University Transportation Research Center - Region 2

Final Report

Environmental Impacts of Oil and Gas Brine Applications for Dust and Ice Control in New York

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University Transportation Research Center - Region 2

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16. Abstract

Transportation agencies are required to treat roads for dust and ice control to ensure adequate safety for travelers. This is commonly achieved through application of solid and liquid chemicals. These materials can be conventional rock salt, brine from rock salt, natural brine, or oil and gas brine. Due to the high cost of treating roads for the removal of snow and ice, in states with active oil and gas wells such as New York, the potential for using this brine to control dust or ice on roads is currently being explored.

Environmental concerns exist over the use of conventional oil and gas brines due to their potential high total dissolved solids and metals concentrations[1,2] They can also be elevated in organic compounds and can contain certain chemical additives[3]. If conventional or unconventional oil and gas brine is applied to roadways for dust or ice control, there is the potential for runoff to impact receiving water or roadside soil. The environmental impact of the leaching of chemical components from soil impacted with oil and gas brine applied for transportation purposes is unknown.

The goal of this work was to determine the potential for components found in oil and gas brine to leach from soil to groundwater. The potential for components found in other alternative brines (agricultural based and plant based) was also investigated.

Three brines were characterized based on their physical and chemical parameters. Toxicity characteristic leaching potential (TCLP) tests were conducted to compare the potential for the release of metals from three brines commonly applied for dust and ice control in New York. Results show that the plant-based brine has the least potential to leach metals from a soil/brine mixture, while the oil-based brine has the highest potential to impact the environment through the leaching of metals. Results from the leaching tests for all experiments show that the concentrations of certain metals would be found in groundwater that are elevated above the maximum contaminant levels set forth by the USEPA.

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Table of Contents

List of Figures

List of Tables

List of Abbreviations and Symbols

TCLP – Toxicity Characteristic Leaching Potential
NYSDOT – New York State Department of Transportation
USEPA – United States Environmental Protection Agency
TS – Total Solids
TDS – Total Dissolved Solids
TSS – Total Suspended Solids
bbls - barrels
mg/L – Milligrams per Liter
µg/L – Micrograms per Liter
mg/kg – Milligrams per Kilogram

Executive Summary

Transportation agencies are required to treat roads for dust and ice control to ensure adequate safety for travelers. This is commonly achieved through application of solid and liquid chemicals. These materials can be conventional rock salt, brine from rock salt, natural brine, or oil and gas brine. Due to the high cost of treating roads for the removal of snow and ice, the potential for using this brine to control dust or ice on roads is currently being explored.

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The goal of this work was to determine the potential for components found in oil and gas brine to leach from soil to groundwater. The potential for components found in other alternative brines (agricultural based and plant based) was also investigated.

Three brines were characterized based on their physical and chemical parameters (properties). Toxicity characteristic leaching potential (TCLP) tests were conducted to compare the potential for the release of metals from three brines commonly applied for dust and ice control in New York. Results show that the plant-based brine has the least potential to leach metals from a soil/brine mixture, while the oil-based brine has the highest potential to impact the environment through the leaching of metals. Results from the leaching tests all experimental show that result in concentrations of certain metals would be found in groundwater that are elevated above the maximum contaminant levels set forth by the USEPA.

Background

The most common roadway anti-icing or anti-dust chemicals include brine, calcium chloride, magnesium chloride, potassium acetate, and agricultural products such as beet juice and molasses. The use of brine as an anti-icing or pre-wetting agent has gained popularity in the U.S. due to its cost-effectiveness, better road conditions, lower accident rates, and lower costs for winter road maintenance. An alternative source of salt brine for ice control is brine generated during oil and gas well drilling. This brine is produced alongside the oil and gas and contains sodium and calcium chloride, which are effective deicing agents. However, these brines can contain elevated metal and suspended solids concentrations which may have detrimental effects on the environment.

In New York State, approximately 30 percent of the oil/gas brine is disposed via road spreading. From the 2012 New York State Oil, Gas and Mineral Resources report summary provided by the NYS Department of Environmental Conservation, New York State natural gas production was 26.4 billion cubic feet (bcf) and oil production was 394,507 barrels (bbls). Most production brine in New York comes either from shallow oil wells or from deep gas wells. The oil wells are present in the Alleghany and Cattaraugus counties while the gas fields are located in the Chautauqua County.

According to the NYSDOT, the Village of Fayetteville in Onondaga County has applied conventional oil and gas brines during the winter months since 2011. A comparative study has shown brines to be more effective than typical rock salt in reducing the number of roadway accidents after heavy precipitation. New York State currently has over 9,000 active wells generating large quantities of well effluent[4].

Although effective in its purpose, conventional oil and gas brine contain high quantities of suspended solids including trace metals and organic matter. The characteristics of the brines from gas and oil producing areas vary significantly. The differences are primarily in the chloride and total dissolved solids (TDS) content. The shallow oil production waters allow for dilution, resulting in lower chloride concentrations in comparison to deep gas wells.

Table 1 shows a comparison of certain components of oil-field brine with a conventional deicer[5]. Oil field brine is elevated in calcium, magnesium, potassium, strontium, and manganese. Sulfate is much lower in oil-field brine than conventional deicer, which is expected as most of the salt in oil-field brine is chloride and sodium.

Table 1. Comparison of concentration of components of oil-field brine versus conventional deicer.

Component	Oil-field brine	Conventional deicer
	Concentration (mg/L)	
Chloride	150,000	150,000
Sodium	42,800	107,300
Calcium	36,200	1,400
Magnesium	6,190	19.1
Potassium	1,460	45.2
Strontium	1,070	9.2
Manganese	14	0.41
Sulfate	229	2,300

Table 2 shows the ranges of trace metal concentrations for Ohio production brines[5]. Barium and zinc are found in the highest concentrations, with the other metals found at much lower concentrations.

Table 2. Metal concentrations in Ohio Oil-field brine.

Metal	Range
Barium	0.1 – 255 mg/L
Zinc	0.05 – 4.1 mg/L
Cadmium	0.4 – 181 µg/L
Chromium	0.6 – 644 µg/L
Cobalt	0.4 – 155 µg/L
Copper	0.3 – 200 µg/L
Lead	5 – 1300 µg/L
Mercury	0.915 – 0.70 µg/L
Nickel	0.7 – 637 µg/L
Vanadium	0.6 – 30 µg/L

There is a potential for heavy metals to leach from soil to groundwater during applications of deicing agents. Deicing agents can infiltrate soil either directly through the melting of snowbanks, salt stockpiles, and salt spray and splash, or indirectly through surface runoff in ditches. Much of the research conducted on the mobilization of heavy metals has been conducted on solid rock salts (sodium chloride, magnesium chloride). Salt may mobilize trace metals in soil and subsequently affect groundwater and terrestrial organisms[6]. Deicing salts can affect soils by exchanging sodium cations with the magnesium and calcium cations already in the soil, affecting structure, pH, and mobilization of trace metals. Research has shown that sodium chloride from road salt application can migrate through the soil can cause osmotic stress and mobilization of nutrients and metals[7,8]. Other research has shown that components of brine including sodium, chloride, magnesium, and calcium may displace heavy metals already bound to soil particles after which the metals may resorb onto other soil sites, interact with soil organic material, bioaccumulate, or move with the hydraulic gradient in groundwater with eventual discharge to surface water. Mobilized metals are more biologically available than soil-bound metals and pose a greater risk. The potential for mobilization is greater when the soil already contains high levels of metals[6]. Other research by Nelson et al 2009 found that immediately after salt application, metals could have concentrations 50 to 1000 percent greater than normal, with sodium chloride salt application leading to a larger increase in lead and copper than magnesium chloride salt application, and magnesium chloride salt leading to a larger increase of cadmium[9]. Research by the Transportation Association of Canada in 2013 showed a large part of the lead, copper, and zinc in roadside soils is vulnerable to leaching when exposed to high sodium chloride concentrations[6]. Other research by Backstrom in 2004 found increased heavy metal concentration during the winter at sites where sodium chloride had been used for deicing[10]. Some lab experiments suggest that chloride can displace heavy metals from soil to groundwater[11,12], however field studies have not confirmed results.

With the increasing use of brine as a deicing or pre-wetting agent, there is a need to study the leaching potential of metals from soil to groundwater during brine applications for winter roadway maintenance or for dust control. To accomplish this, a toxicity characteristic leaching potential (TCLP) test for metals was performed on soil samples that were amended with different volumes of brine. Leaching potential tests were conducted for three different brines (Table 3). The brines were purchased from Road Solutions Inc., and were selected based on their current use for deicing roads in New York State. Brine A is an agricultural based product that is derived from a sugar beet process that is blended with sodium chloride. Brine B is an oil-based brine that is blended with Brine A. Brine C is a corn-based chloride free deicer that is non-harmful in natural surroundings.

Table 3. Characteristics of brines in this study.

Brine	Description
Brine A	Natural surface treatment that is an agricultural based product. Derived from renewable resources. Blended with sodium chloride.
Brine B	Derived from oil brine and blended with Brine A for deicing.
Brine C	Plant-based, chloride-free, product of novel biochemical technologies. Contains no chloride, no sulfate, no nitrite and is proved to be non-toxic and non-harmful in natural surroundings, where 100% degradation can be achieved in soil.

Objectives

The goal of this work is to determine the potential for components found in oil and gas brine to leach from soil to groundwater. The potential for components found in other alternative brines (agricultural based and plant based) were be investigated. Leaching studies were conducted to compare three brines commonly applied for dust and ice control in New York. The objectives for this work are:

Objective 1: Conduct a literature review on brine applications for dust and ice control.
Objective 2: Determine the leaching potential of constituents of concern from soil samples amended with three types of brines commonly applied to roads for dust and ice control in New York State.

Experimental Section

Physical and chemical characterization of brine and soil

First, the physical and chemical characteristics of the three brines and the soil were determined following Standard Methods and EPA Methods as outlined in Table 4. Table 4 lists these characteristics along with the Standard Methods used for the analyses. These analyses were also performed on the soil sample that were used for the leaching studies. The soil sample was collected next to exit 12 off I-87 in the Bronx, NY.

Table 4. Standard methods and constituents for brine and soil analysis.

Class	Constituents	Standard Method
Major anions	Chloride Sulfate Bromide	EPA Method 300.1[13]
Major metals	Barium Zinc Cadmium Chromium Cobalt Copper Lead Mercury Nickel Vanadium Sodium Calcium Magnesium Potassium Strontium Manganese Iron	Standard Method 3111[14] EPA Method 3050B[15]
Solids	TS TDS TSS	Standard Method 2540 Series[16]
Other	Alkalinity pH	Standard Method 2320[17] EPA Method 3050b[15] EPA Method 150.1[18]

Detailed methods and information on quality control are provided in Appendix A and Appendix B. For the soil, acid digestion was performed to determine the initial metals concentration following EPA Method 3050B. The digest was then analyzed for metals using Standard Method 3111.

Toxicity potential leaching tests (TCLP)

To determine the potential of brine to leach from soil to groundwater, EPA Method 1311 for the toxicity potential leaching test (TCLP) for metals was performed. In brief, for this work the TCLP test was used to determine the mobility of metals in soil amended with different volumes of brine. Preliminary evaluations on the soil brine mixture include determination of percent solids and pH so that the appropriate type and mass of extraction fluid is selection (see Figure 1). The extraction fluid was then added to the sample and agitated end over end for 18 hours at 30 rpm. The sample was then filtered and the extract is collected and acidified and analyzed for metals following Standard Method 3111. Figure 1 shows the experimental setup for the TCLP procedure.

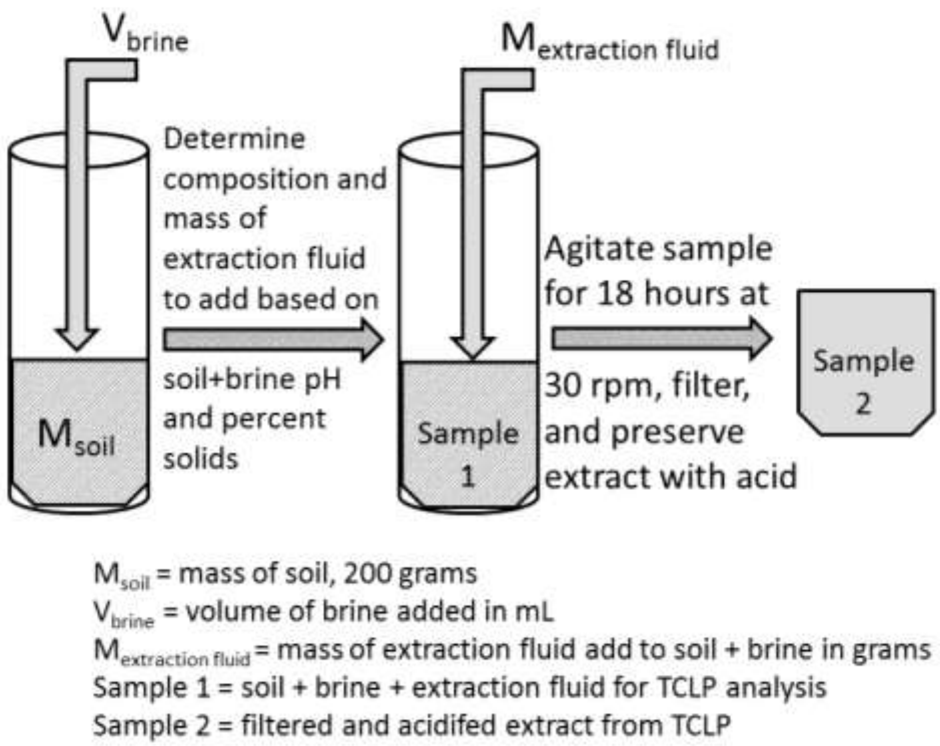

Figure 1. TCLP experimental setup.

Table 5 shows the experimental conditions for the soil and brine along with the determined percent solids, pH, and mass of extraction fluid. A total of 18 combinations of soil and brine were analyzed. Details regarding the determination of percent solids and extraction fluid is found in Appendix A.

Table 5. Experimental conditions for TCLP.

Sample #	Mass soil (g)	Volume Brine A (mL)	Percent solids	pH	Mass of extraction fluid added (g)
1	200	200	60.44	4.99	48.2
2	200	100	73.92	5.18	44.2
3	200	50	84.15	5.18	41.6
4	200	25	90.86	5.28	40.6
5	200	10	96.05	5.41	40.4
6	200	1	98.91	5.56	39.8
Sample #	Mass soil (g)	Volume Brine B (mL)			
7	200	200	65.80	5.40	55.3
8	200	100	79.28	5.60	48.8
9	200	50	86.89	5.44	44.0
10	200	25	91.45	5.34	41.7
11	200	10	96.03	5.20	40.5
12	200	1	98.88	5.46	39.8
Sample #	Mass soil (g)	Volume Brine C (mL)			
13	200	200	66.88	6.94	56.3
14	200	100	78.04	6.71	48.4
15	200	50	86.51	6.43	44.6
16	200	25	92.01	6.02	42.1
17	200	10	96.81	5.84	N/A
18	200	1	98.86	5.86	N/A

The TCLP test was selected because the procedure involves the addition of an acid to lower pH which favors the dissolution of metals. In New York, precipitation has a pH between 4 and 4.5, which indicates that it will contribute to the potential for metals to leach from the soil/brine mixture to groundwater[19].

Results and Discussion

Brine characterization

Total solids, total suspended solids, and total dissolved solids are physical characteristics of a sample. Dissolved solids are organic and inorganic constituents that are dissolved in solution. Suspended solids are small solid particles that remain in suspension in solution. Figure 2 shows the concentrations of total solids (TS) and total dissolved solids (TDS) for the three brines. Total suspended concentrations (TSS) were excluded as the concentrations of TSS were negligible compared to the TS and TDS concentrations. All raw data can be found in Appendix B. As shown in Figure 2, Brine B, which is the blended oil brine, has the highest total solids and total dissolved solids, followed by Brine C (plant-based, chloride free brine) and then Brine A (agricultural based brine).

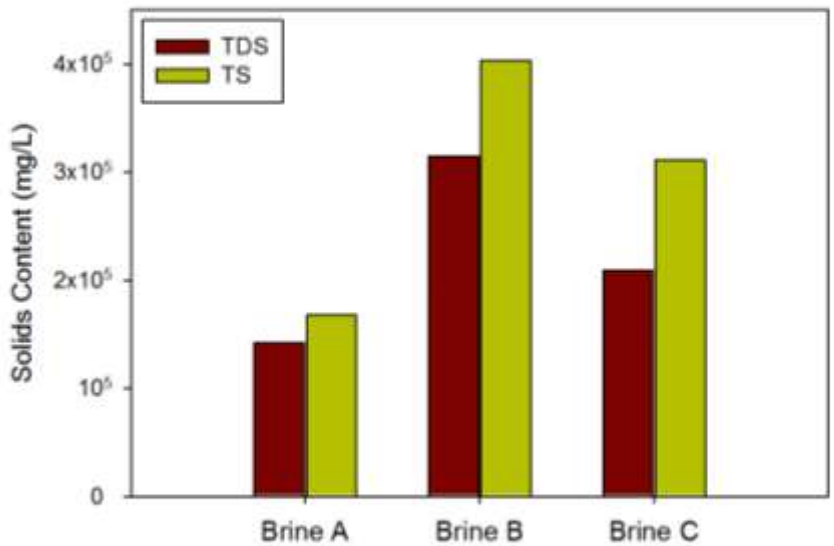

Figure 2. Solids concentration (mg/L) for brines.

Table 6 shows the pH measurements of the brines. pH is a measure of the acidity or basicity of a sample. Solutions with a pH below 7 are considered acidic while solutions with a pH above 7 are considered basic. pH was determined using a Thermo Electron Orion 3 Star pH benchtop meter. The procedure for determining pH is found in Appendix A. Based on these results, the pH of the three brines varies and Brine C has the highest pH while the Brine A has the lowest pH.

Table 6. pH readings for each brine.

Brine	pH
Brine A	5.50
Brine B	6.42
Brine C	8.37

Alkalinity was also determined for the three brines. Alkalinity is a measure of the buffering capacity of a solution, or its resistance to changes in pH. Alkalinity was determined using a Hach alkalinity test kit (TNT870). The procedure for determining alkalinity is found in Appendix A. Based on these results, the alkalinity of the three brines varies and Brine C has the highest alkalinity while Brines A and B have similar Alkalinity

Table 7. Alkalinity data for brines.

Brine	**Alkalinity (in mg/L as $CaCO_3$)**
Brine A	184
Brine B	180
Brine C	275

To determine the major anions present in the brine, ion chromatography (Dionex DX-120, Sunnyvale CA) was used. Figure 3 shows the concentration in mg/L of four major anions (fluoride, chloride, nitrate, and sulfate) present in the brines. Concentrations were determined from a calibration curve (range 1 mg/L to 100 mg/L). Sample dilutions were performed where necessary.

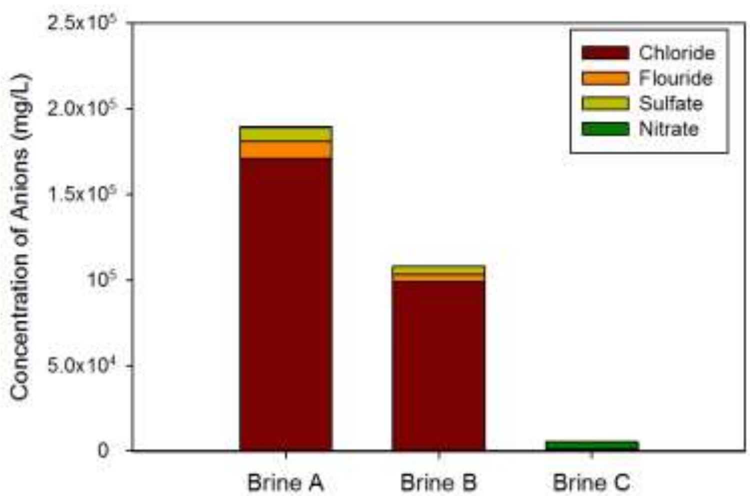

Figure 3. Anion concentrations (mg/L) for brines.

Brine A, which is the agricultural based product blended with sodium chloride, has the highest concentration of all major anions except for nitrate, which is found at the highest concentration in Brine C. Brine C is an all-natural product, and should not contain any chloride or sulfate, however, analysis shows that Brine C does contain some chloride and sulfate, although at a lower concentration than nitrate. Brine B contains the lowest concentration of nitrate and also contains a significant concentration of chloride, which is expected, as Brine B is the oil-brine that is blended with Brine A.

The concentration of several metals was determined for the three brines following Standard Method 3111 (Metals by flame atomic absorption). These results are shown in Table 8 and Figure 4. Most metals were not detected in the brine, however, potassium and lead were found in all three brines. Potassium showed the highest concentrations in all brines, with higher concentrations in Brines A and B than Brine C. Compared to oil-field brines, brines A-C show much lower concentration of potassium, but higher concentrations than conventional deicers. All brines show higher concentrations of lead than found in oil-field brines.

Analytical difficulties were experienced in the determination of metals concentrations in these brines due to the high total dissolved solids concentrations. It is possible that these concentrations are being underestimated or are not able to be detected using flame AAS.

Table 8. Metal concentration (mg/L) in brines. ND indicates the metal was not detected (below instrument detection limit; see Appendix A).

Metal Concentration (mg/L)	Brine		
	Brine A	Brine B	Brine C
Zinc	ND	ND	4.5
Potassium	206	213	46
Lead	8.9	11.7	9.31
Nickel	ND	ND	11.0
Manganese	ND	3.87	ND
Copper	ND	ND	ND
Cobalt	ND	ND	ND
Cadmium	ND	ND	ND
Chromium	ND	0.63	0.06

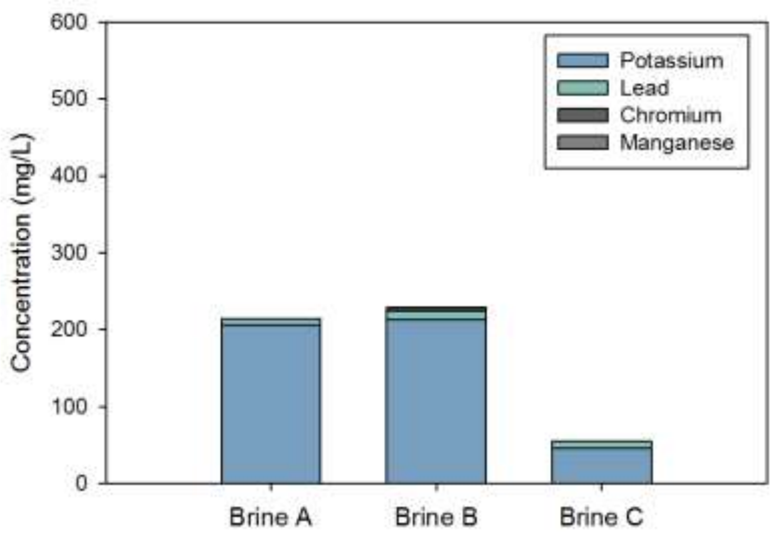

Figure 4. Metal concentrations (mg/L) in brines.

Soil characterization

After the brines were characterized, the physical and chemical characteristics of the soil used in the leaching tests were determined. The percent solids of the soil sample was determined following Standard Methods 2540 and was found to be 98.94%. The pH of the soil was determined to be 5.66 by using a pH meter and was verified using pH strips.

The concentration of metals were determined in the soil by analysis of an acid digested soil sample with flame AAS. The metal concentrations are shown in Table 9 and Figure 5. The concentration of nickel found in the soil is much higher than any of the other metals. Nickel is a naturally occurring element that can exist in various mineral forms. Nickel generally accumulates at the surface of soil from deposition by industrial and agricultural activities. Nickel's content in soil can range from 3 to 1000 mg/kg[20,21] and is primarily a concern in urban areas, which is where this soil sample was collected. Chromium shows the second highest concentration in the soil at a concentration of 59.1 mg/kg. In the U.S., chromium concentrations in soil range from 1 to 2000 mg/kg with a mean of 37.0 mg/kg[22].

Table 9. Metal concentrations (mg/L) in soil.

Metal	Concentration (mg/kg)
Zinc	ND
Potassium	0.323
Lead	6.02
Nickel	309
Manganese	21.1
Copper	5.49
Cobalt	2.77
Cadmium	ND
Chromium	59.1

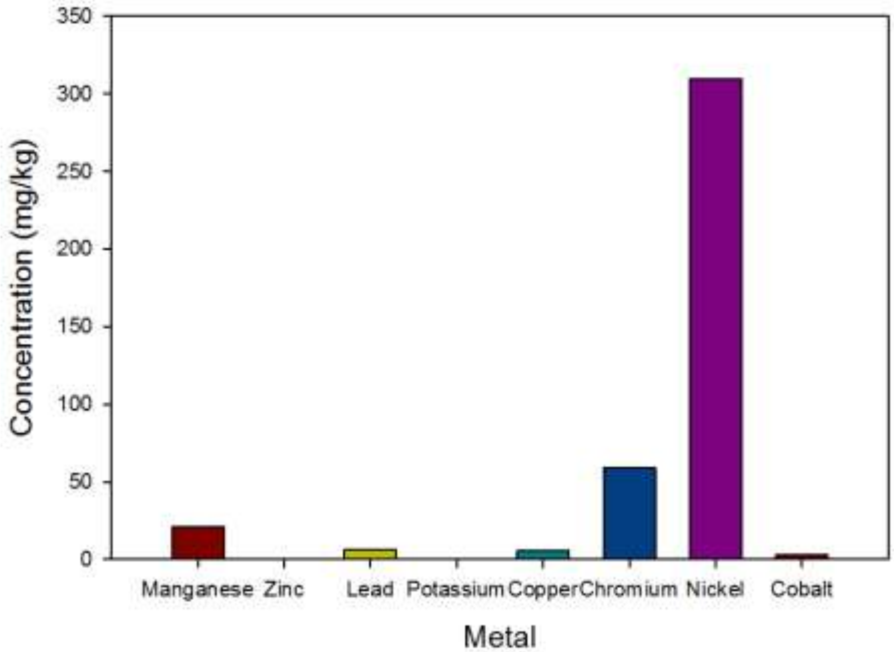

Figure 5. Metal concentrations (mg/kg) in soil.

Leachability studies

The potentials for metals to leach from a soil/brine mixture to groundwater were tested following the experimental conditions in Table 5. No data is shown for the samples that had 1 mL and 10 mL of brine added. This was due to difficulties in extracting the fluid from the mixture. Additionally, results for the leaching tests for 200 mL of brine added were inconclusive and need to be repeated to ensure they meet quality control conditions.

These results show that, in general, as the volume of brine added to the soil increases, the leachability of metals from the soil/brine mixture also increases. Brine B (oil-based brine) shows the highest concentration of metals in the TCLP extracts regardless of the amount of brine added to the soil. Manganese showed the highest concentrations in the TCLP extracts, followed by zinc and lead. This is surprising as manganese, lead, and zinc were found at relatively low concentrations in all brines and soil.

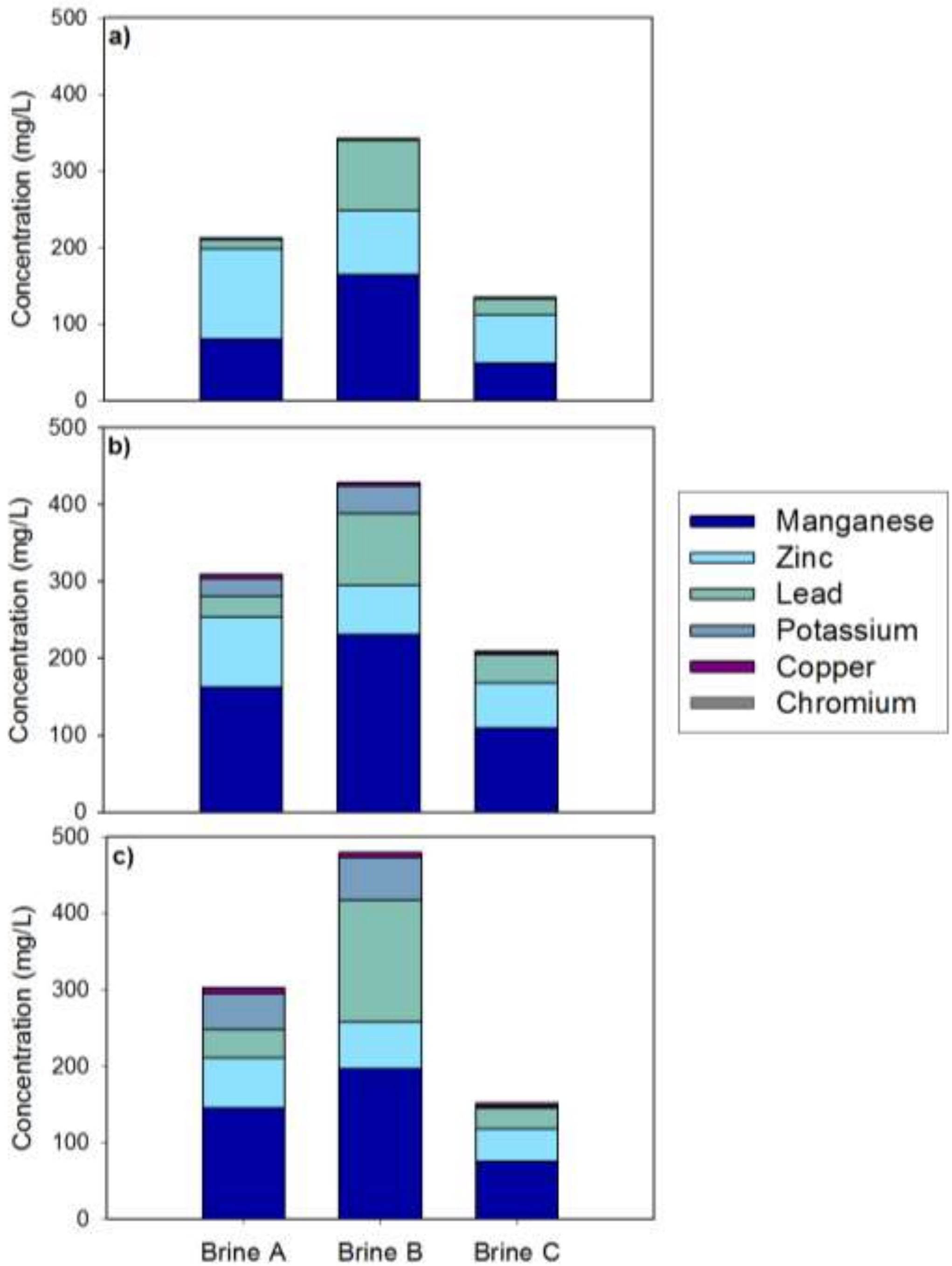

Figure 6. Metal concentration (mg/L) in TCLP extracts. a) 25 mL brine addition; b) 50 mL brine addition; c) 100 mL brine addition.

Tables 10, 11 and12 show a summary of the metal concentrations in the TCLP extracts compared to the concentrations in each brine and soil. For Brine A (Table 10) the extracts show much higher concentrations than the brine except for potassium. It is probable that the concentrations of metals in the brine are underestimated due to the analytical interferences with high total dissolved solids as previously discussed. The metal concentrations in the extracts are also higher than those found in the soil, which indicates that their contributions are likely from the brine and not the soil. Chromium was not detected in any extracts despite showing a relatively high concentration in soil. Zinc was also present in the TCLP extracts, but with increasing brine concentration the extracts showed a decrease in zinc concentration, which is surprising. This likely indicates that Brine A is not contributing to zinc, and that the soil may contain higher zinc, or that the lower pH used in the TCLP extractions results in a leaching of zinc from minerals in the soil.

Table 10. Summary table for metals from Brine A leaching tests, Brine A characterization, and soil characterization.

Metal	25 mL Brine A	50 mL Brine A	100 mL Brine A	Brine A	Soil
Manganese	80.4	162	145	ND	21.1
Lead	12.1	27.0	37.2	8.90	6.02
Zinc	117	91.6	66.5	ND	0.73
Potassium	ND	22.2	46.4	206	0.32
Copper	2.87	5.85	7.81	ND	5.49
Chromium	ND	ND	ND	ND	59.1

Table 11 shows a summary for the leaching tests for Brine B. Manganese showed the highest concentrations in the extracts, followed by lead. Again, this is surprising because Brine B and the soil showed low concentrations of both manganese and lead. Brine B shows much higher concentrations of lead in the TCLP extracts than Brine A.

Table 11. Summary table for metals from Brine B leaching tests, Brine B characterization, and soil characterization.

Metal	25 mL Brine B	50 mL Brine B	100 mL Brine B	Brine B	Soil
Manganese	165	231	196	3.87	21.1
Lead	91.7	93.6	159.6	11.7	6.02
Zinc	83.6	63.3	42.8	ND	0.73
Potassium	ND	35.6	55.6	213	0.32
Copper	2.63	4.31	6.59	ND	5.49
Chromium	ND	ND	ND	0.63	59.1

Table 11 shows a summary for the leaching tests for Brine C. Manganese showed the highest concentrations in the extracts, followed by zinc and lead. Manganese and zinc were not detected in Brine C likely due to interferences with dissolved solids. Compared to Brines A and B, Brine C showed the lowest potential for the leaching of metals. Brine C is the plant-based brine and in general showed the lowest concentrations of all metals, anions, and solids. These results indicate that Brine C may have the lowest potential to affect metal concentrations in the environment if it is used for deicing or dust control.

Table 12. Summary table for metals from Brine C leaching tests, Brine C characterization, and soil characterization.

Metal	25 mL Brine C	50 mL Brine C	100 mL Brine C	Brine C	Soil
Manganese	48.9	109.3	75.5	ND	21.1
Lead	21.1	37.5	26.6	9.31	6.02
Zinc	62.8	58.5	42.8	ND	0.73
Potassium	ND	0.08	2.90	45.6	0.32
Copper	1.87	2.84	2.77	ND	5.49
Chromium	0.97	1.39	1.59	0.060	59.1

Table 13 shows the drinking water maximum contaminant levels[23] for the metals that were found in the TCLP extracts (and thus likely to be found in groundwater after leaching). Manganese, zinc, and copper are not primary drinking water contaminants because they do not cause a direct effect on human health, however, they can contribute to taste and odor impacts in drinking water.

Table 13. Maximum contaminant levels (mg/L) for metals in drinking water.

Contaminant	Concentration (mg/L)
Manganese[a]	0.05
Lead	0.015
Zinc[a]	5.0
Potassium	Not regulated
Copper[a]	1.0
Chromium	0.1

[a]Secondary drinking water contaminant. Non-enforceable suggested regulated concentration.

Based on the results from the leaching tests all experimental conditions would result in concentrations in groundwater that are elevated above the maximum contaminant levels set forth by the USEPA. Of particular concern to human health are the concentrations of lead and chromium that would be found in groundwater. Lead can bioaccumulate in the body over time and is harmful to human health even at low exposure levels. Lead exposure has been linked to physical and behavioral effects (damage to the nervous system, learning disabilities, etc.)[24]. With the results of the leaching tests, the lead concentrations in groundwater are much higher than the MCL for drinking water.

Although chromium toxicity depends on the oxidation state (Cr(III) is not toxic, while Cr(VI) is carcinogenic[25] the EPA regulates total chromium (Cr(III) plus Cr(VI) in drinking water. Based on the results of the leaching tests, it is unknown whether the brines ad soil contained the toxic Cr(VI) or nontoxic Cr(III), as the Standard Method is used to determine total chromium. Based on these results, the concentrations of total chromium in groundwater would exceed the MCL of 0.1 mg/L for total chromium.

Given these results, it is recommended that brines be evaluated for their physical and chemical properties before they are applied for dust and ice control. Additional tests should be conducted with smaller volumes of brine addition to find the maximum amount that can be applied so that the drinking water MCL is not exceeded.

Conclusions

The objective of this work was to determine the potential for metals found in oil and gas brine to leach from soil to groundwater. The potential for metals found in other alternative brines (agricultural based and plant based) was also be investigated. Results show that the plant-based brine has the least potential to leach metals from a soil/brine mixture, while the oil-based brine has the highest potential to impact the environment through the leaching of metals. In New York, the pH of precipitation is acidic (pH 4 to 4.5), and as such will increase the potential for metals to leach from a soil that has been amended with a brine. Future applications of brine for dust and ice control should consider their potential environmental impacts.

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Appendix A. Experimental Section and Materials and Methods

A1: Solids

Total Solids

Evaporating dishes were clean by rinsing them with deionized water and then heating in a 103-105°C oven for 1 hour. They were then stored and cooled in desiccator until they reached room temperature. The weight of the evaporating dishes (in grams) was recorded using a laboratory calibrated balance. A sample volume of 15mL was measured using an automatic pipettor and placed in the clean evaporating dishes. These brines were analyzed in duplicate for quality control, and a blank (deionized water) and standard solution (600 mg/L NaCl) were also analyzed for quality control.

The samples were then placed in a 103-105°C oven for 1-2 hours or until they were completely evaporated. The dishes were cooled in desiccator until they reached room temperature and weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained, or until the weight change was less than 4%.

Total Dissolved Solids and Total Suspended Solids

Evaporating dishes were clean by rinsing them with deionized water and then heating in a 180 ± 2°C oven for 1 hour. They were then stored and cooled in desiccator until they reached room temperature. The weight of the evaporating dishes (in grams) was recorded using a laboratory calibrated balance.   Filters were rinsed with deionized water and dried on aluminum weighing dish in a 103-105°C oven for 1 hour. The filter was inserted wrinkled side up into a filtration apparatus. A vacuum was applied to the apparatus and the filter was washed with three successive 10-mL of deionized water. Continued suction was applied to remove all traces of water. The washings were discarded. A sample volume of 15mL was used and placed in the filtration apparatus with an additional 10-mL washing of deionized water to ensure the sample is completely rinsed off from the apparatus. Total filtrated (with washings) was then transferred to an evaporating dish and then placed in a 180 ± 2°C oven for 1-2 hours or until they were completely evaporated. The dishes were cooled in desiccator until they reached room temperature and weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained, or until the weight change was less than 4%. The filters were carefully removed from the filtration apparatus and transferred back to the original aluminum weighing dishes that they were weighed on. The filters were then placed in a 103-105°C oven for 1-2 hours or until they were completely dried. The filters were cooled in desiccator until they reached room temperature and weighed. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained, or until the weight change was less than 4%.

A2: pH

A 20 mL sample was collected from each brine. The pH was measured using a Thermo Electron Corporation Orion 3 Star pH Benchtop meter. The meter was calibrated using three standard pH solutions (4, 7, and 10, VWR International). The pH of each brine sample was determined using this meter. The electrode tip was rinsed with deionized water between the pH measurements of each brine.

A3: Alkalinity

The brine samples were filtered through a filter apparatus with 0.45 µM filter paper. The samples were diluted by adding 2.5 mL of each sample into a 50 mL Erlenmeyer flask with deionized water. The solutions were mixed by inverting the flasks. 2.0 mL of Solution A was added (Solution A from the Alkalinity Test kit provided by Hach Company) to the TNTplus™870 vial. 0.5 mL of the sample was added (Brine A and Brine B) to the test vial. 0.25 mL of Brine C and 0.25 mL of deionized water was added to another vial. The vials were inverted until completely mixed. The vials were left to complete the reaction for 5 minutes. After 5 minutes, insert each vial into the cell holder and measure the alkalinity. Calculate the exact alkalinity after the dilutions.

A4: TCLP experimental procedure

According to the EPA Method EPA Method 1311 (TCLP) the type amount of extraction fluid to be added to the sample is a function of the sample's percent solid content. Therefore in order to determine the amount of extraction fluid required for each test a method similar to a Total Solids (TS) analysis was conducted. Samples were prepared and heated to 103°C then cooled in a desiccator and weighed. This process was repeated until the weights were either within 5% or 0.0005 mg (smaller or the two) of the previous weighing. Once the percent solids for each soil to brine ratio was known, the amount of extraction fluid per sample was determined using Equation 1:

$$\text{Weight of extraction fluid} = \frac{20 * \text{percent solids} * \text{weight of sample}}{100} \quad (1)$$

The type of extraction fluid was determined based on sample pH and for all analyses extraction fluid #1 was used (EPA Method 1311).

A5: Metals

Metals were analyzed following Standard Method 3111 using flame atomic absorption spectrometry. The method detection limits determined are shown in Table A1. Sample pH was lowered to pH 2 using HNO_3.

Table A1. Method detection limits for metals.

Metal	Detection Limit (mg/L)
Zinc	0.05
Potassium	0.5
Lead	0.5
Nickel	0.5
Manganese	1.25
Copper	0.1
Cobalt	0.5
Cadmium	0.5
Chromium	0.05

Appendix B. Data and Quality Control

B1: Solids

According to Standard Methods, duplicate samples must agree within 5% of their average weight. All samples meet quality control for total solids and total dissolved solids, and results from the total suspended solids meet quality control for the Brine A brine only. The tests for brines B and C were repeated three times but still did not meet quality control. The concentrations for all brines is found in Table B1 and quality control data is found in Table B2.

Table 14. Solids concentration data (in mg/L) for DI water, standard solution, and brines.

Sample	Total Solids (mg/L)	Total Dissolved Solids (mg/L)	Total Suspended Solids (mg/L)
Deionized Water	267	67	ND[a]
Standard Solution	580	600	ND[a]
Brine A	166,853	139,500	153
Brine A (duplicate)	169,533	145,393	433
Brine B	408,180	315,400	2,320[b]
Brine B (duplicate)	398,600	314,267	1,973[b]
Brine C	315,920	193,300	696 [b]
Brine C (duplicate)	305,973	225,133	360 [b]

[a]ND = data below detection limit. No noticeable solids concentration.

[b]Data did not meet quality control parameters. For brine B, duplicate samples were within 6% of their average weight. For brine C, duplicate samples with within 32% of their average weight.

Table B2. Quality control for solids analysis.

Sample	Total Solids (mg/L)	Average	5% of average	Difference from average	Meet QC? (Y/N)
Brine A	166853	168193	8409.65	-1340	Y
Brine A (duplicate)	169533			1340	Y
Brine C	315920	310946.5	15547.325	4973.5	Y
Brine C (dup)	305973			-4973.5	Y

Sample	Total Dissolved Solids (mg/L)	Average	5% of average	Difference from average	Meet QC? (Y/N)
Brine A	139500	142446.5	7122.325	-2946.5	Y
Brine A (duplicate)	145393			2946.5	Y
Brine C	193300	209216.5	10460.825	-15916.5	**N**
Brine C (dup)	225133			15916.5	**N**

Sample	Total Suspended Solids (mg/L)	Average	5% of average	Difference from average	Meet QC? (Y/N)
Brine A	153	293	14.65	-140	**N**
Brine A (duplicate)	433			140	**N**
Brine C	773	596.5	29.825	176.5	**N**
Brine C	420			-176.5	**N**

B2: Anions

Sample	Fluoride (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
Brine A	10,082	170,738	570	8,243
Brine B	4,393	98,721	135	4,786
Brine C	ND[a]	922	4,320	100

[a]ND = data below detection limit (1 mg/L)

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