

EFFECTIVENESS AND SIMULATED IMPACTS OF PRODUCED WATER AS A DUST
ABATEMENT IN WESTERN NORTH DAKOTA

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North Dakota State University's regulations and meets the accepted
standards for the degree of

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ABSTRACT

A road dust abatement alternative that has been considered in the Bakken and Three Forks formations is oil-well produced waters. Three previously untreated gravel roads were selected and passive dust collectors were utilized. The objectives of this study were to: 1) simulate produced water's potential impacts to gravel road materials; 2) compare dust loading at abated and control sites to determine effectiveness; and 3) identify the elemental differences in the dust at abated and control sites. Electrical conductivity has the greatest influence on dispersion probability and clay mineralogy of the road influences the probability of dispersion. Produced water failed to reduce dust on two of the three roads that were tested. Elements that were found to be significantly different included Mo, Mn, Fe, As, Au, and Hg. Results of this study are important to road managers who are contemplating the usage of produced waters to reduce dusts from gravel roads.

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DEDICATION

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PREFACE

Chapters two and three are written as manuscripts to be submitted to a peer-reviewed journal. Both chapters are written following the style and formatting guidelines of the *Water, Air, & Soil Pollution* journal.

TABLE OF CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	iv
DEDICATION.....	v
PREFACE.....	vi
LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW.....	1
Introduction.....	1
Literature Review.....	2
Fugitive Dust.....	2
Externalities of Dust.....	3
Fugitive Road Dust Factors.....	5
Road Dust Abatement.....	6
Abatement Impacts.....	10
Traffic Impacts from Bakken Oil Development.....	12
Conclusions.....	13
Literature Cited.....	13
CHAPTER 2: SIMULATED EFFECTS OF SAR, EC, AND CA:MG RATIOS ON GRAVEL ROAD FINE FRACTIONS.....	20
Introduction.....	20
Methods.....	22
Gravel Road Samples.....	22
Clay Equilibration and Dispersion.....	23
Statistical Analysis.....	24
Results and Discussion.....	25

Conclusions.....	29
Literature Cited.....	30
CHAPTER 3: EFFECTIVENESS OF OIL-WELL PRODUCED WATER AS A ROAD DUST ABATEMENT	32
Introduction.....	32
Methods.....	34
Study Area & Design.....	34
Statistical Analysis.....	37
Results and Discussion	38
Conclusion	43
Literature Cited	44
CHAPTER 4: CONCLUSIONS	47
APPENDIX. ELEMENTS TESTED BY BUREAU VERITAS COMMODITIES CANADA LTD LAB USING ICP-MS ANALYSIS	48

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1.1. Summarized produced water major ions, trace elements and nutrients. Adapted from NDDoH (2007).....	9
2.1. Dun County road clay speciation and concentration (% of clay fraction) analysis from Activation Laboratories Ltd. (Ancaster, ON, Canada).....	23
2.2. Predicted probability dispersion equations for each road.....	27
3.1. Monthly precipitation in millimeters (mm)..	34
3.2. Dunn County road clay speciation and concentration (% of clay fraction) analysis from Activation Laboratories Ltd. (Ancaster, ON, Canada).....	35
3.3. Dunn County dust control study traffic summary using the Federal Highway Association classification system.....	39

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2.1. Map of Dunn County, North Dakota with study locations.	22
2.2. Amount of dispersed clay at each respective SAR and EC level.	26
2.3. Estimated probability of membership to dispersed category at the various SAR and EC levels from the modeled logistic equation.....	28
3.1. Map of Dunn County, North Dakota with study locations.	34
3.2. Overall average dust loading in each section by distance from the road.....	40
3.3. Average dust loading for all control and abated sections.	42

CHAPER 1: INTRODUCTION AND LITERATURE REVIEW

Introduction

Rural gravel roads are widespread in the Great Plains and much of the United States. Energy development (oil and natural gas) in the Bakken and Three Forks regions of North Dakota, Montana, and south-central Canada utilizes these roads to move equipment for well drilling, hydraulic fracturing processes, and for transporting produced oil and oil-related byproducts (Goodman et al., 2016; Tolliver, 2014). During the peak of the recent development, road dust was found to increase 355% 10 m from gravel roads in areas of elevated traffic compared to typical western North Dakota travel (Creuzer et al., 2016). In order to reduce dust production and deposition in surrounding areas, abatements are applied to the roads. A potential road dust and ice abatement option under consideration in North Dakota is oil well produced water, also known as “brine” (NDDoH, 2007). However, literature is lacking on the quantified effectiveness of produced water as an abatement option. Additionally, the composition of the released dust from abated roads is unknown. It is also possible that the application of produced water will have impacts on road materials.

The specific objectives of this study were to:

1. Simulate produced water’s potential impacts to gravel road materials.
2. Compare dust loading at abated sites to control sites to determine effectiveness.
3. Identify elemental differences in the dust collected at abated and control sites.

Literature Review

Fugitive Dust

Fugitive road dust is a significant non-point pollution source and contains particulate matter (PM) that is emitted into the atmosphere via natural or anthropogenic influences such as the wind or vehicle traffic (EPA, 2006). When a vehicle is driven, tires grind road material into fine particles which are then entrained into the atmosphere (EPA, 2006). These particles are then transported away from the source via wind or turbulent wake from the vehicle and can cause ecological and anthropogenic externalities.

Particulate matter is one of the six principal pollutants that the United States Environmental Protection Agency (EPA) established National Ambient Air Quality Standards to reduce (EPA, 2015). The EPA categorizes particulate matter into two main size fractions: particles smaller than 2.5 μm (microns) are categorized as $\text{PM}_{2.5}$ and larger particles up to 10 μm are categorized as PM_{10} . In a 2011 report from the National Emissions Inventory, PM_{10} emissions from unpaved roads were estimated to be approximately 6,985,322.5 Mg (7.7 million tons) per year which makes PM_{10} the largest contributor to non-point pollution emissions in the United States (EPA, 2015).

Studies from Tamm and Troedsson (1955) and Everett (1980) both found that finer particles deposit further away from roads. Additionally, Everett (1980) found that the elemental deposition of the dust did not decline as quickly as particle size, meaning that although particles larger in size were depositing closer to the roads, various elements were still found to be depositing further away. Both the size and composition of particles have externalities associated with them.

Externalities of Dust

Fugitive dust can have both acute and chronic ecological and anthropogenic impacts. Dust can cause physical stress to plants by plugging the stomata, covering the vegetation which leads to a decrease in light reception and ultimately photosynthesis, or by the force of impact as it hits the vegetation after being propelled off of a road surface (Farmer, 1993; Mohamed and Bassouni, 2007).

Aluminum, which can be toxic to plants, has been shown to be a major component of fugitive road dust in some geographic areas (Williams, Shukla, and Ross, 2008). Additionally, a study completed by Brumbaugh, Morman, and May (2011) found that vegetation near the Delong Mountain Transportation System haul road in Alaska had greater changes of increased lead and cadmium. As dust deposits on the vegetation or the surrounding soils, the dust constituents may eventually leach into the soil profile and cause alterations to both the soil profile and the invertebrate communities present (Farmer, 1993). Many of the studies that have been completed looking at dust impacts on vegetation used cement dust and externalities of fugitive unpaved road dust are not yet well documented (Farmer, 1993).

Creuzer et al. (2016) did not find any significant impacts to wetland water quality near high traffic, unpaved roads in North Dakota. However, there is still potential for the dust deposits to be transported into a waterbody via runoff or be re-transported via wind (Zhu et al., 2014). Impacts to water could have subsequent impacts to surrounding vegetation, livestock, and wildlife.

Livestock and wildlife will likely forage on the vegetation that is covered by fugitive dust. Dorn et al. (1975) found that livestock suffered from lead poisoning after consuming pasture vegetation that had been covered with dust from smelting operations. There is an

absence of literature concerning vegetation impacted by road dust consumption by livestock. Inhalation of dust by livestock and wildlife could have consequences such as asthma, lung cancer, cardiovascular issues, and premature death since in humans a number of illnesses have been linked to dust inhalation (Stetler and Stone, 2008).

Previous studies regarding the health effects of dust to humans have considered both coarse and fine particles. However, it is usually fine particulate matter (PM_{2.5}) that has been correlated to a number health effects in humans as the particles at this size become aerosolized. These size particles are also the particles that travel further and stay in the atmosphere longer. A study by Zanobetti and Schwartz (2009), found a significant relationship between fine particulate pollution and mortality for all myocardial infarction, cardio vascular disease, stroke, and respiratory disease cases investigated. Younger children, those with respiratory diseases, and older adults are more at risk to be affected by particulate matter (Mohamed and Bassouni, 2007).

In addition to illnesses caused or enhanced by dust, there is also the hazard of decreased visibility from fugitive dust which can cause problems while driving (Lunsford and Mahoney, 1998; Mohamed and Bassouni, 2007). Another side effect of decreased visibility from fugitive dust could be aesthetic damage in the areas where it occurs. If there is a high amount of fugitive road dust being produced in a known tourist attraction area it could cause a decrease in visitors to these areas and local areas may suffer reduced income from tourists. There have been new regulations introduced to reduce the amount of PM to protect visibility at national parks, forests, and wilderness areas (Kuhns et al., 2010)

Ultimately, there is an economic loss that is incurred from fugitive road dust. If an unpaved road is generating dust, there is a loss of road materials. A study by Sanders et al. (1997) in Colorado found that untreated roads experience an estimated annual aggregate loss of

approximately 766,066 kg/km (1,395 ton/mile). This study also found that untreated sections experienced two to three times more aggregate loss compared to sections that received dust control treatments.

Fugitive Road Dust Factors

Road type plays a major part in road dust emissions. There are two main types of roads. Paved roads are hard surfaced roads and typically do not lead to high amounts of dust emissions in comparison to unpaved roads (Farmer, 1993). Unpaved roads typically consist of a loose material, usually from a local gravel source, that is graded and compacted to create a road surface. Gravel for unpaved roads in Dunn County, North Dakota, include clinker (“Scoria”), carbonate caprock of the Killdeer Mountains, and other local gravel pit sources that originate from glacial deposits that have been reworked during glacial melting (Murphy, 2001). The texture (i.e., percent sand, silt, and clay) of unpaved roads also has an impact on the quantity of particles available to become fugitive dust (EPA, 2006; Kuhns et al., 2010).

Vehicular traffic also influences fugitive dust released from roads. Vehicle speed and weight have been found to be dominant vehicular factors that influence dust emissions. Gillies et al. (2005) found that unpaved road emissions are linearly correlated with vehicle speed and weight. Kuhns et al. (2010) found the same consistent trends as Gillies et al. (2005). For both of these factors, as speed and weight increase there is an increase in fugitive dust emissions. Additionally, a study by Williams et al. (2008) found that within the dust emissions released with increasing vehicle speed, there was an increase in small sized particles.

A third main factor that influences road dust is climate. In particular, moisture content in both the gravel material and the geographic region are important factors when it comes to both dust emissions and abatement effectiveness. Where lighter weight vehicles are present, moisture

content in the road surface materials may be more of a driving factor (EPA, 2006). Kuhns et al. (2003) found a positive linear correlation between unpaved road dust emission potential and days since precipitation. Wind has also been found to influence the spatial spread of dust. Gillies et al. (1999) found that most of the fugitive PM generated moved horizontally with the dominant wind direction and that concentrations decrease downwind in relation to proximity from the road.

Road Dust Abatement

There are a number of options available to managers for controlling road dust emissions. One option is to administratively regulate and enforce more strict speed limits or weight restrictions; however, this option can be difficult to enforce (EPA, 2006). Another option is to constructively change the road type from an unpaved to a paved road; however, this option has a high initial cost and may not be the best option for heavy vehicle haul roads (EPA, 2006). Paved roads have significantly less fugitive dust compared to unpaved roads (Roberts et al., 1975). Chemical surface treatments for dust abatement are an alternative option to the administrative and constructive options. This type of dust abatement has been used for many years but is becoming more popular (Piechota et al, 2004).

Chemical dust abatements use materials to limit particulate emissions by binding surface particles together (EPA, 2006). Common physical materials used as dust abatements are clay additives such as bentonite and montmorillonite, mulch, and other fiber mixtures such as paper mulch with a gypsum binder or wood fiber mulches mixed with seeds (Bolander, 1999; Piechota et al., 2004). Common chemical abatements used are water; water absorbing products such as calcium chloride (CaCl_2) and magnesium chloride (MgCl_2); petroleum-based organics such as asphalt emulsion and cutback solvents; non-petroleum based organics such as vegetable oils, molasses, and lignin sulfate; synthetic polymers such as polyvinyl acetate and vinyl acrylic;

electrochemical products such as enzymes, ionic products, and sulfonated oils; and other industry by-products (Bolander, 1999; Piechota et al., 2004). According to Travník (1991) chloride salt abatement products are the most common type of chemical abatement. These abatements can be mixed into or sprayed over the top of the road surface and are usually applied when dust has been deemed undesired or hazardous and can be applied several times a year as needed.

Magnesium chloride is a hygroscopic compound which means that it has the ability to absorb moisture (Addo et al. 2004). Magnesium chloride is created through seawater evaporation or industrial waste byproducts (Piechota et al., 2004). When it is applied, $MgCl_2$ hardens the road surface when it is dry. It is usually applied 1-2 times a year at the approximate rate of 2.26 L/m^2 (0.5 gal/yd^2) for the initial application. Following applications are typically applied at half the initial application rate (Bolander, 1999). Material Safety Data Sheets are provided for dust abatements but do not give a chemical composition breakdown (Piechota et al., 2004).

There are several industry created by-products under investigation to be used as dust abatement options, one of which is oil-well produced water (MDoNR, 1983; NDDoH, 2007; ODoNR, 2004; PDoEP, 1998). According to a study completed by Kondash and Vengosh (2015), oil development has produced approximately 775 million m^3 of produced water which has to be stored after it is produced. Oil-well produced water is usually defined as having greater than 35,000 mg/L Total Dissolved Solids (TDS) but produced water from the Williston Basin has been found to have greater than 450,000 mg/L TDS (Kalkhoff, 1993; Otton, 2006). However, the amount of TDS depends on location. TDS concentrations vary from less than 30,000 mg/L along the east side to greater than 300,000 mg/L in the more central locations of the Williston Basin formation (Iampen and Rostron, 2000). Additionally, produced water from the

Williston Basin has been found to be highly saline, be sodium, chlorine, and bromine rich, and have other toxins present such as selenium, vanadium, strontium, boron, manganese, nickel, cadmium, copper, zinc, barium, lead, radium, and ammonia (Iampen and Rostron, 2000; Lauer, Harkness, and Vengosh, 2016).

In order to authorize the usage of oil-well produced water in North Dakota, the North Dakota Department of Health (NDDoH) (2007) analyzed ten oil-well produced waters (brine) produced in North Dakota as a potential de-icer and dust abatement option. Analysis of the waters showed varying amounts of total dissolved solids (TDS), major ions, nutrients, and trace elements (Table 1.1). The variability of these findings is due to the age and formation from which the water was produced and the high ionic nature of the produced water which had to be diluted prior to sample processing. Copper, selenium, nickel, zinc, arsenic, chloride, barium, and boron in multiple produced water samples exceeded ND chronic aquatic life criteria established by the North Dakota Water Quality Standards. Additionally, at road side water sites where produced water had been applied, selenium exceeded the standard at two sites, copper exceeded at one site, and lead exceeded at one site. Furthermore, at road side soil sites where produced water had been applied, phosphorus exceeded the standard at all sites, chloride exceeded at one site, and sulfate exceeded at two sites. As a result of this study, the NDDoH recommended that application of oil-well produced water be suspended until further investigations were completed (NDDoH, 2007).

Table 1.1. *Summarized produced water major ions, trace elements and nutrients. Adapted from NDDoH (2007)*

<u>Major Ions</u>	<u>Range (mg/L)</u>
Total Dissolved Solids (TDS)	85,300 - 317,200
Sodium (Na)	28,800 - 123,000
Calcium (Ca)	2,990 - 47,700
Magnesium (Mg)	234 - 3,640
Chlorine (Cl)	52,200 - 171,000
Sulfate (SO ₄)	135 - 750
<u>Trace Elements</u>	<u>Range (µg/L)</u>
Boron (B)	65,000 - 366,000
Nickel (Ni)	<1,000 - 2,180
Copper (Cu)	<1,000 - 1,530
Zinc (Zn)	<1,000 - 2,180
Arsenic (As)	<1,000 - 1,530
Selenium (Se)	<1,000 - 9,070
Barium (Ba)	<1,000 - 52,300
<u>Nutrients</u>	<u>Range (mg/L)</u>
Ammonia (NH ₃)	85 - 1,490
Phosphorus (P)	<0.004 - 23
Potassium (K)	481 - 9,560

Although dust abatements have been used for some time, there still is a lack of literature and no consistent methodologies for determining effectiveness. Previous qualitative studies regarding dust abatements effectiveness have used visual estimations and operator surveys (Johnson and Olson, 2009). Previous quantifiable studies have used dust collections by vehicle-mounted devices and passive samplers to determine dust emissions and effectiveness of select abatement treatments (Gillies et al., 1999; Sanders et al., 1997). A few studies have also considered the relationship between the dust generated and various road characteristics such as moisture content and fine particle content (Gillies et al., 1999). These studies have found varying results for the abatements that they tested.

Sanders et al. (1997) found a 50-70% reduction in fugitive dust emissions with lignosulfonate, CaCl₂, and MgCl₂. Flocchini et al. (1994) found a 98% effectiveness rate for MgCl₂ observing PM₁₀ emissions (grams) five days after application to a road in the San Joaquin Valley, California. However, the effectiveness was not revisited after a longer period of time. Gillies et al. (1999) also observed PM₁₀ emissions to test the efficiencies of four dust abatements. They concluded that the decrease in relative efficiency for each tested abatement varied and was related to time from application. A general decrease in efficiency over time is supported by other studies (Sanders et al., 1997).

A study completed in Minnesota investigating the role of aggregate moisture content in abatement effectiveness found a general reduction in dust levels with higher moisture content but did not reveal any other strong relationships between the study variables (application rate, average daily traffic, conductivity, and percent passing through a 75 µm (#200) sieve) (Johnson and Olson, 2009). Johnson and Olson (2009) also found a weak negative correlation between abatement effectiveness and the sand content in the roads they tested which suggests that gravel roads with sandier texture will see a lower effectiveness level.

Abatement Impacts

There is limited literature regarding the environmental impacts associated with the utilization of dust abatements (Evans and Frick, 2001; Goodrich, Koski, and Jacobi, 2009b; Piechota et al., 2004). Soil and vegetation alongside the road may suffer through both direct and indirect application contact. Vegetation and soil on the roadside can be directly sprayed as abatements are applied and there is also a chance that after the abatement is applied, before it completely dries, that it will spread into the immediate roadside which could lead to uptake or leaching of ions by the surrounding vegetation and soil profile (Goodrich, Koski, and Jacobi,

2009a). As early as the 1950s, effects from sodium chloride were noticed in Minnesota as trees along city boulevards began to express salt-related injuries such as burn and dieback (French, 1959). In more recent $MgCl_2$ studies conducted by Trahan and Peterson (2007) and Goodrich et al. (2009a), chloride has been linked to foliar damage.

Salts tend to be easily leached during heavy rains and can be transported into nearby areas (Bolander, 1999; Lunsford and Mahoney, 1998). A study completed in Colorado by Goodrich et al. (2009) that investigated $MgCl_2$ found that higher concentrations of chlorine, magnesium, aluminum, boron, calcium, potassium, sulfate, and sodium at several of the study sites although they were all under levels considered harmful. Additionally, they found that as the average application rate of $MgCl_2$ increased on the roads, there was a subsequent increase in magnesium and chlorine concentrations in the adjacent streams. It is possible that water sources may be impacted abatement and become harmful for livestock and wildlife to utilize (Gleason and Tangen, 2014; Gleason et al., 2011).

Blading the road surface can lead to an increase in sediment to rivers and streams. However, dust abatements help decrease the need of blading unpaved roads (Edvardsson, 2009). Johnson and Olson (2009) found that 80% of the road departments they surveyed decreased their blading requirement by 50% after dust abatements had been applied. Literature indicates that the possibility of dust particles generated after application containing chemical constituents from abatement treatments has not yet been fully explored (Piechota et al., 2004).

The main monetary reasons for controlling fugitive dust on unpaved roads is to prevent the loss of particles and to reduce the need for maintenance to keep the road surface in good condition (Addo et al., 2004). James et al. (1999) estimated the cost of $MgCl_2$ to be approximately US \$1500/hectare (2.5 acres). In a North Dakota report by Schwindt (2012), a

MgCl₂ application to unpaved roads for dust control was estimated to cost US \$8,000 per 1.6 km (1 mile) for the first treatment and \$4,900 for additional treatments. Schwindt (2012) also estimated the cost of applying oil-well produced water as a dust abatement to be \$135-500 per hour to apply since there was no cost for the product. For comparison, Schwindt (2012) also estimated the cost of cement, which is a more permanent option for dust control, to be US \$60,000-\$250,000 per 1.6 km (1 mile) depending on depth.

A study by Sanders et al. (1997) in Colorado, found that although there is a high initial cost with abatement applications after an estimated average daily travel (ADT) of 120 vehicles, abatements were cost effective. To increase the cost effectiveness of abatements, it may be beneficial to lay new material before abatements are applied. Although Sanders et al. (1997) found that abatements became cost effective after an ADT of 120 vehicles, they did not consider larger vehicles such as semi-trailer trucks. Additionally, Bolander (1999) recommended that above an ADT of 500, chip seal coating or asphalt would be more cost effective.

Traffic Impacts from Bakken Oil Development

Drilling and hydraulic fracturing operations for an oil well create short and long term road utilization by heavy vehicles such as semi-trailer trucks (Goodman et al., 2016). There are approximately 2,300 drilling related vehicle trips for every well that is drilled and hydraulically fractured (Tolliver, 2014). Before drilling and fracture can occur, a well pad must first be constructed. Then the process of transporting the fracking solution to the well for fracking operations begins. There is then the subsequent removal of solution and oil production begins. Over the course of time there may also be a need to re-frack a location (Goodman et al., 2016). The majority of active wells in Dunn County, North Dakota have products transported by truck (NDIC, 2015). The estimation given by Tolliver (2014) does not include vehicle trips for

hauling produced products such as crude oil or produced waters. If these products are subsequently transported by road, there will be an increase in heavy vehicle road traffic.

Conclusions

Although there have been studies attempting to model fugitive road dust and its impacts, there is still little known about the quantity, composition, sizes, and transport distances of fugitive unpaved road dust. Most of the previous work has been completed in either laboratory settings, arid regions such as New Mexico and Arizona, or Alaska (Brumbaugh et al., 2011; Pinnick et al., 1985; Rushing et al., 2006; Walker and Everett, 1987; Williams et al., 2008). Furthermore, the effectiveness and potential impacts to the roads themselves that could be experienced from using new industry by-products, such as oil-well produced water, as abatements are unknown.

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CHAPTER 2: SIMULATED EFFECTS OF SAR, EC, AND CA:MG RATIOS ON GRAVEL ROAD FINE FRACTIONS

Introduction

Particulate matter released from unpaved roads by vehicles were estimated to be approximately 6,985,322.5 Mg (7.7 million tons) per year in a 2011 National Emissions Inventory report, making it the largest contributor to non-point pollution emissions in the United States (EPA, 2006; EPA, 2015). Fugitive dust can have both acute and chronic ecological and anthropogenic impacts. For example, dusts can cause physical stress to plants by plugging the stomata, covering the vegetation which leads to a decrease in light reception and ultimately photosynthesis, or by the force of impact after being propelled off of a road surface (Farmer, 1993; Mohamed and Bassouni, 2007). Inhalation of dust has been linked to both respiratory and cardiac diseases (Zanobetti and Schwartz, 2009). In addition to illnesses caused or enhanced by dust, there is also the hazard of decreased visibility from fugitive dust while driving (Lunsford and Mahoney, 1998; Mohamed and Bassouni, 2007).

Dust abatements are applied to roads once to several times a year to reduce fugitive dust (Bolander, 1999; Piechota et al., 2004). There are physical abatement options such as clay additives. However, chemical abatements such as chloride-based compounds are more common but tend to be expensive (Travnik, 1991; Bolander, 1999; Piechota et al., 2004). For example, in 2016 approximately 331.5 km (206 mi) of $MgCl_2$ was applied to road surfaces in Dunn County, North Dakota for a total cost of about US \$1.64 million (D. Schwartzenberger, personal communication, 2016, Dunn County Road Department, ND, USA).

One potential road dust and ice abatement option under consideration in North Dakota, due to the energy developments in the Bakken and Three Forks regions of the United States and

Canada, is oil-well produced water also known as “brine” (NDDoH, 2007). Produced water is a byproduct that is created when it is separated from the oil in holding tanks and is normally disposed of into deep-injection wells. Other US states have considered produced water as a dust abatement option (MDoNR, 1983; PDoEP, 1998; ODoNR, 2004). There have been approximately 775 million m³ of produced water generated in the United States and finding alternative uses is more desired in contrast to the costs for disposal (Kondash and Vengosh, 2015).

The produced water in the Bakken and Three Forks region has concentrations of Na and Cl often exceeding 123,000 and 186,000 mg/L, respectively (NDDoH, 2007). Sodium is a known dispersant and the potential for dispersion is largely controlled by the concentration of Na on the exchange sites, the electrical conductivity (EC) of the soil solution, and clay mineralogy (Zhang and Norton, 2002). Therefore, after application as an abatement, the exchange sites of the road’s clay binder or clay-sized particles will likely become Na-saturated due to mass action. As long as the roads EC remains above the flocculation threshold, dispersion will not occur. However, after rainfall events up to 67% may run off of the road carrying soluble salts with it, thus reducing the flocculation potential and possibly yielding increased dust generation (Kohl, Carlson, and Wangemann, 1994). The relationship between gravel road clay-sized fractions and produced water has not yet been investigated. Therefore, the objective of this study was to simulate the potential impacts of produced water on gravel road fine fractions using varying Na, EC, and Ca:Mg ratios to determine flocculation thresholds for three gravel roads having different mixed clay mineralogies.

Methods

Gravel Road Samples

Gravel road materials, to a depth of 5 cm, were collected from three gravel roads in Dunn County, North Dakota prior to the application of dust abatements (Figure 2.1). Each sample was air dried at 25 °C and sieved to less than 250 µm. Representative samples were then sent to Activation Laboratories Ltd. (Ancaster, ON, Canada) for clay speciation and concentration analysis using quantitative X-ray Diffraction (XRD). The first site, 1st St NW (47°25'48.06", 102°49'44.01"), mainly consisted of smectite and illite (Table 2.1). The second site, 12th St SW (47°14'27.98", 102°58'47.03"), also mainly consisted of smectite and illite (Table 2.1). The third site, 14th St SW (47°12'46.11", 102°32'55.40"), differed from the other two roads in that it mainly consisted of illite (Table 2.1).

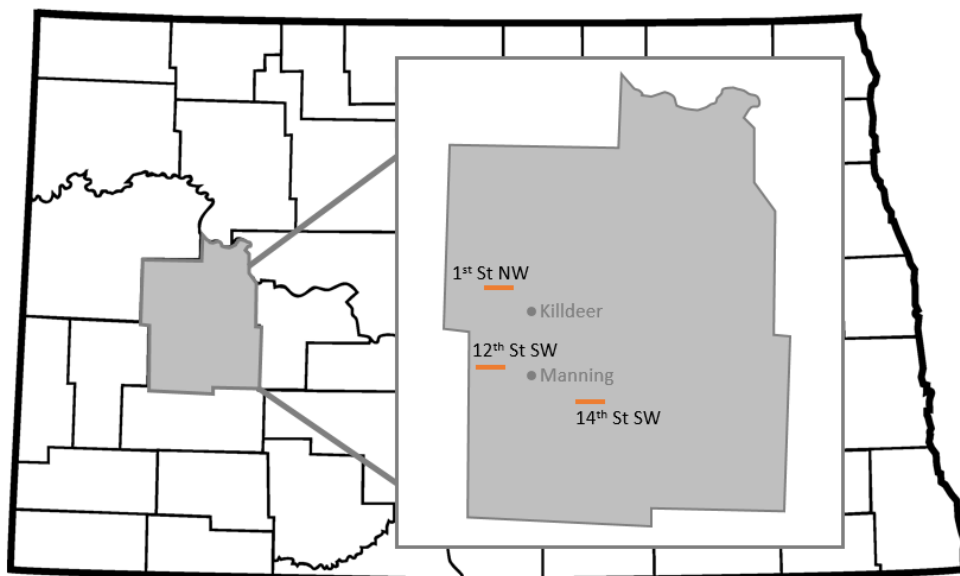


Figure 2.1. Map of Dunn County, North Dakota with study locations.

Table 2.1. *Dunn County road clay speciation and concentration (% of clay fraction) analysis from Activation Laboratories Ltd. (Ancaster, ON, Canada).*

Clay Type	1st St NW	12th St SW	14th St SW
Smectite	63%	51%	ND ¹
Illite	27%	34%	83%
Chlorite	5%	7%	17%
Kaolinite	5%	8%	Trace

¹ Not Detected

Clay Equilibration and Dispersion

The clay equilibration and clay dispersion methods used in this study were modeled after He et al. (2013). Anhydrous salts of sodium chloride (NaCl), calcium chloride (CaCl₂), and magnesium chloride (MgCl₂) were mixed into deionized water (DI) to create the equilibration solutions. The equilibration solutions used consisted of the highest targeted EC (16 dS/m) and respective sodium adsorption ratio (SAR) levels (0, 1, 5, 12, 24, and 48) and Ca:Mg ratios (1:0, 1:2, 2:1, and 0:1). Each <250 µm road sample was equilibrated by agitating 30 g of sample with 150 mL of equilibrating solution (1:5 ratio) on a mechanical shaker (225 oscillations/min) for 12 h and centrifuged (RCF 647 x g) for 20 min. The supernatant was decanted and discarded after each centrifugation. Each equilibration step was repeated three times. After equilibration the samples were washed four times with 150 mL of 95% ethanol (shaken for 15 min; centrifuged for 15 min) to remove excess ions. The equilibrated samples were air dried at 25 °C and ground with a mortar and pestle to pass through a 75 µm sieve.

The varying EC, SAR, and Ca:Mg solutions were prepared using anhydrous salts of NaCl, CaCl₂, and MgCl₂ into DI water for the dispersion solutions. For the dispersion solutions the targeted SAR levels consisted of 0, 1, 5, 12, 24, and 48, the targeted EC levels consisted of

0.5, 2, 4, 6, 8, 12, and 16, each having targeted Ca:Mg ratios of 0:1, 2:1, 1:2, and 1:0. Each solution was analyzed for cations using an atomic absorption spectrophotometer (210VGP, Buck Scientific, CT, USA) and EC determined using a conductivity probe (Sension 378, Hach Co., CO, USA). To simulate dispersive reactions, 30 mL of dispersive solution was mixed with 1 g of <75 μm sample in 50 mL plastic centrifuge tubes. The samples were shaken (225 oscillations/min) for 16 h and allowed to settle at 25 °C for approximately 90 min according to Stoke's Law. A 5 mL aliquot was then removed from a depth of 2 cm after the required settling time (Curtin, Steppuhn, and Selles, 1994) and placed into 20 mL glass scintillation vials and then transferred into spectrophotometer cuvettes to determine absorbance at 640 nm (V-1200, VWR International, PA, USA). Clay absorbance was converted to a concentration utilizing calibration curves that were prepared for each gravel road fine fraction similar to He et al. 2013 and Curtin et al., 1994. The clay concentration in the 5 mL aliquot was used to determine the amount of dispersion caused by each solution. When a higher concentration was recorded, it signified that more dispersion of the sample had occurred. The concentrations were then plotted to determine where a flocculation/dispersion threshold appeared to exist.

Statistical Analysis

Since there is a threshold effect for dispersion, a designated g/L or greater dispersed level was considered dispersed while levels below that were considered not dispersed. A cutoff of 5 g/L acting as the dispersion threshold was chosen to conservatively determine the probability of dispersion and may change with further investigation. With the dataset ordered in a binary fashion, dispersed or undispersed, a logistic regression was used to model the response of Ca:Mg ratio, SAR, and EC for each of the three roads. The model was developed to estimate the probability of membership to the dispersed category. The PROC LOGISTIC routine was used

with a forward selection procession where inclusion in the model required a p value of 0.15 or less as implemented in SAS/STAT® software (Version [9.4] of the SAS System Copyright (c) 2002-2012 by SAS Institute Inc., Cary, NC, USA). After the model was fit, estimated probability membership to the dispersed category was calculated for each EC and SAR level. A Hosmer and Lemeshow Goodness-of-Fit test is reported to determine if further inclusion of other factors or nonlinear effects are warranted in the logistic beyond the original three factors.

Results and Discussion

An examination of the data indicates that for all the roads, the Ca:Mg ratios, SAR, and EC levels resulted in varying clay concentrations. The reactions varied with the dispersed clay concentration readings ($>5\text{g/L}$) among the road samples with 14th St SW having the highest, then 12th St SW, and then 1st St SW which only had a few readings above the dispersion threshold (Figure 2.2). After categorizing the data into dispersed ($>5\text{g/L}$) or undispersed categories ($<5\text{g/L}$), the influence of the three factors, Ca:Mg ratio, SAR, and EC, were found to be similar to the findings of Curtin et al. (1994) and He et al. (2013) . In the forward selection process, at no time were the Ca:Mg ratios included in the logistic models as an effective explanatory factor ($p<0.15$) (Table 2.2). The different forward selected logistic models show that the levels of Ca or Mg did not increase the explanatory ability of the logistic models. However, both SAR and EC were necessary factors in the logistic model explaining the probability of membership to the dispersal category. As long as the EC is high, the higher SAR values did not result in an inclusion in the dispersal category. All of the individual logistic models for the three roads after forward selection were found to have a Likelihood Ratio test of $p<0.001$ demonstrating that the effect of the factors in the model were not zero. The Hosmer and Lemeshow tests for each road

were greater than $p > 0.8$ signifying that there was little chance that inclusion of additional factors or including nonlinearities in the explanatory factors would improve the logistic model.

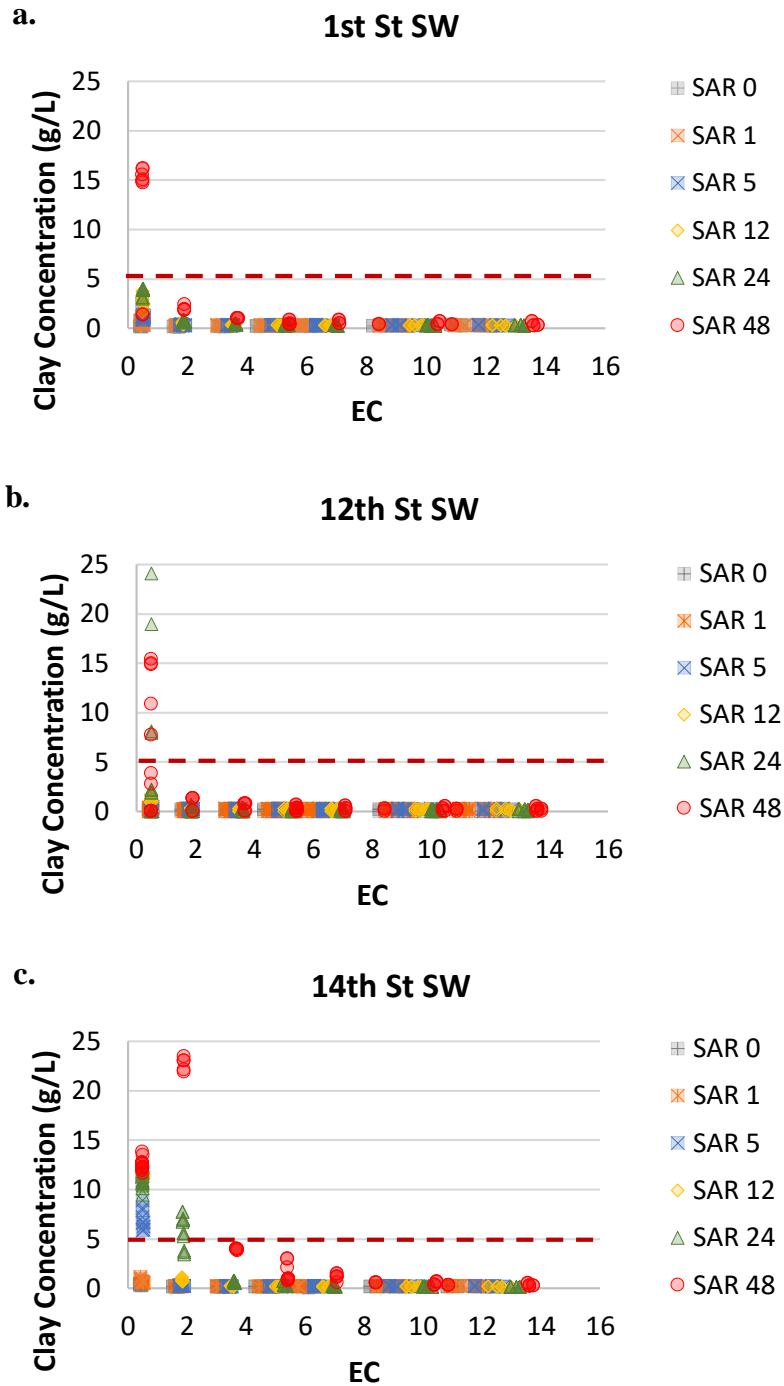


Figure 2.2. Amount of dispersed clay at each respective SAR and EC level. Dotted line indicates the chosen dispersion threshold of 5 g/L.

Table 2.2. Predicted probability dispersion equations for each road. The prediction equations model the estimated probability of membership to the dispersion category.

Road	Dispersion Prediction Equation
1 st St NW	$\hat{\pi} = 1/(1 + e^{-(-18.34+0.49(SAR)-8.37(EC))})$
12 th St SW	$\hat{\pi} = 1/(1 + e^{-(-1.07+0.16(SAR)-7.18(EC))})$
14 th St SW	$\hat{\pi} = 1/(1 + e^{-(-15.58+3.91(SAR)-57.55(EC))})$

The estimated probabilities calculated from the different EC and SAR levels changed for each road and combination of EC and SAR (Figure 2.3). For 1st St NW only one set of conditions resulted in a high probability (>0.74) of membership to the dispersal category, SAR of 48 and EC of < 0.51. For 12th St SW one set of conditions resulted in a high probability (>0.94) of membership to the dispersal category, SAR of 48 and EC of <0.51, while a SAR of 24 and EC of <0.51 resulted in a probability of 0.3 of membership in the dispersal category. For 14th St SW there are varying levels of SAR and EC that result in different probabilities of membership to the dispersal category. The lowest SAR level of 5 and an EC of <0.53 resulted in a high probability (>0.98) of membership to the dispersed category. At the higher levels of SAR 12 and 24 and an EC of <0.57 there was a high probability (>0.99) of membership to the dispersed category. At higher EC levels between 1.85 and 1.9 and a SAR of 24 the probability of membership to the dispersed category varied between 0.95 and 0.57. The highest SAR level of 48 and an EC of <1.91 resulted in a high probability (>0.99) of membership to the dispersed category. This demonstrates that with 14th St SW road type, as EC increases, it can result in membership to the dispersal category combined with decreasing SAR levels beyond what is found with 12th St SW and 1st St NW.

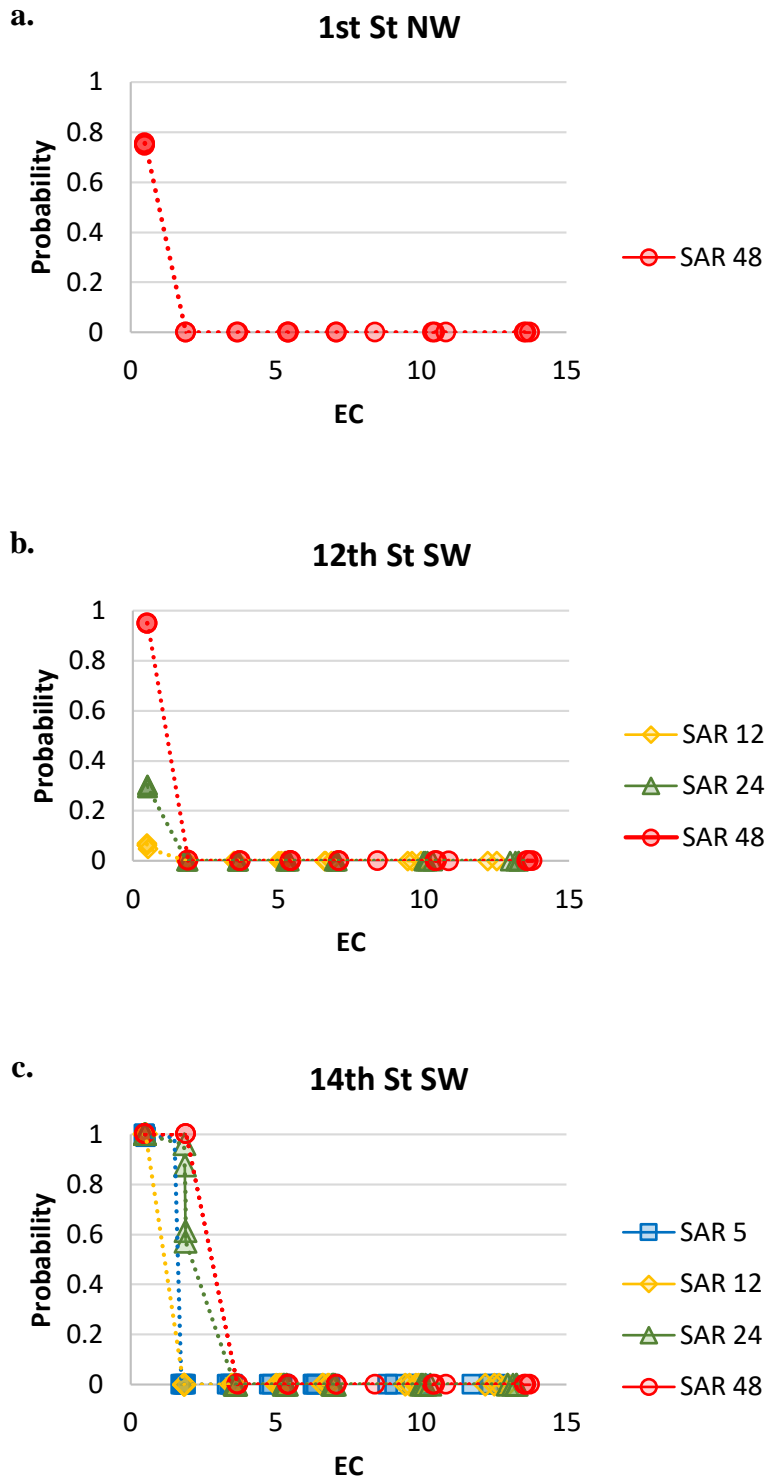


Figure 2.3. Estimated probability of membership to dispersed category at the various SAR and EC levels from the modeled logistic equation. The SAR levels with no high estimated probability are not shown to reduce clutter in the graph.

The road samples analyzed for clay species present in the gravel indicated that both 1st St NW and 12th St SW had 50% or more of smectite. However, 14th St SW had a much higher percentage of illite detected. There was no smectite clay detected on 14th St SW. The occurrence and probabilities of dispersion differed between the roads. Roads similar in mineralogy to 14th St SW have the highest probabilities for dispersion to occur. Roads similar in mineralogy to 12th St SW will have the probability of dispersion occurring at lower levels of EC but not as great as roads similar to 14th St SW. However, roads similar in mineralogy to 1st St NW will have almost no probability of dispersion with the exception of very low EC levels. This demonstrates that the application of solutions, such as produced water, to roads with differing mixed mineralogy should be carefully considered before application. The probability of dispersion will be dependent on how the actual application rate/spread of produced water interacts with the road materials to determine if the levels of SAR and EC can be realized that can result in dispersion.

Conclusions

Ca:Mg ratios were found to have no significant influence on the outcome of dispersion. However, the influence of SAR and especially EC were much more pertinent to the occurrence of dispersion. Even at higher SAR values, EC still remained the dominant factor for when dispersion would occur. Additionally, each road type reacted differently to the varying solutions which demonstrates that the probability of dispersion is dependent on the mineralogy of the road. These findings and predicted probabilities present important implications for managers to consider in regards to the gravel sources that have been used to create the roads that may receive produced waters as an abatement.

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CHAPTER 3: EFFECTIVENESS OF OIL-WELL PRODUCED WATER AS A ROAD DUST ABATEMENT

Introduction

Rural unpaved (gravel) roads are widespread in the Great Plains and typically utilized for domestic and agriculture purposes. However, energy development (oil and natural gas) in the Bakken and Three Forks regions of North Dakota, Montana, and south-central Canada has greatly increased the use of these roads to move equipment for well drilling, hydraulic fracturing processes, and for transporting oil and oil-related byproducts (Tolliver, 2014; Goodman et al., 2016). An undesired consequence of increased traffic has been an increase in dust production from these gravel roads. In a recent study, road dust was found to increase 355% at 10 m from gravel roads in areas servicing current oil-well development compared to typical domestic and agriculture use roads (Creuzer et al., 2016).

To help reduce dust production and deposition on nearby areas, dust abatements are utilized. These abatements can be mixed into the road surface, but are typically sprayed onto the road surface and may be applied several times a year (Bolander, 1999; Piechota et al., 2004). Although there are physical abatement options such as clay additives, chemical abatements such as chloride-based compounds are more common but can be expensive (Travnik, 1991; Bolander, 1999; Piechota et al., 2004). Magnesium chloride ($MgCl_2$) is commonly used throughout the United States as a dust abatement and is widely used in the northern Bakken and Three Forks regions. For example, in Dunn County, North Dakota approximately 331.5 km (206 mi) of $MgCl_2$ was applied to road surfaces for a total cost of about US \$1.64 million in 2016 (D. Schwartzenberger, personal communication, 2016, Dunn County Road Department, ND, USA).

A potential road dust and ice abatement option under consideration in the region is oil-well produced water, also commonly known as “brine” (NDDoH, 2007) which is a byproduct that is separated from the oil in holding tanks. Produced water is also a dust abatement option in other states of the US, including but not limited to Ohio, Michigan, and Pennsylvania (MDoNR, 1983; PDoEP, 1998; ODoNR, 2004). These waters can contain naturally occurring radioactive materials, toxic trace elements, and over 300,000 mg/L total dissolved solids (TDS) (Iampen and Rostron, 2000). In the Bakken and Three Forks regions produced water is mostly composed of sodium and chloride, and has been found to be up to 123,000 mg/L and 186,000 mg/L, respectively (NDDoH, 2007). Oil development in the United States has produced approximately 775 million m³ of produced water and finding alternative uses is desired as opposed to costs for disposal (Kondash and Vengosh, 2015).

There is little to no knowledge regarding the utilization of produced water as an abatement option. Based on the dispersion probabilities created in the laboratory study, it is possible after the application of produced water that roads may disperse, depending on their mineralogy, leading to greater amounts of dust being generated. To date, the authors are not aware of any quantifiable studies that have determined the effectiveness of using produced water as a dust abatement. Additionally, the possibility of dust particles generated after abatement application containing chemical constituents have not been readily documented (Piechota et al., 2004). As road managers consider the use of produced water as a dust abatement option it is important to investigate its effectiveness and potential impacts. The objectives of this study were to determine the effectiveness of produced water for dust control and to determine the chemical constituents of the generated dust from treated and untreated roads.

Methods

Study Area & Design

The study was conducted in Dunn County, North Dakota, United States during the summer of 2015 (Figure 3.1). Precipitation during the study period was typically above the 30-yr average with the exception of July (Table 3.1). Additionally, June also experienced a greater amount of precipitation than the 30-yr average (NDAWN, 2016).

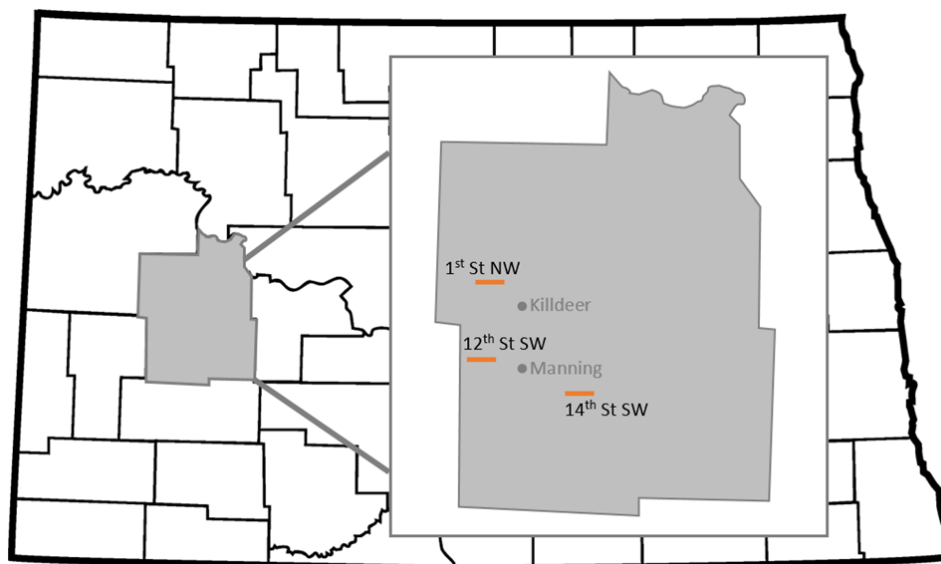


Figure 3.1. Map of Dunn County, North Dakota with study locations.

Table 3.1. Monthly precipitation in millimeters (mm). Number in parentheses denotes departure from the monthly 30-year average.

Month	Rainfall (mm)
June	158.6 (76.8)
July	51.6 (-11.1)
August	59.5 (23.2)
September	49.0 (15.8)
October	39.9 (4.8)

Within Dunn County there are 1408 km (875 mi) of gravel roads (Dunn County Road Department, 2011). Three previously untreated gravel roads with elevated traffic due to oil development related activities were selected for this study (Figure 3.1). Bulk samples of the road materials were sent to Activation Laboratories Ltd. and analyzed for clay species present (Clay Speciation; Activation Laboratories Ltd., Ancaster, ON, Canada). The first site, 1st St NW (47°25'48.06", 102°49'44.01"), was located north of Killdeer. This road consisted of gravel from the Killdeer Mountains which are located to the northwest of this site. The second site, 12th St SW (47°14'27.98", 102°58'47.03"), was located to the northwest of Manning and consisted of a local, glacial-derived gravel pit source with some clinker present in it. Both 1st St NW and 12th St SW consisted of 50% or more of smectite (Table 3.2). The third site, 14th St SW (47°12'46.11", 102°32'55.40"), was located southeast of Manning. This road consisted of clinker gravel sourced from a pit located nearby. There was no smectite present in the 14th St SW gravel, but consisted of a much higher percentage of illite (Table 3.2).

Table 3.2. *Dun County road clay speciation and concentration (% of clay fraction) analysis from Activation Laboratories Ltd. (Ancaster, ON, Canada).*

Clay Type	1st St NW	12th St SW	14th St SW
Smectite	63%	51%	ND ¹
Illite	27%	34%	83%
Chlorite	5%	7%	17%
Kaolinite	5%	8%	Trace

¹ Not Detected

On July 17th the selected roads (each approximately 4.8 km in length) were watered and bladed with a grader. Each road had a 1.6 km (1 mi) section that was treated and another 1.6 km (1 mi) section that was untreated, each road section being approximately 1.6 km long and 7.3 m

wide). Produced water was applied at an approximate rate of 2.3 L/m² (0.5 g/yd²) to the road surface via spraying the same day and were not re-treated for the remainder of the study. Well data analysis for the produced water used in this study indicates that the total dissolved solids (TDS) was approximately 286,000 mg/L, of which calcium was 74,900 mg/L, magnesium was 4,320 mg/L, and sodium was 10,900 mg/L, thus having a sodium absorption ratio (SAR) of approximately 55. Therefore, approximately 660 g TDS were applied per m² of road.

The passive dust collectors and methods used in this study were the same as Creuzer et al. (2016). The basic design of the collectors consisted of a funnel leading into a small collection bucket (diameter = 30 cm, height = 37 cm) inside of a larger bucket (diameter = 24 cm, height = 24 cm), all fastened to the top of a steel post. The top of the bucket was positioned 1.5 m above the soil surface (see Creuzer et al. (2016) for full collector design). Ten grams of cupric sulfate were placed in each collection bucket to help minimize potential biological activity (Environmental Defender's Office (New South Wales), 2010).

The collectors were placed 10, 20, 40, and 60 m from the road on the prevailing downwind side (south side) at each of the three roads immediately after the abatement applications on July 17th. Dust samples were collected 28, 56, and 84 days after application (DAA). After each collection period the funnels were rinsed with deionized water and the collection buckets were removed, sealed, and transported to North Dakota State University for analysis. Cleaned collection buckets were installed for the next sampling period. Dust samples were dried at 29.4 °C (85 °F) with no air flow. After drying, dusts were quantitatively transferred into 118 mL (4 oz) specimen cups and dried at 105 °C for 24 h or until the sample was completely dry (ASTM Standard D2216-10, 2010). The samples were then placed into a desiccator filled with silica beads for a minimum of 24 h to equilibrate all samples to the same

water content before they were weighed using a 0.01 g scale. The weight of the cupric sulfate was subtracted from the dust samples to yield the weight of dust collected.

After the samples were weighed, they were ground in a porcelain mortar and pestle. The samples were then sent to Bureau Veritas Commodities Canada Ltd. and analyzed for the elements present in the collected dust using aqua regia digestion and Inductively coupled plasma mass spectrometry (ICP-MS) (AQ250-EXT; Bureau Veritas Commodities Canada Ltd, Vancouver, BC, Canada). A list of elements that Bureau Veritas analyze for can be found in Appendix A. However, only the elements of molybdenum, manganese, iron, arsenic, gold, and mercury were found to have enrichment and chosen to be further investigated.

Picocount 2500 traffic counters were placed on each road the same day as the dust collectors and remained on the road for the extent of the study (Counting Cars, St. Louis Park, MN, USA). Traffic data was retrieved on the same days as the dust collections (every 28 d). The counters recorded the vehicle size, speed, and time and date of occurrence.

Statistical Analysis

Paired t-tests were used to compare average dust loading amounts within 20 m (10 and 20 m samples were treated as different pairs in the analysis) from the road in each of the treatment sections using the time periods as replications. A significance level of $p < 0.1$ was chosen due to the limited number of periods that sampling can be used as replications. The three roads were analyzed separately due to the differences of gravel type. Using a randomized block design, differences in loading amounts through the duration of the project at each distance and differences in dust loading for each of the treatment sections at each distance were tested using PROC GLM with a Tukey test for means comparison in the SAS/STAT[®] software (Version [9.4] of the SAS System Copyright (c) 2002-2012 by SAS Institute Inc., Cary, NC, USA).

Additionally, elements that were detected by Bureau Veritas Commodities Canada Ltd analysis and were found to have an average enrichment factor of 1.5 were tested using paired t-tests to compare if significant changes were seen in the dust from the produced water sections compared to the dust from the control sections.

Results and Discussion

During each sampling period, traffic on individual roads remained fairly consistent but rates varied between the roads with 1st St NW generally experiencing greater amounts than the other two roads. Using the Federal Highway Association (FHWA) classification system, all vehicles were sorted by axle counts into the appropriate class by the traffic counter (Table 3.2). Larger vehicles create more axle counts due to their size, which typically corresponds with an increase in weight. All of the roads experienced higher rates of larger vehicles (Class 4 and higher) such as semi-trailer trucks than smaller vehicles such as cars or pickups. The average speeds were 54.7 km/h (34 mph), 61 km/h (38 mph), and 72 km/h (45 mph) for 1st St NW, 12th St SW, and 14th St SW, respectively. Vehicle speed and weight have been found to be dominant factors in dust production and if there is an increase in either, there is an increase in fugitive dust production (Gillies et al., 2005; Kuhns et al., 2010). Although there were visible amounts of dust collected, the dust loading was not as heavy as found previously in North Dakota oil producing areas (Creuzer et al., 2016). This is most likely due to the differences in traffic levels during each study as traffic levels have decreased in the area due to decreasing oil prices since the study completed by Creuzer et al. (2016). However, abatements are still used even with lower traffic.

Table 3.3. *Dunn County dust control study traffic summary using the Federal Highway Association classification system. The number of vehicles in each class were totaled and averaged for each time period (28 d).*

Road Location	Vehicle Classification	Days 1-28	Days 29-56	Days 57-84	Total Average Vehicle Count
1st St NW	1-3 ¹	839	700	1314	951
	4-13 ²	2881	2653	3134	2889
	Total	3720	3353	4448	3840
12th St SW	1-3 ¹	422	473	246	380
	4-13 ²	1263	1929	1701	1631
	Total	1685	2402	1947	2011
14th St SW	1-3 ¹	168	90	118	125
	4-13 ²	533	528	745	602
	Total	701	618	862	727

¹ Classes 1-3 are smaller passenger vehicles.

² Classes 4-13 are larger commercial vehicles.

The dust loading at each individual distance for each treatment section were not different throughout the duration of the project. When all control sections were averaged together to compare distance loading, only the 10 m distance was significantly different from the remainder of the distances (Figure 3.2a). In the produced water sections, the 10 m distance loading amount was also significantly different from the remainder of the distances. However, the 20 m distance was not significantly different from the 40 m or 60 m distances, but the 40 m and 60 m distances were significantly different from each other (Figure 3.2b). The trend of decreasing dust amounts further from the road has been previously documented (Tamm and Troedsson, 1955; Everett, 1980; Walker and Everett, 1987; Creuzer et al., 2016). This indicates that the roadside biota and adjacent water and soil mediums will be mostly impacted by the road dust. It is also worth noting that the roadside environment or local aquifers will also see runoff impacts from the road

after application in addition to the heavier dust loading (Kohl et al., 1994; Goodrich et al., 2009a; Eckstein, 2011).

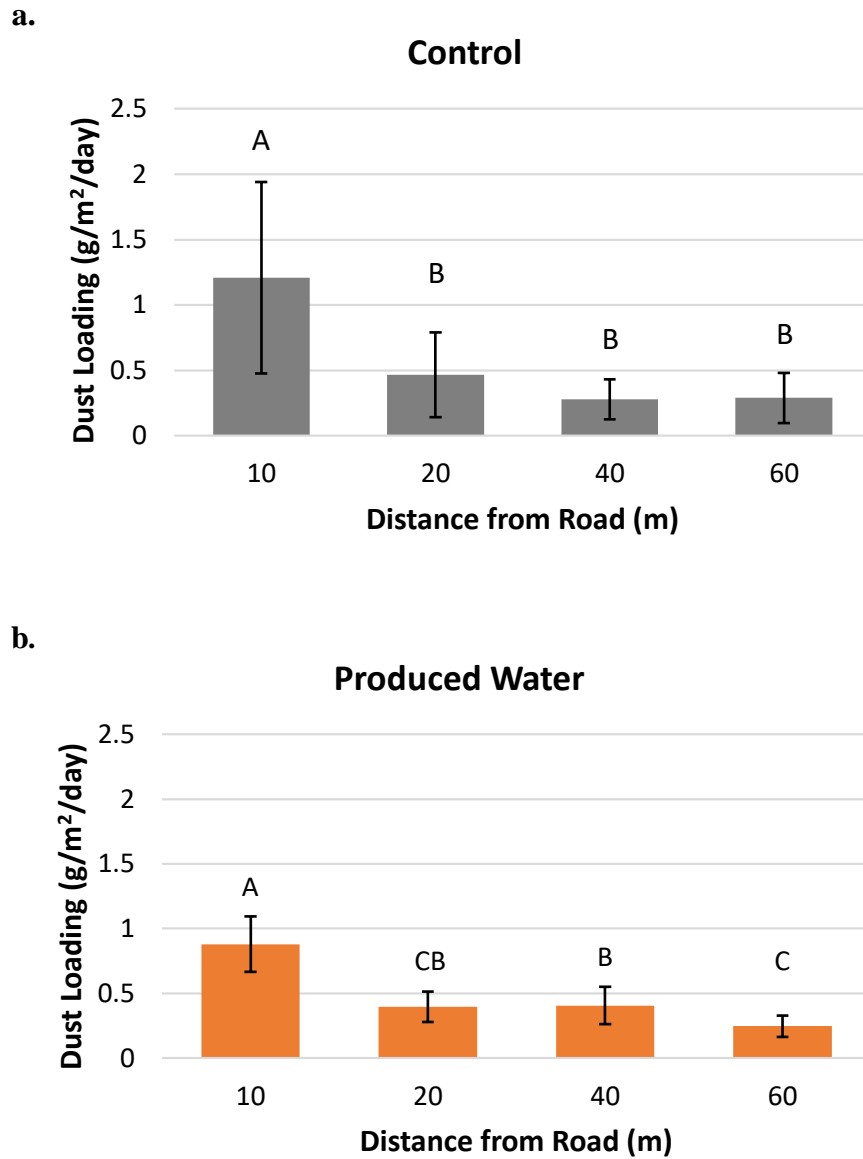


Figure 3.2. Overall average dust loading in each section by distance from the road. Error bars represent the standard deviation for each distance.

Even with the lowest amount of traffic throughout the study, using the 10 and 20 m dust collections, produced water failed to reduce dust compared to the control section on 14th St SW ($p=0.44$) (Figure 3.3c). Produced water additionally failed to reduce dust on 12th St SW ($p=0.19$) which also saw less traffic than 1st St NW (Figure 3.3b). On 1st St NW the dust loading from the produced water section was less than the control ($p=0.005$) (Figure 3.3a). The likelihood of 12th St SW and 14th St SW failing to reduce dust is supported by our predicted probabilities of dispersion found during our laboratory study. Additionally, this indicates that whether produced water is effective for dust abatement or not is not likely to be traffic dependent. Furthermore, this demonstrates that a single application of produced water, although cheap, may not be cost effective enough to be beneficial in reducing dust. It is possible that additional applications may help reduce dust production, but as there are more applications, there could be buildup of elements that could be transported by dust particles or solution movement (runoff) from the road surface into nearby areas.

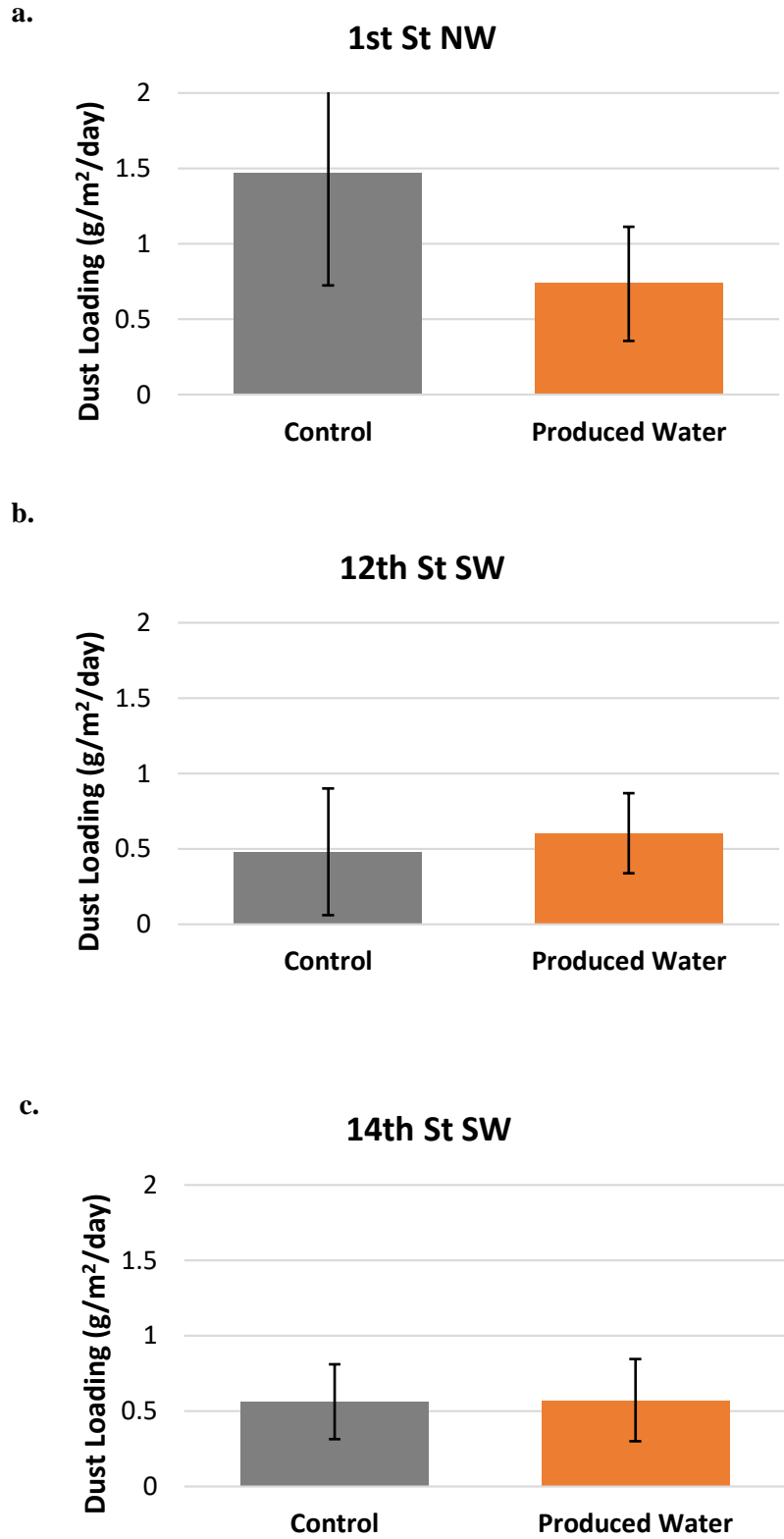


Figure 3.3. Average dust loading for all control and abated sections. Error bars represent the standard deviation for each treatment.

Elements that are known to be present in produced water were considered but showed no enrichment, due to this we chose to focus on elements that showed an enrichment between control and abated sites after being analyzed. When comparing the control and abated dust elemental analysis, using the 10 and 20 m dust collections, the elements that had an enrichment factor of 1.5 were molybdenum (Mo), manganese (Mn), iron (Fe), arsenic (As), gold (Au), and mercury (Hg). Mo ($p=0.0047$), Mn ($p=0.0022$), Fe ($p=0.0043$), and As ($p=0.0028$) were significantly different on 12th St SW. On 14th St SW only Hg was significantly different ($p=0.000031$). There were no differences found on 1st St NW with these elements. The changes in these elements demonstrate that elements in the dust able to be transported via road dust and may vary road to road. With additional applications of produced waters there could be an increase in the elements in the released dust.

Conclusion

This study is the first of its kind to quantitatively compare dust loading from unpaved roads abated with produced water to control sites. Even when differing traffic levels were observed, produced water failed to reduce dust on two of the three roads in this study (12th St SW and 14th St SW). This demonstrates that one application of produced water as a dust abatement is generally ineffective. It is possible that additional applications of produced water could aid in a greater effectiveness outcome. However, with additional use of produced water there is more likely to be impacts to the terrestrial and aquatic ecosystems that surround the road. Information from this study is informative to road and land managers that are considering produced waters as a dust abatement option.

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CHAPTER 4: CONCLUSIONS

This study simulated produced water's potential impacts to gravel road materials, compared dust loading at abated to control sites to determine effectiveness, and identified elemental differences in the dust collected at abated and control sites. When it comes to the potential impacts to gravel road materials, the mineralogy of the road vastly influences the probability of dispersion. Additionally, produced water was not effective as a dust abatement treatment. Furthermore, there were changes in elemental composition found between dust collected at abated sites compared to control sites. These findings are the first of their kind and establish a baseline of knowledge regarding the usage of produced waters as a dust abatement. Future research should explore the impacts of multiple applications of produced waters to a road as a dust abatement and explore other mixed mineralogy roads.

APPENDIX. ELEMENTS TESTED BY BUREAU VERITAS COMMODITIES CANADA

LTD LAB USING ICP-MS ANALYSIS

Element	Symbol	Detection Limit	Element	Symbol	Detection Limit
Aluminum	Al	0.01 %	Nickel	Ni	0.1 ppm
Antimony	Sb	0.02 ppm	Niobium	Nb	0.02 ppm
Arsenic	As	0.1 ppm	Palladium	Pd	10 ppb
Barium	Ba	0.5 ppm	Phosphorus	P	0.001 %
Beryllium	Be	0.1 ppm	Platinum	Pt	2 ppb
Bismuth	Bi	0.02 ppm	Potassium	K	0.01 %
Boron	B	20 ppm	Rhenium	Re	1 ppb
Cadmium	Cd	0.01 ppm	Rubidium	Rb	0.1 ppm
Calcium	Ca	0.01 %	Scandium	Sc	0.1 ppm
Cerium	Ce	0.1 ppm	Selenium	Se	0.1 ppm
Cesium	Cs	0.02 ppm	Silver	Ag	2 ppb
Chromium	Cr	0.5 ppm	Sodium	Na	0.001 %
Cobalt	Co	0.1 ppm	Strontium	Sr	0.5 ppm
Copper	Cu	0.01 ppm	Sulfur	S	0.02 %
Gallium	Ga	0.1 ppm	Tantalum	Ta	0.05 ppm
Germanium	Ge	0.1 ppm	Tellurium	Te	0.02 ppm
Gold	Au	0.2 ppb	Thallium	Tl	0.02 ppm
Hafnium	Hf	0.02 ppm	Thorium	Th	0.1 ppm
Indium	In	0.02 ppm	Tin	Sn	0.1 ppm
Iron	Fe	0.01 %	Titanium	Ti	0.001 %
Lanthanum	La	0.5 ppm	Tungsten	W	0.1 ppm
Lead	Pb	0.01 ppb	Uranium	U	0.05 ppm
Lithium	Li	0.1 ppm	Vanadium	V	2 ppm
Magnesium	Mg	0.01 %	Yttrium	Y	0.01 ppm
Manganese	Mn	1 ppm	Zinc	Zn	0.1 ppm
Mercury	Hg	5 ppb	Zirconium	Zr	0.1 ppm
Molybdenum	Mo	0.01 ppm			