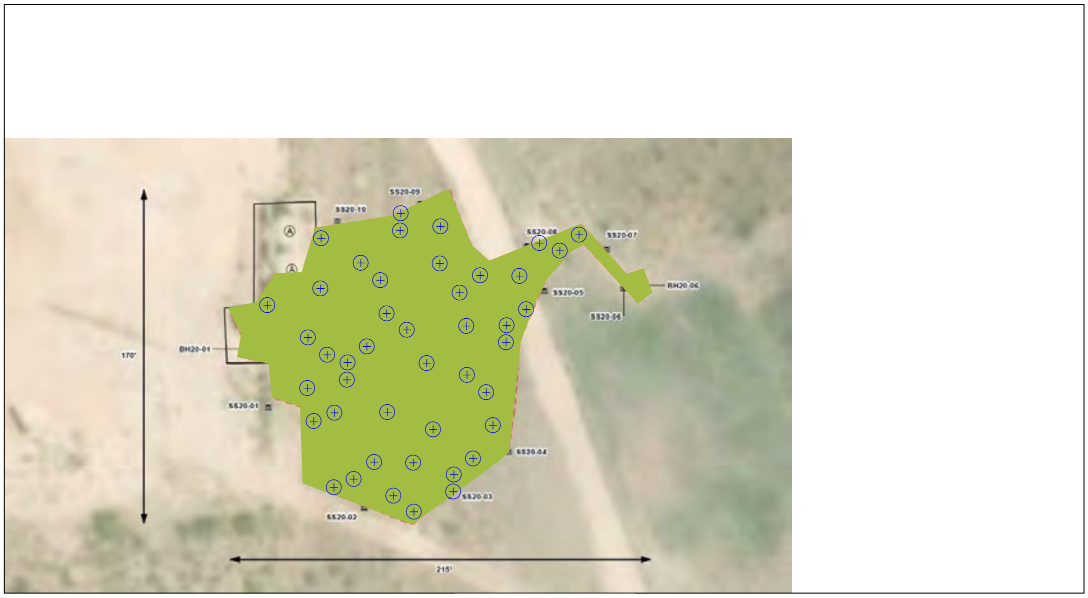
This report summarizes the sampling design developed by VSP based on inputs provided by the VSP user. The following table summarizes the sampling design developed by VSP. A figure that shows the sample placement on the map and a table that lists the sample locations are also provided below.

SUMMARY OF SAMPLING DESIGN	
Primary Objective of Design	Use a nonparametric (distribution-free) one-sided upper tolerance limit (UTL) to test if the true P^{th} percentile of a population exceeds the action level
Required fraction of the population to be less than the action level	0.9 (P=90)
Required percent confidence on the decision made using the UTL	99%
Method used to compute the number of samples, *n*	Hahn and Meeker (1991, page 169) (See equations below)
Sample placement method	Simple random point sampling
Calculated total number of samples	44
Number of samples on map [a]	44
Number of selected sample areas that are not rooms	1
Total sampling surface area [b]	17978.86 ft^2
Total cost of sampling [c]	$5,708.00

[a] This number may differ from the calculated number because of 1) grid edge effects, 2) adding judgment samples, or 3) selecting or unselecting sample areas (rooms).

[b] This is the total surface area of all selected rooms and other selected sample areas on the map of the site.

[c] Including measurement analyses and fixed overhead costs. See the Cost of Sampling section for an explanation of the costs presented here.



Floor Plan Map

Area: Area 1

X Coord	Y Coord	Label	Value	Type	Historical	Sample Area
-322.3678	-251.1862			Random		
-281.6677	-232.1210			Random		
-335.9345	-174.9255			Random		
-227.4009	-117.7300			Random		
-363.0680	-213.0558			Random		
-254.5343	-155.8603			Random		
-288.4511	-147.3869			Random		
-342.7179	-242.7127			Random		
-315.5845	-166.4521			Random		
-274.8844	-198.2273			Random		
-329.1512	-141.0318			Random		
-356.2846	-179.1622			Random		
-247.7509	-121.9667			Random		
-302.0178	-217.2925			Random		
-291.8427	-249.0678			Random		
-346.1096	-191.8723			Random		
-264.7093	-172.8071			Random		
-318.9762	-115.6116			Random		
-386.8097	-153.7419			Random		
-359.6763	-145.2685			Random		
-305.4094	-183.3989			Random		
-285.0594	-164.3337			Random		
-366.4596	-196.1090			Random		
-257.9260	-138.9135			Random		
-312.1928	-234.2393			Random		
-271.4927	-215.1742			Random		
-325.7595	-157.9787			Random		
-352.8929	-246.9494			Random		
-298.6261	-132.5584			Random		
-298.3081	-113.4933			Random		
-352.5750	-208.8191			Random		
-325.4415	-208.5053			Random		
-284.7414	-189.4401			Random		
-339.0082	-132.2446			Random		
-366.1417	-170.3749			Random		
-311.8748	-259.3457			Random		
-291.5248	-240.2806			Random		
-345.7916	-183.0850			Random		
-237.2579	-125.8895			Random		
-264.3914	-164.0199			Random		

-318.6582	-106.8244			Random		
-277.9581	-138.5997			Random		
-332.2249	-233.9255			Random		
-359.3583	-119.5345			Random		

Primary Sampling Objective

The primary objective of this sampling effort is to make a decision whether an unacceptably large portion (fraction) of a specified surface area (target population) is contaminated above a specified action level (AL) or is otherwise defective. It is presumed that suitable actions have been identified to be implemented for either way the decision may go.

Population Parameter of Interest

The population parameter of interest is the true P^{th} percentile of the population of contaminant concentrations, where $0 < P < 100$, in this case, the 90th percentile ($P = 90$). The true P^{th} percentile is the value above which (100 - P)% of the population lies and below which P% of the population lies. The objective is to reject the null hypothesis if the true P^{th} percentile exceeds the specified action level (AL). But, the true P^{th} percentile will never be known with 100% confidence because all possible measurements from the population cannot be obtained. Hence the decision whether to reject the null hypothesis is made using the computed upper tolerance limit (UTL) for the P^{th} percentile, that is, by computing the upper 100(1-α)% confidence limit on the P^{th} percentile (see Decision Rule below). For the current design α is 0.01, which means that the decision will be made using the computed UTL for the 99% confidence limit on the 90th percentile.

Hypothesis Being Tested

The null hypothesis (baseline assumption) is as follows:

H_o: The true P^{th} percentile $\leq$ AL

or equivalently,

H_o: Less than P% of the population < AL

The H_o is rejected if UTL < AL, in which case the alternative hypothesis (H_a) is accepted as being true, where:

H_a: More than P% of the population < AL

Sampling Design Options

VSP offers many options to determine the locations at which measurements are made or samples are collected and subsequently measured. For this design, simple random point sampling was chosen. Locating the sample points randomly provides data that are separated by varying distances, providing good information about the spatial structure of the potential contamination. Knowledge of the spatial structure is useful for geostatistical analysis. However, it may not ensure that all portions of the site are equally represented.

Decision Rule and Number of Samples, *n*

The null hypothesis is rejected and the alternative hypothesis is accepted if the nonparametric (distribution-free) UTL for the P^{th} percentile is less than the specified action level (AL). The nonparametric UTL is simply the maximum of the n measurements obtained from the population of interest, where n is computed using the following equation

$$n = \frac{\ln(\alpha)}{\ln(P/100)}$$

(from Hahn and Meeker 1991, page 169). These authors discuss the statistical meaning, use, and computation of nonparametric tolerance limits and the number of samples required (pages 91, 92,169, and 326).

The following table displays the values of the input parameters used for this design:

Parameter	**Value**
Input	
P	90
α	0.01 (1%)
Confidence (1-α)	99%

Output	
n	44

Statistical Assumptions

1. Representative measurements have been obtained from a defined target population using simple random sampling or a systematic grid pattern that has a randomly selected starting location.
2. The *n* measurements are statistically independent, i.e., there is no spatial correlation (no spatial patterns) of contaminant levels throughout the target population.
3. The maximum of the *n* measurements is not an invalid value, i.e., it is not a mistake or an unacceptably uncertain value due to faulty sample handling, transport, treatment, storage, or measurement.

Sensitivity Analysis

The sensitivity of the calculation of number of samples was explored by varying the required percent of the population to be less than the action level. and confidence level (1-α) (%). The following table shows the results of this analysis.

Number of Samples					
	CL=99	**CL=97**	**CL=95**	**CL=93**	**CL=91**
P=85	29	22	19	17	15
P=90	44	34	29	26	23
P=95	90	69	59	52	47

P = Required Percent of the Population to be Less Than the Action Level.
CL = Confidence Level (1-α) (%)

Cost of Sampling

The total cost of the completed sampling program depends on several cost inputs, some of which are fixed, and others that are based on the number of samples collected and measured. Based on the numbers of samples determined above, the estimated total cost of sampling and analysis at this site is $5,708.00, which averages out to a per sample cost of $129.73. The following table summarizes the inputs and resulting cost estimates.

COST INFORMATION			
Cost Details	**Per Analysis**	**Per Sample**	**44 Samples**
Field collection costs		$7.00	$308.00
Analytical costs (Analyte 1)	$100.00	$100.00	$4,400.00
Sum of Field & Analytical costs		**$107.00**	**$4,708.00**
Fixed planning and validation costs			$1,000.00
Total cost			**$5,708.00**

Recommended Data Analysis Activities

Post data collection activities generally follow those outlined in EPA's Guidance for Data Quality Assessment (EPA, 2000). The data analysts should become familiar with the context of the problem and goals for data collection and assessment. The *n* data should be verified and validated before being used to test the null hypothesis. The VSP user should enter the validated and verified *n* data values into the VSP dialog box and click on appropriate tabs to obtain the following statistical summaries of the data. If there is strong evidence that the *n* data are normally distributed, the VSP user may want to use VSP to determine the number of samples, *n*, required to compute the normal distribution UTL and then use that UTL (rather than the nonparametric UTL) to test the null hypothesis.

Summary statistics: *n*, minimum and maximum of the *n* measurements, range of the *n* data, mean, median, standard deviation, variance, skewness, percentiles, and the interquartile range

Statistical Tests of Normality Assumption: Shapiro-Wilk test (if $n \leq 50$) (Gilbert 1987), Lilliefors test (if $n > 50$) (EPA 2000).

Graphical Displays of the Data: Histogram, box-and-whisker plots and quantile-quantile (probability) plots (EPA 2000).

References

EPA. 2000. *Guidance for Data Quality Assessment, Practical Methods for Data Analysis*, EPA QA/G-9, EPA/600/R-96/084, July 2000, Office of Environmental Information, U.S. Environmental Protection Agency.

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