CHEMICAL ANALYSIS OF MAJOR CONSTITUENTS AND TRACE CONTAMINANTS OF ROCK SALT

Robert V. Titler, Environmental Chemist and Paul Curry, Water Program Specialist

Pennsylvania Department of Environmental Protection
Bureau of Water Standards and Facility Regulation

Executive Summary

The main purpose of this study is to analyze various rock salt sources to determine the existing composition of rock salt. The results will then be compared to the chemical composition of the salt produced from Shale Gas Extraction Wastewater (SGEW) evaporation. Naturally occurring rock salt was formed from the evaporation of inland seas. Its primary constituents are sodium, chloride, calcium, magnesium, potassium, and sulfate. Rock salt generally contains between 90 to 98% sodium chloride. The salt content in SGEW may exceed 200,000 mg/l or approximately 7 times saltier than sea water.

In the United States, approximately 77% of the rock salt domestically produced, and imported, is used for highway de-icing. In order to compare the differences or similarities of salt obtained from treated SGEW to "conventional" rock salt currently being used for de-icing in Pennsylvania, it is necessary to analyze conventional rock salt samples from various sources. At room temperature, rock salt is in the solid state; therefore, an aqueous solution must be prepared for analysis. The high content of sodium in the rock salt can result in interference issues for metal analysis using Inductively Coupled Plasma analysis. In this study, the high sodium and chloride content of the rock salt also caused interferences in the gross alpha and beta analyses as well.

Rock salt in its native form should not contain any synthetic organic compounds. The chemical composition findings in this study are supported by the Assale and Khewra rock salt studies. Calcium was detected in only one of the samples. If the detection limits of calcium were lower, it should have been detected in all of the DEP's rock salt samples. The trace chemicals in rock salt samples could vary depending upon the location and geologic time when the salt deposit was formed.

The chemical composition of rock salt, compared to SGEW, yielded very low concentrations of barium and strontium. Conversely, data reviewed from SGEW analyses indicate that high concentrations of both barium and strontium are usually detected. The low concentrations of the few organic compounds detected in this study could have resulted from contamination during transportation of the rock salt or at its storage location.

Introduction

The Marcellus Shale Play is estimated to contain more than 500 trillion cubic feet of recoverable natural gas (Engelder, 2008). The process of hydraulic fracturing employed to facilitate extraction of the gas from the deep Marcellus Shale formations uses large quantities—typically millions of gallons per well—of fresh water. A variety of chemicals and sand are intentionally added to the water to produce a proprietary hydro-fracturing fluid. The added chemicals act to reduce friction, inhibit corrosion or scale formation, and serve as proppants (EPA, 2011). This water also becomes laden with contaminants that are introduced into this mixture below ground as a result of contact with natural formations. A significant portion of this fracking fluid is not retained underground but, due to underground pressure, returns to the surface where it is referred to as flowback water. The drilling/hydrofracturing process also brings large quantities of highly saline water, previously trapped underground, to the surface. The release of these waters, referred to in this document as Shale Gas Extraction Wastewater (SGEW), untreated into surface waters is prohibited. This restriction has created a significant industry in the processing or treatment of SGEW. One product, or byproduct, of the treatment processes is concentrated brine or, in some cases, solid salt.

The main purpose of this study is to analyze rock salt from various sources to determine the composition. The results will then be compared to the chemical composition of the salt produced from SGEW evaporation. This will provide data to determine what, if any, additional pollutants may be introduced into the water column from the fracking practices.

Research from the Pennsylvania Department of Environmental Protection (PADEP), Bureau of Oil and Gas Management, shows a high concentration of the metals barium and strontium along with other heavy metals in SGEW. In the crystallization process of SGEW, these metals have to be removed to an acceptable concentration.

Rock salt is a sedimentary rock, which is classified as an evaporate. Naturally occurring rock salt is formed from the evaporation of inland seas. The rock salt contains the minerals found in that particular body of water; mostly sodium, chloride, calcium, magnesium, potassium, and sulfate. These are the major elements found in rock salt. All of these substances are highly soluble in water. Shale is also a sedimentary rock; however, it is classified as a clastic rock layer. Clastic sedimentary rocks are composed predominantly of broken pieces of older weathered and eroded rocks and are classified based on grain size, clastic and cementing material (matrix) composition, and texture. Shale is a fine-grained, clastic sedimentary rock composed of mud that is a mix of flakes of clay minerals and tiny fragments (silt-sized particles) of other minerals, especially quartz and calcite. Many of the minerals that make up shale are insoluble in water. Marcellus Shale is black shale, which is dark, thinly laminated carbonaceous shale, exceptionally rich in organic matter and sulfide and often containing unusual concentrations of certain trace elements such as uranium, vanadium, copper, and nickel.

Background

There are a variety of methods employed to manage the SGEW. These range from disposing of it (untreated) deep underground in injection wells, treating as necessary to allow it to be re-used in other hydrofracturing procedures, and treating it to a degree necessary that it can be discharged to surface waters. Some facilities are dedicated solely to treating SGEW. Until early 2011, some publicly-owned treatment works (POTWs) in Pennsylvania accepted a limited amount of SGEW that was treated along with their domestic wastewater flow.

When treatment is utilized, dealing with the significant quantity of highly saline SGEW is a challenge. The salt content may exceed 200,000 mg/l, about 7 times saltier than sea water. The treatment processes result in the concentration of salt in the brine being increased to the point where it precipitates out. Some evaporation/crystallization treatment processes produce salt cake that can be further processed to produce granular salt. Early estimates (circa 2009) were that as the Marcellus shale "play" nears its potential full production volume, sufficient treatment facility capacity for twenty million-gallons-per-day of SGEW could be required, which would result in the production of 7,500 – 12,500 tons of salt per day [1]. It is desirable to identify a beneficial use for the concentrated salt solution, or brine, as well as the dried salt cake that may be produced by the various treatment processes. One apparent possible use is the application to roads as a winter de-icing agent.

Brine from "traditional" oil and gas drilling has been used for years as a de-icing agent. There are also brine wells specifically for brine production. Traditional, in this sense, generally means drilling that does not use the hydraulic fracturing process (no chemical additives) and overwhelmingly involves wells that are not completed in the Marcellus Shale formation. However, concern has been raised that the brine, or salt cake obtained from treated SGEW may contain trace amounts of chemicals from the hydrofracturing process as well as constituents dissolved in the produced water and brought to the surface by the gas extraction. Research from the Bureau of Oil and Gas Management indicates that SGEW includes a high content of hazardous heavy metals, such as barium and strontium. There is also concern about radioactivity. The Marcellus Shale play is known to generally be more radioactive relative to other geologic formations.[2] Of course, the radioactivity of deeply buried shale is of no concern. However, what is natural or normal at that depth is not natural on the surface of the ground and concern is being expressed about the radioactivity of products resulting from Marcellus Shale extraction. These previously buried materials are referred to as "naturally occurring radioactive materials" (NORMs). When materials containing NORMs are processed or refined, the radioactive material may become more concentrated to create "technologically enhanced naturally occurring radioactive materials" (TENORMs). The primary radionuclides of concern are Radium 226 (Uranium-238 decay series) and Radium 228 (Thorium-232 decay series).

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[1] Chapter 95 – Wastewater Treatment Requirements, PowerPoint presentation given by John Hines, former Pennsylvania DEP Deputy Secretary for Water Management As of this writing, current trends such as improved drilling techniques, recycling, policy changes, etc. will likely result in less SGEW being sent to treatment facilities. While an accurate calculation of a revised salt quantity estimate would be difficult, it is now recognized that earlier estimate is improbably high.

[2] Attributed to Terry Engelder (PSU) in Sumi,L., Shale Gas: Focus on the Marcellus Shale

Radium is slightly soluble and may become mobilized in fluid phases of the Marcellus formation.

Salt Production

For the purpose of tracking production, there are four types of salt (sodium chloride) classified according to the methods of extraction or recovery used to obtain it. Rock salt (halite) is obtained from underground room and pillar mining, or surface mining of bedded halite, or halite domes. Solar salt is obtained in areas of low precipitations and high evaporation rates from solar evaporation of seawater or inland salt water lakes. Brine salt is obtained from solution mining of underground salt formations. This brine salt is used as a feedstock for mechanical evaporation processes that produce vacuum pan salt, which is in flake rather than cubic form and is preferred for food applications.

The least expensive source production method of salt is by solar evaporation. However, the limited areas where this method is viable means it cannot provide the quantity of salt necessary for many purposes. Underground mining of rock salt is relatively inexpensive and can produce vast quantities of salt. Consequently, this is the source of the overwhelming majority of rock salt used for winter road de-icing in the United States.

Rock Salt Production and Usage in the U.S.

Appendix Table A.1 presents a table of U.S. rock salt producer locations and the production volumes in 2009. It should be noted that the various sources of data for salt production/consumption (e.g. USGS reports, industry data, Salt Institute data) are in approximate agreement; however, there are some variations. Also, a significant amount of salt is imported. While specific figures for rock salt imports are not readily available, the United States imported 14.7 million metric tons of salt from 48 countries in 2009 (U.S. Census Bureau statistics). Canada was the leading source of imports, representing about 40% of total imports, followed closely by Chile (35%). Notably, the International Salt Company with headquarters in Pennsylvania and affiliated with the Chilean salt producer Sociedad Punta de Lobos, imports rock salt mined from the Tarapaca´ Salt Flat. This salt is mined in open pits which is possible due to the extremely arid climate.

In the United States, approximately 77% of the rock salt domestically produced and imported is used for highway de-icing. As may be expected, the quantity used varies from year to year with the severity of the winter weather. According to the 2009 United States Geological Survey Minerals Yearbook, (Yearbook) about 22.6 million metric tons was consumed nationally for this purpose in 2008-2009. Pennsylvania (PA DOT and municipalities) used about 1.7 million metric tons that winter. Appendix Table A.2 presents a summary of highway (rock) salt volumes and sales from 2000 - 2009.

Rock Salt Supply and Availability

Although salt is generally regarded as an inexpensive, widely available commodity, there have been shortages with accompanying price fluctuations in the highway salt market. The Yearbook reports that in late 2008 many municipalities nationwide were reporting difficulties in obtaining salt, and prices had increased significantly from 2007. The situation became so severe that an investigation into price-fixing was initiated by officials of several state governments. It was discovered that there was little evidence of price-fixing, but rather a problem caused by customers waiting too long (mid-Summer) to place their orders. This created a "seller's market" because many municipalities had placed orders earlier when salt companies had time to schedule production and deliveries. As a result, some municipalities had no choice but to pay premium prices as they were competing for a dwindling supply and timely delivery. There are a variety of reasons for shortages including shipping delays, contract requirements, and a series of unusually harsh, unexpected winter storms. Normally, inability of production, *per se*, to keep pace with demand is not generally regarded as a limiting factor.

A significant factor in the price of highway salt is transportation. In some cases, it may be the predominant factor and may be higher than the cost of the salt itself. This is where the market, particularly in areas proximate to a sea coast, favors bulk shipment of huge quantities such as those carried by large ocean vessels. Where ports of sufficient depth such as those near Philadelphia are available, imports of salt are growing because domestic transportation costs by truck or rail are not competitive.

Highway Salt Suppliers Prices (Pennsylvania)

Appendix Map 1 depicts the 2009/2010 renewal prices and the suppliers by county for highway salt. All but one of these sources (International Salt Company) supplies salt of domestic origin. Appendix Map 2 depicts the locations of the supplier's mines in close proximity to Pennsylvania. The average of the prices is $58.76. As indicated previously, prices for bulk rock salt fluctuate with supply and demand. In 2008, PA DOT paid an average of $56/ton. However, due to severe winter weather, there were also reports of shortages and prices as high as $185/ton were quoted to municipalities (Source: Pennsylvania Department of General Services). This resulted in PA DOT making a one-time emergency offering of 82,000 tons of rock salt to municipalities at a much lower fixed price. Hence, there are times when localized shortages may create a market for emergency surplus supplies.

Highway (Rock) Salt Specifications

Naturally occurring rock salt was formed from the evaporation of inland seas. The rock salt contains the minerals found in that body of water; mostly sodium, chloride, calcium, magnesium, potassium, and sulfate. Rock salt typically contains 90 to 98% sodium chloride. There are several published technical papers that provide some insight into what may constitute the trace components of a rock salt sample. The Appendix Table 2 provides an example of an analysis for Khewra rock salt mined in Pakistan. However, it must be understood that there are regional and certainly global variations in these trace components. Thus, it cannot be stated that these results are "typical." The standard specification for highway salt supplied to PA DOT is ASTM D632 (Grade 1). The chemical requirement of this standard is simply that the product must be a minimum of 95% sodium chloride (there is a post-delivery allowance of 0.5% - i.e. a minimum of 94.5% may be acceptable). It is likely salt production companies do quality control testing that identifies trace chemical components; however, this information is not typically provided to purchasers of rock salt for de-icing.[3] Producers may provide technical product information such as shown in the Appendix, Figure 1. PA DOT performs quality control analysis on the materials they purchase; however, information regarding the methods used, what analytes are looked for, and the results of these analyses were not made available for this study.

Purpose of Study

Huge quantities of rock salt mined from different sources are sold in bulk to the Commonwealth of Pennsylvania and municipalities for winter road application as an anti-icing agent. The suppliers who sell bulk rock salt also sell packaged rock salt for home and commercial use. The goal of this study is to provide chemical constituent guidelines for the beneficial reuse of salt obtained from processing SGEW as a de-icing agent. This study does not provide a determination of environmental or public health impacts of de-icing agents nor is it intended to advocate for their use.

Study Method

In order to compare the differences or similarities of salt obtained from treated SGEW in relation to "conventional" rock salt currently being used for de-icing in Pennsylvania, it is necessary to analyze conventional rock salt samples from various sources. The analyte list must include chemicals or elements that have been reported as constituents in the SGEW (Appendix Table A.10). The results of the chemical analyses will provide the data needed to establish the guidelines. While it may have been desirable to obtain rock salt samples from all of the suppliers to PA DOT or municipalities, there was an expectation at the onset of the study that there would not be a wide range of concentrations found in the various samples (sources). There were also budget constraints that limited the procurement of samples to the central Pennsylvania area as well as limiting the number of samples analyzed. The environmental impact of applying rock salt for road de-icing has been previously studied and determined to have minimal impact if prescribed application rates are followed. A decision was made to obtain a total of eight samples, some from municipal stockpiles and some from packaged rock salt available from retail locations. Two additional samples, table salt and deionized water, were used for quality control. Table 1 below presents the sample information.

[3] Telephone contact with Morton Satin, Vice-President of Science and Research, Salt Institute, Alexandria, VA

Table 1 – Sources of Rock Salt Samples for Study			
Source	**Vendor**	**Collector**	**Brand or Source**
Bagged Product	Agway-Davis	BT	Halite Rock Salt (Cargill)
Bagged Product	Hornung's True Value	BT	Ice-Away (Cargill)
Bagged Product	Yankee Hardware	BT	Morton Crystal Rock Salt
Bagged Product	Coles	RM	Halite Winter Melt (Cargill)
Bulk Stockpile	Sunbury Borough	RM	Cargill
Bulk Stockpile	Watsontown Borough (Northumberland County)	RM	American Rock Salt
Bulk Stockpile	East Buffalo Township (Union County)	RM	American Rock Salt
Bulk Stockpile	South Middleton Township (Cumberland County)	DA	International Salt (Chile)
Food Grade Package (field blank)	Giant Foods	BT	Non-iodized table salt (source unknown)

Limitations of the Analyses

At room temperature, rock salt, which generally contains between 90 to 98% sodium chloride, is in the solid state. Before proceeding with the chemical analysis of most solid substances, they must first be converted to their liquid state. With the exception of some radiological analyses, most of the testing in this study was performed after the rock salt was dissolved in water to form a solution. When analyzing pure substances, the solution has to be diluted so as to not over-saturate the detector used for analysis. This dilution will result in higher detection limits for the analytes. In other words, very small concentrations of some constituents may not be detected.

The high content of sodium in the rock salt can result in interference issues for metal analysis using Inductively Coupled Plasma analysis.

Quality Control Samples

Quality control samples are analyzed to ascertain whether anything that happened in the field or that nothing about the sample itself would affect the analytical results. One field blank was taken. The purpose of the field blank is to assess the potential of cross contamination of samples due to insufficient decontamination of sampling equipment. For this study, a sample of commercial non-iodized table salt was analyzed as a field blank. Equipment blanks were prepared with deionized water in the sampling containers.

Results

Rock salt in its native form should not contain any synthetic organic compounds. If SGEW is re-crystalized, it should not contain a high content of Volatile Organic Compounds (VOC's) or semi VOC's because in the drying process these organic substances would be released into the atmosphere. Occasionally, polychlorinated biphenyls (PCB's) are discarded along with other waste materials because they could possibly go undetected in the disposal of wastes.

From the analysis of SGEW in the "Sampling and Analysis of Water Streams Associated with the Developed of Marcellus Shale Gas" and from data obtained from the Bureau of Oil and Gas Management, the SGEW water contains much higher concentrations of barium and strontium. These are very hard to remove from the SGEW. If strontium and barium are not removed from the "frack" salt, it could have toxic effects on the environment if used as road salt.

Radiological Analysis

The samples were analyzed for the following radioactive isotopes: Total Uranium (U^{238}, U^{235}), Radium-226 and -228 (Ra^{226}, Ra^{228}), Lead-212 and 214 (Pb^{212}, Pb^{214}), Potassium-40 (K^{40}). Additional analyses included Gross Alpha and Gross Beta. The results are presented in Table 1. The high sodium and chloride content of the rock salt caused interferences in the gross alpha and beta analyses. Therefore, the gross alpha and beta data could be suspect. The rock salt samples yielded low levels of radium, lead, and uranium. Potassium 40 is highly soluble in water and is expected to be detected in evaporated rocks. The ranges of the concentrations detected are listed in Table 1.

Table 2 - Radioactive Analysis Results

Isotope	Concentration Range pCi/kg
Radium-226	668+/-82 to155+/-44
Radium-228	Only one detection - 17±11
Potassium-40	807+/-60 to 90+/-40
Lead-212	31+/-15 to 36+/-15
Lead-214	No detections
Uranium-238	872+/-225 to 0
Uranium-235	No detections
Gross Alpha	No detections
Gross Beta	No detections

Metal Analysis

All metal analyses were performed using an Inductively Coupled Plasma (ICP) methodology except for strontium. Strontium analysis was performed by Inductively Coupled Plasma - Mass Spectrometry (ICP/MS). Note the correlation between the results and the following list, Table 3, of the most abundant metals found in the earth's crust aluminum, iron, calcium, sodium, potassium and magnesium. Also, note that calcium was detected in only one of the samples. The detection limit for calcium was 579 mg/kg, which was rather high. If the detection limits were lower, calcium should have been detected in all of the samples. More precise results may have been determined if flame Atomic Adsorption (AA), or a graphite furnace, methodology been utilized. Table 3 presents the results for the metals analyses.

Table 3 – Metals Analysis Results

Element	Concentration Range in mg/kg
Aluminum	41.6 to 256
Antimony	No detect
Arsenic	No detect
Barium	4.18 to 5.2
Beryllium	No detect
Boron	No detect
Cadmium	No detect
Calcium	3473 (one sample only)
Chloride	590000 to 606,000
Chromium	No detect
Chromium +6	No detect
Cobalt	No detect
Copper	No detect
Iron	18.1 to 324
Lead	No detect
Lithium	No detect
Magnesium	256 to 1386
Manganese	2.0 to 5.2
Molybdenum	No detect
Nickel	No detect
Potassium	119 to 295
Selenium	No detect
Silver	No detect
Sodium	371,606 to 400,015
Strontium	11.9 to 138
Thallium	No detect
Tin	No detect
Titanium	No detect
Zinc	No detect

Non Metal Analysis

Ion chromatography was used to analyze the halides, fluoride, chloride, bromide, and iodide. A substantial dilution of the sample was necessary due to the significant chloride concentration. This resulted in non-detects of the other halides.

Organic Analysis

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes, and various aromatic hydrocarbons. Most of the organic analysis was of synthetic organic compounds. Humans were not in existence when halite was formed, therefore no synthetic organic substances should be present in rock salt. If organic substances are detected, they were probably introduced to the rock salt after it was mined or at the storage location. In the Shale Gas Extraction process, many organic additives are added to increase the efficiency of the drilling. In the re-crystallization process of flow back water, all the VOC's and most of semi VOC's will evaporate under heat and pressure and be released into the atmosphere. A few organic compounds (Table 4) were detected and are found in gasoline and diesel fuel. These contaminants were probably acquired during transportation or storage of the rock salt. Acetone, used as a solvent, was detected in only one sample. Another sample contained ethylene glycol, which is a component of antifreeze.

Table 4 - VOC Analysis Results

Compound	Concentration Range in ug/kg
1,2,4-Trimethylbenzene	15.6
o-Xylene	16.8
m/p Xylene	30.2
Acetone	190
Benzene	16.4
Ethylene Glycol	39
Toluene	31.2 - 55.2

Comparison of the DEP study to the Assale Study yields similar results for chloride and sodium (Table 5). However, the analytical methods used in the Assale Rock Salt are different from the DEP study. The metal analysis was performed by AA (Atomic Absorption). The chemical composition of the trace metals should be different.

Table 5 – Comparison of DEP Rock Salt Analysis to Assale Rock Salt Study		
Element	Ave. % Composition of 8 Rock Salt Samples	Chemical Composition of rock salt in Assale Rock Deposit
Chloride	60.23 (60.3#)	60.68
Sodium	38.49 (39.7#)	37.47
Sulfate	0.374	0.09
Calcium	0.0434	0.018
Magnesium	0.0520	0.010
Potassium	0.0166	0.020
Iron	0.0157	NA
Aluminum	0.0093	NA
Strontium	0.0050	NA
Barium	0.0005	NA
Manganese	0.0004	NA

Theoretical percentage chemical composition of pure sodium chloride

Quality Control Analysis

The trip blanks yielded non-detections for all analytes. If detections had occurred, this would have indicated that the sample had been contaminated. Since the trip blank did not have reportable detections of the analytes of interest, one can conclude that the samples had not been contaminated during transportation or sampling and that the values actually reported were detected in the sample itself.

A sample of table salt was analyzed to provide evidence that the analytical methods employed could in fact detect trace elements in the rock salt samples. In the study, table salt yielded fewer trace elements than rock salt.

Conclusion

The chemical composition of rock salt, compared to SGEW, yields very low concentrations of barium and strontium. Conversely, data reviewed from SGEW analysis indicated that high concentrations of both barium and strontium are usually detected. The chemical composition findings in this study are supported by the Assale and Khewra rock salt studies (Table A.10). The major elemental constituents were very similar in all three studies.

If the detection limits of calcium had been lower, calcium would have been detected in all of the DEP's rock salt samples. Trace amounts of bromides and iodides should have been detected as well. However, due to the high concentration of chloride in rock salt, the laboratory had to dilute the rock salt sample to determine the concentration of the chloride using EPA Method 300.0. The trace chemicals in rock salt samples could vary depending upon the location and geologic time when the salt deposit was formed. Although the bromide and iodide concentrations could have been determined using another analytical method, this study did not utilize that methodology.

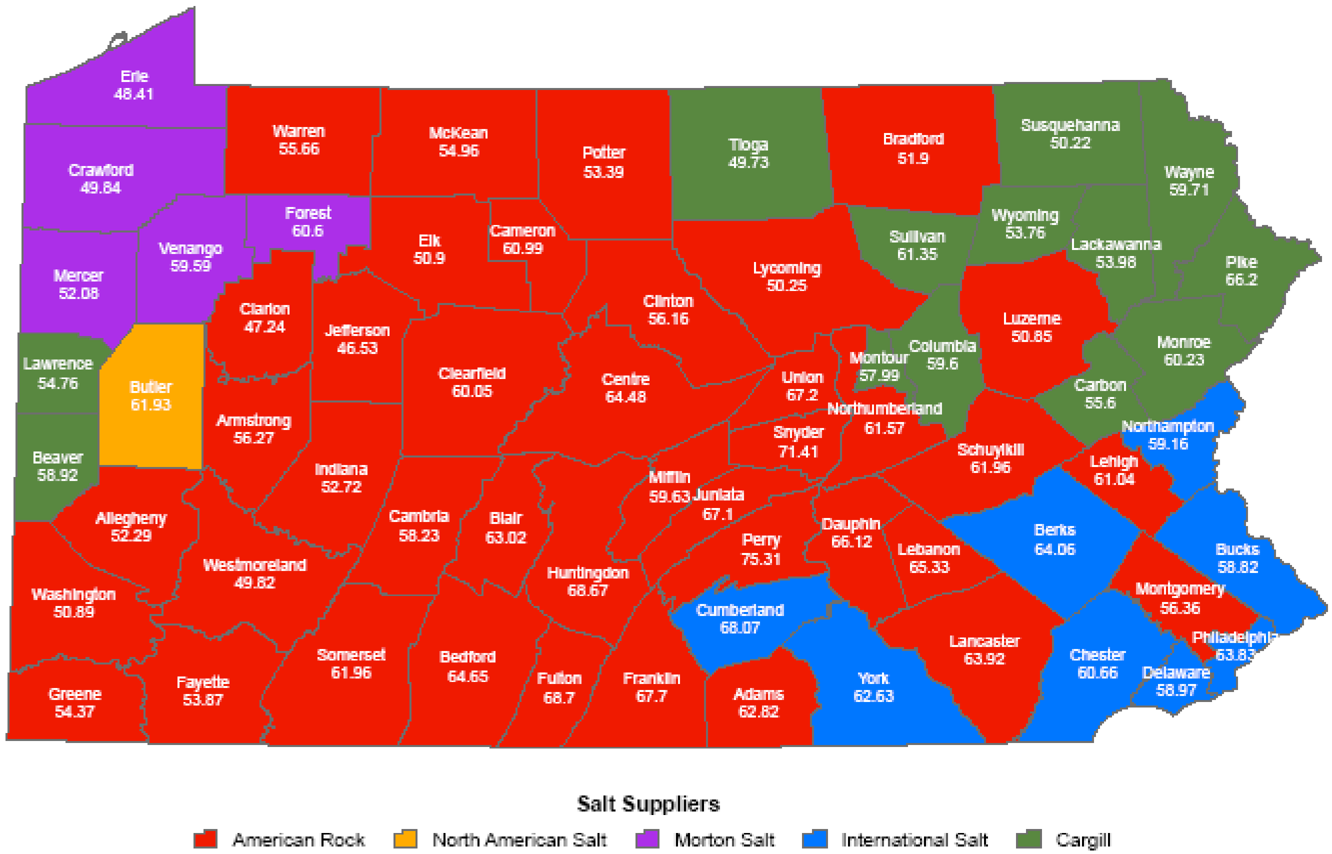
The low concentrations of the few organic compounds detected in this study could be from gasoline or diesel fuel. The contamination probably occurred during bulk transportation of the rock salt or at its storage location. Acetone is a synthetic organic solvent. The origin of the acetone contamination is unknown.

APPENDICES

Table A.1 - 2009 U.S. Rock Salt Producers, Locations and Production Volume	
Company and Location	Production (thousands of tons)
American Rock Salt Company	
Hampton Corners, NY	4,500
Cargill Incorporated	
Avery Island, LA	2,700
Cleveland, OH	4,000
Lansing, NY	2,400
Detroit Salt Company	
Detroit, MI	1,500
Huck Salt Company	
Fallon, NV	20
Hutchinson Salt Company	
Hutchinson, KS	750
Independent Salt Company	
Kanapolis, KS	750
Lyons Salt Company	
Lyons, KS	600
Morton International, Incorporated	
Fairport, OH	2,000
Grand Saline, TX	400
Weeks Island, LA	1,800
North American Salt Company	
Cote Banche, LA	3,500
Redmond Clay & Salt Company	
Redmond, UT	150
United Salt Corporation	
Hockley, TX	150
Total	**25,200**

Table A.2 – Highway (De-icing) Salt Sales and Volume		
Calendar Year	Sales (thousand of dollars)	Volume (thousands of tons)
2000	365,146	18,101
2001	362,350	16,845
2002	336,553	13,391
2003	479,431	19,359
2005	388,836	16,014
2005	543,214	20,483
2006	307,763	12,129
2007	585,700	20,252
2008	766,928	22,185
2009	714,139	16,535

Sodium Chloride 2009/2010 Renewal Prices



Map 2. – Rock salt sources close to Pennsylvania (symbolized by crossed pickaxes)

Source: http://www.saltinstitute.org/content/download/561/3308

Table A.3 Analysis of Rock Salt (Source: Khewra Salt Mine, Pakistan)			
Table a. Chemical Analysis of Rock Salt Samples (wt% on dry basis)			
Component	Sample-1	Sample-2	Sample-3
NaCl	93.6	91.84	94.180
Ca^{2+}	0.849	1.120	0.934
Mg^{2+}	0.438	0.848	0.974
K^{+}	1.300	1.670	0.733
SO_4^{2-}	2.016	1.632	2.160
Table b. Chemical Analysis of Trace Metals in Rock Salt Samples (mg/kg on dry basis)			
Component	Sample-1	Sample-2	Sample-3
Ag (Silver)	0.632	0.594	0.215
Al (Aluminum)	26.121	38.127	28.510
B (Boron)	19.500	29.193	41.484
Ba (Barium)	25.157	13.276	23.987
Bi (Bismuth)	7.141	13.436	8.649
Cd (Cadmium)	8.947	0.634	5.865
Co (Cobalt)	0.766	1.049	7.985
Cr (Chromium)	3.769	1.223	1.379
Cu (Copper)	1.984	2.317	19.480
Fe (Iron)	49.844	24.890	19.650
Ga (Gallium)	9.782	4.665	7.762
In (Indium)	6.710	5.963	4.958
Li (Lithium)	3.821	5.942	7.894
Mn (Manganese)	6.748	9.056	3.805
Ni (Nickel)	6.096	4.786	0.983
Pb (Lead)	9.714	17.743	28.976
Sr (Strontium)	37.894	61.567	34.567
Ti (Tellurium)	11.560	18.765	41.987
Zn (Zinc)	17.548	6.895	17.896

Figure 1 – PDF of Cargill Technical Information Sheet

Cargill™

Technical Information

Bulk Ice Control Salt

DESCRIPTION:

Bulk Ice Control Salt is a coarse screened, translucent to white crystalline solid obtained from underground bedded salt deposits by physical mining. The salt is exploited by drilling and blasting with explosives in a manner similar to that used in other types of mineral mining. The mined salt is then crushed, screened and hoisted to the surface where it is stockpiled awaiting distribution as a highway deicing product.

COMPLIANCE:

Bulk Ice Control Salt is not approved for human or animal consumption. It is intended for use only as a chemical deicer on roadways and thoroughfares. This salt complies fully with ASTM Specification D 632-99 Type 1, Grade 1.

ADDITIVES:

Bulk Ice Control Salt may contain Yellow Prussiate of Soda, which is added to improve caking resistance.

APPLICATIONS:

Bulk Ice Control Salt is intended for use as an ice and snow removal agent on highways and other roadways.

PACKAGING AND SHIPPING:

Bulk Ice Control Salt is available only in bulk form. Bulk quantities are shipped by rail or truck.

METHODS OF ANALYSIS:

Methods of analysis and product performance evaluation are taken from the ASTM designations D 632-99 and E 534-98.

CHEMICAL ANALYSIS:

Component	Units	Typical	Specification
Sodium Chloride (dry basis)[1]	%	95.8	95.0 min.
Calcium & Magnesium (as Ca)[1]	%	1.1	--
Sulfate (as SO_4)[1]	%	2.7	-
Water Insolubles[1]	%	0.4	2.0 max.
Surface Moisture[2]	%	0.1	1.0 max.
Yellow Prussiate of Soda[3]	ppm	50	100 max.

[1]By difference of impurities before conditioning.
[2]110ºC for 2 hours before conditioning.
[3]Optional anticaking agent (sodium ferrocyanide decahydrate).

SIEVE ANALYSIS:

U.S.S. Mesh	Opening Inches	Opening Microns	Typical	Specification
1/2"	0.500	12500	100	100 min.
3/8"	0.375	9500	98	95 – 100
4	0.187	4750	71	20 – 90
8	0.0937	2360	39	10 - 60
30	0.0232	600	11	15 max.

Note: Sieve analysis is reported as percent passing.

BULK DENSITY:

Parameter	Typical	Specification
Pounds per Cubic Foot	75	71 - 79
Grams per Liter	1200	1135 - 1265

Note: Bulk density is reported as loose (uncompacted).

PRODUCING LOCATION: CLEVELAND, OH

No. 4700 Revised May 2007

CARGILL SALT
P.O. Box 5621
Minneapolis, MN
55440
1-888 385-7258

Table A.4 - Inorganic Parameters and Methods	
Parameters	Methods
pH	SM 4500H-B
TOC	SM 5310C
Alkalinity	SM-2320B
Ammonia/Nitrogen	EPA 350.1
Bromide	EPA 300.0
Chloride	EPA 300.0
Fluoride	EPA 300.0
Iodide	EPA 300.0
Chromium VI	EPA SW 846 7199
Cyanide	EPA 335.4/Kelada-01 rev1.2
Hot Acidity	SM 2310-B
MBAS	SM5540-C
Nitrate	EPA 300.0
Nitrite	EPA 300.0
Nitrate/Nitrite	EPA 353.2
Oil and Grease	EPA 9071B
Total phosphorus	EPA 365.1
Sulfide	DIONX 107
Sulfate	EPA 300.0
Total Phenols	EPA 420.1

Table A.5 – Radiological Parameters and Methods	
Parameters	Methods
Gross Alpha/Beta	EPA 900.0
Lead 212	EPA 901.1
Lead 214	EPA 901.1
Radium 226	EPA 901.1
Radium 228	EPA 901.1
Uranium 235	EPA 901.1
Uranium 238	EPA 901.1

Table A.6 - Metals and Methods	
Metal	Method
Aluminum Total	EPA 6010C
Antimony	EPA 6020
Arsenic Total	EPA 6020
Barium Total	EPA 6010C
Beryllium Total	EPA 6020
Boron Total	EPA 200.7
Cadmium Total	EPA 6020
Calcium Total	EPA 6010C
Chromium Total	EPA 6010C
Cobalt Total	EPA 6020
Copper Total	EPA 6010C
Iron Total	EPA 6010C
Lead Total	EPA 6020
Lithium Total	EPA-200.7
Magnesium Total	EPA 6010C
Manganese Total	EPA 6010C
Molybdenum Total	EPA 6020
Nickel Total	EPA 6010C
Potassium Total	EPA 6010C
Selenium Total	EPA 6020
Silver Total	EPA 6020
Sodium Total	EPA 6010C
Strontium Total	EPA 200.8
Thallium Total	EPA 6020
Tin Total	EPA 6010C
Titanium Total	EPA 200.7
Zinc Total	EPA 6010C

Table A.7 – Volatile Organic Compounds and Methods	
VOC	Method
1,1,1,2-Tetrachloroethane	EPA 8260
1,1,1-Trichloroethane	EPA 8260
1,1,2,2-Tetrachloroethane	EPA 8260
1,1,2-Trichloroethane	EPA 8260
1,1-Dichloroethane	EPA 8260
1,1-Dichloroethene	EPA 8260
1,1-Dichloropropene	EPA 8260
1,2,3-Trichlorobenzene	EPA 8260
1,2,3-Trichloropropane	EPA 8260
1,2,4-Trichlorobenzene	EPA 8260

Table A.7 continued	
1,2,4-Trimethylbenzene	EPA 8260
1,2-Dibromo-3-chloropropane	EPA 8260
1,2-Dibromoethane (EDB)	EPA 8260
1,2-Dichlorobenzene	EPA 8260
1,2-Dichloroethane	EPA 8260
1,2-Dichloropropane	EPA 8260
1,3,5-Trimethylbenzene	EPA 8260
1,3-Dichlorobenzene	EPA 8260
1,3-Dichloropropane	EPA 8260
1,4-Dichlorobenzene	EPA 8260
2,2-Dichloropropane	EPA 8260
2-Butanone (MEK)	EPA 8260
2-Hexanone	EPA 8260
4-Isopropyltoluene	EPA 8260
4-Methyl-2-pentanone (MIBK)	EPA 8260
Acetone	EPA 8260
Benzene	EPA 8260
Bromobenzene	EPA 8260
Bromodichloromethane	EPA 8260
Bromoform	EPA 8260
Bromomethane	EPA 8260
Carbon disulfide	EPA 8260
Carbon tetrachloride	EPA 8260
Chlorobenzene	EPA 8260
Chloroethane	EPA 8260
Chloroform	EPA 8260
Chloromethane	EPA 8260
cis-1,2-Dichloroethene	EPA 8260
cis-1,3-Dichloropropene	EPA 8260
Dibromochloromethane	EPA 8260
Dibromomethane	EPA 8260
Dichlorodifluoromethane	EPA 8260
Dichloromethane (methylene chloride)	EPA 8260
Ethylbenzene	EPA 8260
Hexachlorobutadiene	EPA 8260
m/p-Xylenes	EPA 8260
Isopropylbenzene	EPA 8260
MTBE	EPA 8260
Naphthalene	EPA 8260
n-Butylbenzene	EPA 8260
n-Propylbenzene	EPA 8260
o-Chlorotoluene	EPA 8260
o-Xylene	EPA 8260
p-Chlorotolulene	EPA 8260

Table A.7 continued	
PCTFB	EPA 8260
Styrene	EPA 8260
Sec Butyl Benzene	EPA 8260
t-Butyl acetate	EPA 8260
t-Butyl alcohol	EPA 8260
Tetrachloroethene	EPA 8260
Tetrahydrofuran	EPA 8260
Toluene	EPA 8260
trans-1,2-Dichloroethene	EPA 8260
trans-1,3-Dichloropropene	EPA 8260
Tert-Butyl Acetata	EPA 8260
Tert-Butylbenzene	EPA 8260
Tert-Butyl alcohol	EPA 8260
Trichloroethene	EPA 8260
Trichlorofluoromethane	EPA 8260
Vinyl acetate	EPA 8260
Vinyl chloride (Chloroethene)	EPA 8260

Table A.8 – Semivolatile Organic Compounds and Methods	
SVOC	Method
1,2,4,5-Tetrachlorobenzene	EPA 8270
1,2,4-Trichlorobenzene	EPA 8270
1,2-Dichlorobenzene	EPA 8270
1,3-Dichlorobenzene	EPA 8270
1,3-Dinitrobenzene	EPA 8270
1,4-Dichlorobenzene	EPA 8270
1,4-Naphthoquinone	EPA 8270
2,3,4,6-Tetrachlorophenol	EPA 8270
2,4,5-Trichlorophenol	EPA 8270
2,4,6-Trichlorophenol	EPA 8270
2,4-Dichlorophenol	EPA 8270
2,4-Dimethyphenol	EPA 8270
2,4-Dinitrophenol	EPA 8270
2,4-Dinitrotoluene	EPA 8270
2,6-Dichlorophenol	EPA 8270
2,6-Dinitrotoluene	EPA 8270
2-Acetylaminofluorene	EPA 8270
2-Chloronaphthalene	EPA 8270
2-Chlorophenol	EPA 8270
2-Methylnaphthalene	EPA 8270
2-Methylphenol	EPA 8270
2-Nitroaniline	EPA 8270
2-Nitrophenol	EPA 8270

Table A.8 continued	
2-Picoline	EPA 8270
3,3'-Dichlorobenzidine	EPA 8270
3,4-Methylphenol	EPA 8270
3-Methylcholanthrene	EPA 8270
3-Nitroaniline	EPA 8270
4,6-Dinitro-2-methylphenol	EPA 8270
4-Aminobiphenyl	EPA 8270
4-Bromophenyl-phenylether	EPA 8270
4-Chloro-3-methylphenol	EPA 8270
4-Chloroaniline	EPA 8270
4-Chlorophenyl-phenylether	EPA 8270
4-Nitroaniline	EPA 8270
4-Nitrophenol	EPA 8270
5-Nitro-o-toluidine	EPA 8270
7,12-Dimethylbenz(a)anthracene	EPA 8270
Acenaphthene	EPA 8270
Acenaphthylene	EPA 8270
Acetophenone	EPA 8270
Aniline	EPA 8270
Anthracene	EPA 8270
Aramite (total)	EPA 8270
Benz(a)anthracene	EPA 8270
Benzo(a)pyrene	EPA 8270
Benzo(b)fluoranthene	EPA 8270
Benzo(g,h,i,)perylene	EPA 8270
Benzo(k)fluoranthene	EPA 8270
Benzyl alcohol	EPA 8270
bis(2-Chloroethoxy)methane	EPA 8270
bis(2-Chloroethyl)ether	EPA 8270
bis(2-Chloroisopropyl)ether	EPA 8270
bis(2-Ethylhexyl)phthalate	EPA 8270
Butylbenzylphthalate	EPA 8270
Chlorobenzilate	EPA 8270
Chrysene	EPA 8270
Diallate (total)	EPA 8270
Dibenz(a,h)anthracene	EPA 8270
Dibenzofuran	EPA 8270
Diethylphthalate	EPA 8270
Dimethoate	EPA 8270
Dimethylphthalate	EPA 8270
Di-n-butylphthalate	EPA 8270
Dimethyaminoazobenzene	EPA 8270
Di-n-octylphthalate	EPA 8270
Dinoseb	EPA 8270

Table A.8 continued	
Diphenylamine&n-Nitrosodiphenylamine	EPA 8270
Disulfoton	EPA 8270
Ethyl methanesulfonate	EPA 8270
Fluoranthene	EPA 8270
Fluorene	EPA 8270
Hexachlorobenzene	EPA 8270
Hexachlorobutadiene	EPA 8270
Hexachlorocyclopentadiene	EPA 8270
Hexachloroethane	EPA 8270
Hexachloropropene	EPA 8270
Isodrin	EPA 8270
Isophorone	EPA 8270
Isosafrole (total)	EPA 8270
Methyl methanesulfonate	EPA 8270
Naphthalene	EPA 8270
Napropamide	EPA 8270
Nitrobenzene	EPA 8270
N-Nitrosodiethylamine	EPA 8270
N-Nitrosodimethylamine	EPA 8270
N-Nitrosodi-n-butylamine	EPA 8270
N-Nitroso-di-n-propylamine	EPA 8270
N-Nitrosomethylethylamine	EPA 8270
N-Nitrosomorpholine	EPA 8270
N-Nitrosopiperidine	EPA 8270
N-Nitrosopyrrolidine	EPA 8270
o,o,o-Triethylphosphorothioate	EPA 8270
o-Toluidine	EPA 8270
Parathion	EPA 8270
Pentachlorobenzene	EPA 8270
Pentachloroethane	EPA 8270
Pentachloronitrobenzene	EPA 8270
Pentachlorophenol	EPA 8270
Phenanthrene	EPA 8270
Phenol	EPA 8270
Phorate	EPA 8270
Pronamide	EPA 8270
Pyrene	EPA 8270
Pyridine	EPA 8270
Safrole	EPA 8270
Sulfotep	EPA 8270
Thionazine	EPA 8270

Table A.9 – PCBs and Methods	
Aroclor-1221	EPA 8082A
Aroclor 1016	EPA 8082A
Aroclor-1232	EPA 8082A
Aroclor-1242	EPA 8082A
Aroclor-1248	EPA 8082A
Aroclor-1254	EPA 8082A
Aroclor-1260	EPA 8082A

Table A.10 - Summary of Chemical Characteristics of flowback water sampled 5 days following hydraulic fracturing event (Source: Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas December 31 2009)	
Parameters	Median concentration range
Barium	686 mg/l
Boron	12.0 mg/l
Calcium	4,950.0 mg/l
Iron	39.0 mg/l
Lithium	43.0 mg/l
Magnesium	559.0 mg/l
Manganese	2.6 mg/l
Potassium	301.0 mg/l
Sodium	18,000.0 mg/l
Strontium	1,080.0 mg/L
Non metals	
Chlorides	41,850mg/L
Bromides	445 mg/L

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