ASSESSMENT OF SULFATE IN OHIO TRANSPORTATION SUBGRADES

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ASSESSMENT OF SULFATE IN OHIO TRANSPORTATION SUBGRADES

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Thesis

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ABSTRACT

The Ohio Department of Transportation (ODOT) recently implemented global chemical stabilization for new construction or repair involving major road projects. Pavement heave caused the failure of the road surfaces in three projects in Lake County, Ohio. Subsequent soil investigation revealed surface heave was caused by soil swell from the formation of a calcium alumina sulfate hydrate, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) which may occur in sulfate bearing soils chemically stabilized with lime. Failure of pavement in these three projects caused ODOT to question the whether other regions within Ohio had subgrades with high soluble sulfate concentrations. This report is an investigation into natural and anthropogenic sources of sulfate (SO_4) in Ohio soils evaluated via literature review and soil testing. The ODOT provided just under 350 soil samples from 39 different counties throughout the state for assessment of soil chemistry and mineralogy. Soluble SO_4, often the primary controlling factor in degree of ettringite formation, was measured within soils using colorimetric methods. Several soils were additionally tested for total metal (Al, Fe and Cr) concentrations using acid digestion and inter coupled plasma optical emissions spectrometry (ICP-OES). Total Al concentration within soils was analyzed, as Al and SO_4 are the chemicals within ettringite which have their primary source as the prestabilized soil. Total Fe was assessed as a marker for potential areas where sulfate would have formed from the oxidation of pyrite (FeS_2). Total Cr concentration was tested as chromate (CrO_4)

can be a replacement group for SO_4 within the ettringite structure. Additionally initial review of literature identified chromite ore processing residue remediation as a potential source of excess SO_4 in soils. Finally, soil mineralogy was analyzed via x-ray diffraction (XRD).

Results indicate Lake County, Ohio is not the only region with Ohio where ODOT should expect subgrades with problematic soluble SO_4 concentrations. Although further soil testing throughout the state is needed, sufficient sulfate concentration (>3,000 mg/kg) for elevated risk of sulfate-induced heave were identified in a number of soils and three key regions within Ohio: Lake County in the northeast, Paulding and Defiance counties in the northwest and Morrow County in the north central. Within both Lake County soils and the Paulding and Defiance area soils, the primary identified SO_4 bearing minerals were evaporates, gypsum and anhydrite. The natural origin of these mineral is most likely glacial lacustrine deposits. However, there are anthropogenic sources which likely add SO_4 to soils within these regions. The high degree of industrial activities including coal fired power plants add SO_4 to soil in Lake County. Whereas the application of gypsum as a farmland amendment is the likely anthropogenic source in Paulding and Defiance counties. Gypsum and pyrite were identified as the primary and secondary sulfur bearing minerals, respectively, in Morrow County soils. The origin of pyrite within this region is from Devonian Shale bedrock. The oxidation of these pyritic shales was identified as the primary source of $SO_{4,}$ in the form of gypsum, in Morrow County soils.

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CHAPTER I

INTRODUCTION

1.1 Statement of the Problem

The Ohio Department of Transportation (ODOT) predicted cost savings by implementation of a global chemical stabilization strategy (Merklin 2011). However these benefits were challenged by pavement failure cause by the swell of chemically stabilized subgrades containing elevated levels of sulfate. Swell of lime stabilized subgrade caused the failure of three road construction projects in Lake County, Ohio. Cracking, unevenness and undulation of the asphalt surface in addition to vertical displacement between pavement and the median haunch in two projects along State Route (SR) 2 and another project along Interstate Route (IR) 90 caused ODOT to investigate failure of these projects in Lake County (Narsavage 2011). The cost of repairing heaved pavements for one of these SR-2 projects was well over a million dollars (Narsavage 2012). Subsequent soil investigation revealed elevated levels of soluble sulfate (SO_4) and presence of gypsum ($CaSO_4{\cdot}2H_2O$) in the natural subgrade and ettringite in the stabilized subgrade beneath the heaved pavement (Narsavage 2011; Farver et al., 2014). Sulfate-induced heave was not a new phenomenon having gained exposure since the late 1980’s and occurred in: Nevada (Hunter 1988); Texas (Petry & Little 1992; Kota et al., 1996; Burkhart et al., 1999; Harris et al., 2003; Puppula et al., 2005); California (Berger et al., 2002), Louisiana (Wang et al., 2005); Colorado (Little & Nair 2007); Oklahoma (Cerato et al., 2011) and in the United

Kingdom (Abdi & Wild 1993; Rahmat & Kinuthia 2011). However, this was the first time ODOT encountered sulfate-induced heave in a lime stabilized soil project. The financial toll of pavement repairs, inconvenience of lane closures and concerns about failure of future lime stabilization projects caused ODOT to request a study on sources of sulfate in Ohio soils. Understanding the sources of and location of soils with high SO_4 concentrations could assist the planning and supervision of future stabilization projects.

1.2 Research Objective

The primary objective of this research project was to identify the origin and formation of SO_4 and sulfur bearing (S-bearing) minerals in Ohio soils to assist ODOT in selection of proper construction strategies for stabilization of clay soils. This objective was met by thorough literature review on sulfate-induced heave and natural as well as anthropogenic source of SO_4 in Ohio. Additionally, tests were conducted on 350 soil samples from 39 different counties throughout the state provided by ODOT for assessment of soil chemistry (SO_4, Al, Fe and Cr) and mineralogy (S-bearing mineral source). Soluble SO_4, often the primary controlling factor in degree of ettringite formation, was measured within soils using colorimetric methods. Several soils were additionally tested for total metal (Al, Fe and Cr) concentrations using acid digestion and inductively coupled plasma spectrometry (ICP). Total Al concentration within soils was analyzed, as Al and SO_4 are the chemicals within ettringite which have their primary source as the prestabilized soil. Total Fe was assessed as a marker for potential areas where sulfate would have formed from the oxidation of pyrite (FeS_2). Total Cr concentration was tested as chromate (CrO_4) can be a replacement group for SO_4 within the ettringite structure. Finally, soil mineralogy was analyzed via x-ray diffraction (XRD) to ascertain S-bearing minerals in soils.

Investigation of existing research on sulfate-induced heave and sources of SO_4 in Ohio soils in conjunction with the results of soil testing will provide the framework for evaluation of soluble sulfate concentrations in Ohio transportation subgrades.

CHAPTER II

LITERATURE REVIEW

2.1 Background on Sulfate Induced Heave

Expansive clay soils are problematic as pavement subgrades due to volume changes associated with accessibility to water, lack to strength and flexible nature. Often to mitigate these problems clay soils are chemically stabilized with the addition of lime which may reduce shrink/swell potential, increase strength and provide soils a more rigid structure. Although effective at meeting these subgrade issues, chemical stabilization of sulfate bearing clays creates an environment favorable for the formation of ettringite. The reaction has many steps, but the basic constituents are: calcium (Ca); aluminum (Al); sulfate (SO_4) and water (H_2O). Calcium is provided by the addition of lime, Al is a common component of clay soil, sulfate in soil has many origins but is associated with gypsum ($CaSO_4 \cdot 2H_2O$). Water could be introduced during the stabilization process, moisture in soils due to minimal depths to groundwater, precipitation events or water runoff. Under such conditions the expansive mineral ettringite, $Ca_6(Al(OH)_6)_2(SO_4)_3 \cdot 26H_2O$) can form.

2.1.1 Lime Stabilization

Expansive soils, covering approximately 25% of the United States, annually shrink and swell due to seasonal variations and changes in water availability (Adams et al., 2008). This cyclic pattern causes an estimated $15 billion dollars per year in damage to structures and transportation pathways. Numerous researchers have reported the addition of lime to soils improves the physical properties of clay soils through physiochemical alterations (Bell 1996; Cokca 2001; Harris 2006; Cerato 2007; Adams et al., 2008; Little & Nair 2011). Calcium ions from the lime react with metal ions associated with the clay causing flocculation and bonding through ion exchange (Bell 1996). This chemical alteration of clay soils reduces the plasticity of the soil, mitigates volume change potential (Adams et al., 2008), increases soil strength and workability and provides a platform for construction activities (Little and Nair 2011).

2.1.2 Sulfate-Induce Heave

Heaving, or the upward lift, of pavements above subgrades treated with standard lime stabilization practices has become a problem throughout the U.S. in recent years. Several states have investigated failures of soils due to sulfate-induced heave (Hunter 1988; Bredenkamp & Lytton 1995; Kota et al., 1996; Berger 2002; Muckel 2004; Harris 2004 and 2006; Wang et al., 2005; Little 2005; Little & Nair 2007; Cerato et al., 2011). Sulfate-induce heave is a chemical reaction involving clay soils with high concentrations of soluble sulfate which disassociate reacting with calcium ions from the lime stabilization, aluminum ions from the clay fraction of the soil and water. Lime added in the stabilization process raises the pH of the environment to 12.3. At this pH the dissolution of Kaolinite or other clay soil introduces aluminum ions. Water will cause the dissolution of gypsum or other sulfate bearing minerals. The geochemical reaction model was provided by Harris et al., in 2004 as:

Ionization of lime which raises the pH to 12.3 (eq. 1)

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2(OH)^-$$

Dissolution of kaolinite at pH greater than 10.5 (eq. 2)

$$Al_4Si_4(OH)_8 \ + 4(OH)^- + 10H_2O \rightarrow 4Al(OH)_4^- + 4H_4SiO_4$$

Dissolution of gypsum (eq. 3)

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + (SO_4)^{2-} + 2H_2O$$

Formation of ettringite (eq. 4)

$$6Ca^{2+} + 2Al(OH)_4^- + 4(OH)^- + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6(Al(OH)_6)_2 \cdot (SO_4)_3 \cdot 26H_2O$$

Ettringite is not limited to this unique chemical composition. Rather ettringite is the name for a number of minerals with similar composition, replacement of Al by Fe^{3+} or Cr^{3+}. Similarly SO_4 can be replaced by other common oxyanion: CrO_4^{2-}, SeO_4^{2-} or CaO_3^{2-} (Little et al., 2005). In addition to the damage related to soil swell, in the presence of soluble silica and carbonate and at temperatures below 15° C, ettringite can transform into thaumasite, a mineral which provide significantly less strength to the soil (Little et al., 2005). Another complexity of ettringite formation is the length of time after stabilization until ettringite formation and swell reaches completion. Delayed failure occurred in multiple lime stabilization projects in Las Vegas, Nevada (Mitchell 1986). Although minor cracking was recognized after six months, significant swell occurred more than two years after stabilization was completed (Mitchel 1986; Hunter 1988). Although degree of swell usually increases with increasing SO_4 concentration, in some instances soil with lower SO_4 concentration experienced greater degrees of swell. Researchers examining swell of Oklahoma soils found soils with SO_4 concentration of 8,600 mg/kg swelled 2.5 - 3.5% more than soils with much higher concentrations of SO_4 (Adams et al., 2008). Similarly, swell tests on Ohio soils also found degree of swell was not exclusively related to SO_4 concentration (Cutright & Wigdahl 2013). In these cases sulfate may not have been the limiting factor. The amount of available Al has been recognized as a possible and probable limiting factor in swell of certain Colorado soils (Little & Nair 2007).

2.1.3 General Sources of Sulfate

Natural gypsum is the most common natural sulfate mineral. The United States produces 15% of the world's gypsum (Kota et al., 1996) with mining activities throughout the country (Figure 1, Kota et al., 1996). Gypsum and anhydrite are major constituents of many sedimentary rocks (Chikyala 2007).

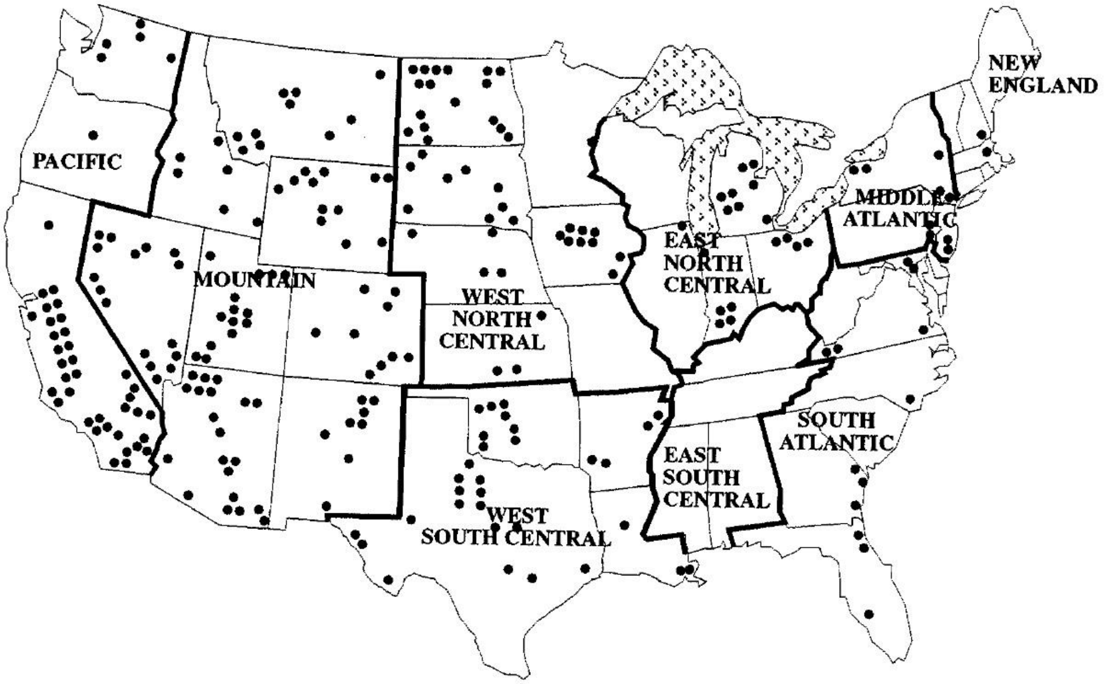


Figure 1 Locations of soils with gypsum and gypsum mines in the United States (Kota et al., 1996)

Sulfates can also occur as the result of the oxidation of pyrite in sedimentary rocks especially shale (Harris et al., 2004; Wild et al., 1999). In pyrite bearing sedimentary rocks the oxidation of pyrite causes the formation of acid sulfate. Calcium also within these rocks reacts with the acid sulfate to form gypsum (Chikyala 2007).

Oxidation of pyrite (eq. 5)

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$$

Dissolution of calcite (eq. 6)

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

Formation of gypsum (eq. 7)

$$Ca^{2+} + (SO_4)^{2-} + 4H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Pyrite is oxidized when exposed to an oxygen source through cuts in the soil during road construction (Kota et al., 1996) or water enriched with oxygen infiltrating the soil (Chikyala 2007). Additionally there are a number of anthropogenic sources of sulfate in soils. Researchers have reported $MgSO_4$ and Na_2SO_4 have been contained in industrial waste (Wild et al., 1999). Ferrous sulfates was used in the remediation of hexavalent chromium contaminated soils subsequently used as fill (Dermatas 2005). Sulfate particulate travel through atmospheric wind currents and can be deposited well away for their original source (Zhao et al., 2007). Sulfate bearing materials have even been used as a road coarse (Wang et al., 2005).

2.1.4 Factor Affecting Swell Potential

In addition to the stoichiometric presence of sulfates, calcium, aluminum and water, there are several factors that influence the rate and degree of ettringite formation. The mineralogy of a soil can vary greatly within a given site and can be changed by external influences such as pollution (Zhao et al., 2007), water sources which may transport deleterious materials such as soluble sulfate (Little & Nair 2009) and fill material during the construction process (Kota et al., 1996; Dermatas et al., 2006). The grain size of sulfate bearing minerals effects the solubility and the rate of sulfate dissolution and hence, ettringite formation (Harris et al., 2004). As grain size is reduced the surface area becomes larger which increases the dissolution rate (Cerato et al., 2011). Conversely, at larger grain sizes, sulfates do not experience complete dissolution quickly and significantly more time is needed for dissolution (Cerato et al., 2011; Little & Nair 2009). Variation in water supply also is an important factor. Seasonal changes in moisture can create sulfates deposits near the soil surface when rainfall is lacking. Then in seasons of high rainfall, water can dissolve these sulfates and transport them to areas of lower elevation through overland flow and infiltration (Little & Nair 2009).

2.1.5 Research into Mitigation of Sulfate-Induced Heave

Additional research found the use of excess water after lime stabilization would reduce the dry density of the soil creating more void space for ettringite crystal to expand (Harris et al., 2004). Several researchers have studied the effects of mellowing time before compaction (Berger et al., 2002; Harris et al., 2004). These researchers found that soils with sulfate concentrations as high as 7,000 mg/kg could be treated with traditional lime stabilization if a mellowing time of 1-3 days was allowed before compaction. Other researchers found mellowing time allow potentially reduce subsequent swell potential adversely impact compressive strength of soils and recommends against mellowing (Rahmat & Kinuthia 2011). Researchers in California studied 1-D swell of two native soils at sulfate concentrations of 0, 5000, 8000, 14,000 mg/kg, (each concentration +/- 1000 mg/kg) with 4% lime addition and exposed to 1, 3 or 5 day cure (Berger et al., 2002). They also studied whether the partial replacement of lime with of Class C Fly Ash would reduce swell. Berger et al., determined the use of a one day mellowing time with 4% lime addition would limit swell and the sulfate concentration was not particularly significant. Addition of 6% lime enable samples to retain pH in excess of 10 insuring the desired chemical reactions were proceeding (Berger et al., 2002). They also stated that Fly Ash did not cause swell to reduce much more than lime alone. In conclusion they recommended that lime be added in a single application, water content of 4% above optimum be used during lime addition and an extended mellowing time could be used to stabilize soils at very high sulfate concentrations. Mitigation of swell by the addition of fly ash was also conducted in Scotland, United Kingdom. Fly addition of up to 24% fly ash was found to be effective for total potential sulfate of 1.5% by mass (15,000 mg/kg) (McCarthy et al., 2012). Researcher in Texas examined the effectiveness of 12 non-traditional stabilizers to see if swell could be reduced in clay soils spiked to 0, 10,000 and 20,000 mg/kg SO_4. Only the treatment of ground granulated blast furnace slag (GGBFS) with lime provided acceptable swell and strength. Researchers recommended use of 5:1 (GGBFS:Lime) per weight of dry soil based on swell and strength testing as well as economic value (Harris et al., 2006). The potential use of non-traditional chemical stabilizers has also been evaluated in Ohio. Using soils from Lake County with visible signs of gypsum, Roadbond EN1 was not effective in reducing swell or increasing strength more than cement stabilization alone (Narsavage 2012).

2.1.6 Risk Thresholds of Sulfate Concentration

Researcher have tested the swell of soils samples subjected to varying concentrations of sulfate to determine if there is a sulfate threshold below which heave will not occur or the can be controlled. Extensive research has been conducted on Texas soils and a threshold of 3,000 mg/kg has been reported as the limit of sulfate concentration below which detrimental effects will not occur (Harris et al., 2004). However, failure of soils has been reported at sulfate concentrations as low as 700 mg/kg (Hunter 1988). Recommended thresholds based on risk levels at varying sulfate concentrations have been offered by researchers Little and Nair in 2009 (Table 1). However they site that swell tests in laboratory fail to completely mimic conditions in the field and swell tests are often are not conducted for long enough periods of time (Little & Nair 2009).

Table 1 Threshold risks levels for sulfate induced heave based on SO_4 concentration (Little & Nair 2009)

Risk Involved	Soluble Sulfate Concentration
Low Risk	Below 3,000 mg/kg
Moderate Risk	Between 3,000 and 5,000 mg/kg
Moderate to High Risk	Between 5,000 and 8,000 mg/kg
High to Unacceptable Risk	Greater than 8,000 mg/kg
Unacceptable Risk	Greater than 10,000 mg/kg

Standardizing threshold levels for soluble sulfate concentration has been a challenge amongst researchers as SO_4 concentration in not the sole factor contributing to extent of soil swell. As mentioned above failures in soils have occurred at sulfate concentrations as low as 700 mg/kg, while other researchers had reported minimal swell in soils with sulfate concentrations in excess of 12,000 mg/kg. In addition to the differing soils chemistries which could lead to these discrepancies, researchers have indicated the use of differing soluble sulfate measuring procedures as a source of variation (Burkhart et al., 1999).

2.2 Measuring Sulfate Concentration

There are many ways to determine the soluble sulfate concentration and resulting concentrations will vary depending on which test is used. This provides challenges in developing threshold concentration for risk of sulfate induced heave. Colorimetric, gravimetric and electrical conductivity methods are briefly described below and a comparison of these different SO_4 testing methods is provided in Table 2. Ion chromatography is and additional method which provides good results for low sulfate concentrations, but is not described here (See Harris et al., 2003 for more information).

Table 2 Comparison of SO_4 Concentration Test Methods

Methods Name	Test Mechanism	Water to Soil Ratio (ml of water:g of soil)	Particle Size	Contact Time	Separation Method
Modified UTA[1]	Gravimetric	10:1	Passing 4.75 mm (No. 4) sieve	1 h	Centrifuge
AASHTO (T290-95)[2]	Gravimetric	3:1	Passing 2 mm (No. 10) sieve	Not Specified	Centrifuge
TEX-146[3]	Conductivity	20:1	Passing 425 μm (No. 40 sieve)	12 h	N/A
OHD L-49[4]	Colorimetry	40:1	Passing 2 mm (No. 10) sieve	16 h	Partial Filtration (>30 mL)
TEX-145E	Colorimetry	20:1	Passing 425 mm (No. 40 sieve)	12 h	Filtration

[1] *Modified UTA: Modified University of Texas at Arlington gravimetric method for assessing sulfate concentration in soil (Talluri et al., 2012).*

[2] *AASHTO 290-95: American Association of State Highway and Transportation Officials gravimetric method for assessing sulfate concentration (Talluri et al., 2012).*

[3] *TEX-146: Texas Department of Transportation conductivity method for screening sulfate in soil (TexDOT 2005b).*

[4] *OHD L-49: Oklahoma Department of Transportation colorimetric method for assessing soluble sulfate concentration in soil (OkDOT 2005).*

[5] *TEX-145E: Texas Department of Transportation colorimetric method for assessing soluble sulfate concentration in soil (TexDOT 2005a).*

2.2.1 Colorimetry

Colorimetry involves the process of mixing an amount of soil with an amount of distilled water (DI) then measuring the amount of sulfate that solubilizes in the solution. The amounts of soil and ratio of soil to water vary among current procedures. Currently the TexDOT mixes 20 grams of soil passing a number 40 (425 µm) sieve and 400 ml of DI for a water to soil ratio of 20:1 (TexDOT 2005a). After adding the soils and water in a jar the sample is shaken vigorously for a minute and then let to stand for a minimum of 12 hours before measuring for soluble sulfate. The Oklahoma department of transportation (OkDOT) colorimetry method, OHD L-49, requires only 5 grams of soil passing a number 10 (2 mm) sieve and 200 ml of DI for a water to soil ratio of 40:1 (Cerato, et al., 2011). After adding the soil and water into a jar the sample is shaken by hand for 15 seconds every five minutes for 15 minutes or on a mechanical shaker for 15 minutes then let to stand for a minimum of 16 hours before measuring for soluble sulfate (OkDOT 2005). Both methods require filtration of the sample after the prescribed sitting time. Then 10 ml of the filtrate is added to a testing vial and is tested for soluble sulfate by adding a barium chloride testing pillow to the vial. This pillow reacts with soluble sulfate within the sample and will change the color of the sample based on the degree of soluble sulfate within the sample. After five minute reaction time the vial is placed in a handheld colorimeter and soluble sulfate is measured. This reading is then multiplied by the initial water to soil ratio to provide the soluble sulfate concentration of the soil in mg of soluble sulfate per kg of soil or parts per million (ppm).

2.2.2 Gravimetric

There are several gravimetric methods for assessing SO_4 content in soils: Modified UTA Method; AASHTO Method T 290-95 and Tex-620J. Gravimetric analysis first requires removal of sulfate from soil via dissolution. The Tex-620J adds heated DI water to assist dissolution followed by filtration (Harris et al., 2003), where the Modified UTA and AASHTO 290-95 required a period of shaking of soil/water solutions; followed by centrifuging for separation and filtration if needed (Talluri et al., 2012). Barium chloride ($BaCl_2$) is then added to the solution in each method and heated until $BaSO_4$ precipitation occurs. The solution again is filtered collecting $BaSO_4$ on the filter paper. Residual chlorides are removed from the precipitate by DI wash and after precipitate dries the weight can be measured and SO_4 content of soil can be calculated (Harris et al., 2003; Talluri et al., 2012).

2.2.3 Electrical Conductivity

Another method for determining soils with high SO_4 content is based on electrical conductivity. Researchers in Texas studied the ability of electrical conductivity to access sulfate concentration and found it could accurately predict soils containing high level of soluble salt. However, results of high conductivity did not necessarily dictate high sulfate content as other soluble salts within the soil could provide high conductivity (Bredenkamp & Lytton 1995). Subsequently the Texas Department of Transportation implemented Method TEX-146-E, Conductivity Test for Field Detection of Sulfates in Soil as a screening test. 100ml of DI water was added to 5 g of soil and shaken vigorously for one minute. Immediately after shaking the conductivity was measure. The solution was then left to sit for 12 h, after which it was shaken again for one minute and then measured for conductivity. If the conductivity of either reading was above 238 μS or the conductivity of the second reading was more than 50 μS the soil would then be tested for SO_4 assessment using the TEX-145-E method (TexDOT 2005b).

2.3 Natural Sources of Sulfate in Ohio

Sulfur, as sulfide (S^{2-}) and sulfate (SO_4^{2-}), both naturally occur in the earths subsurface. Sulfur is the 7th most abundant element in the earth's core and within sedimentary rocks, the global total mass of sulfur is estimated at 1.4×10^{24} g (Rickard

2012). Within these sedimentary rocks shales contain over half of all sulfur deposit and the global total mass of evaporates has been conservatively estimated at 1.2 x 10^{21} g (Rickard 2012). Within Ohio surface soils, sulfur bearing mineral have naturally originate from bedrock, glacial deposition and groundwater movement.

2.3.1 Bedrock

The parent material of surficial soils in Ohio is primarily weathered sedimentary bedrock and glacial till. Natural sources of sulfate these soils can be attributed to Silurian bedrock, containing calcium sulfate evaporates, and Devonian bedrock with sulfide mineral pyrite. Silurian bedrock underlies most of Ohio and is the uppermost bedrock in northwestern Ohio, comprising the Findlay Arch (Figure 2). Silurian bedrock formed over 438 million years ago as sea level rose depositing subtropical carbonate materials and evaporates: halite, gypsum and anhydrite (Coogan 1996). Salina group, within the Silurian bedrock formation, is capped with a thick layer of anhydrite (Tomastik 1997). Gypsum was found in immense bed and nodules in Silurian rocks of Erie, Lucas, Ottawa, Sandusky, Wood and Wyandot Counties (Wolfe 2001). In Sandusky County, drill well investigations revealed gypsum beds as thick as 9 feet at a depth of 272 feet (Jones 1935). Gypsum deposits were abundant enough to support 180 years of mining in the Ottawa County, Ohio. In this region mines were active until 2001 and an estimated 28 million tons of gypsum had been produced in Ohio as of 2000 (Wolfe 2001). Coogan (1996) identified the two bands of Devonian bedrock that flank the Silurian bedrock of the Findlay arch to the northwest and southeast (Figure 2).

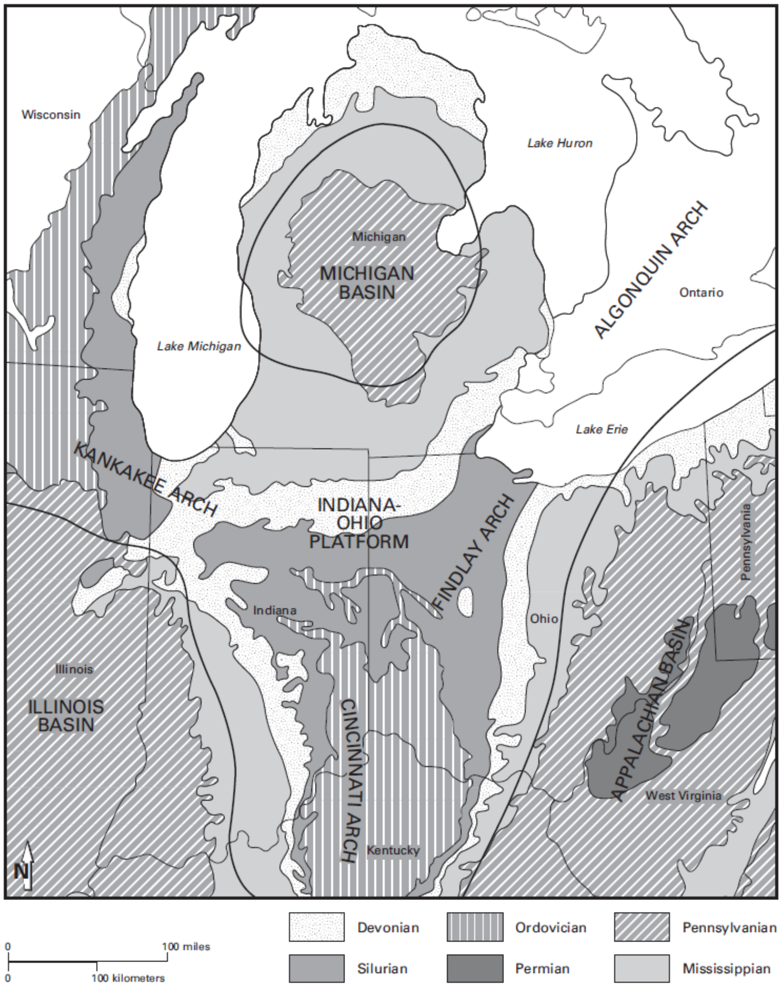


Figure 2 Map of Ohio Bedrock and Geologic Features (Coogan 1996)

The primary band enters the Ohio in the south at the Ohio River in Adams County, continues north to Erie County and then follows Lake Erie east exiting the state in Ashtabula County. Devonian shale contains the sulfur bearing mineral pyrite (FeS_2) (Kane et al., 1990; Schieber & Riciputi 2004; Rimmer et al., 2004; Angle et al., 2005; Leventhal & Hosterman 1982). Oxidation of FeS_2 in soils can occur naturally due to exposure to oxygen (O_2) either from water or air and the rate of oxidation is influence by: pH, microorganisms, organic acids and Fe_3^+ (Kendelewicz et al., 2004). Devonian bedrock has been divided into an upper and lower layer. The Upper Devonian layer is further segmented into the Huron, Chagrin and Cleveland Shale, collectively known as the Ohio Shale. Both the Huron and Cleveland Shales contain significant pyrite deposits (Hoover 1978). Although FeS_2 does not directly contribute to sulfate induced heave, its presence should be considered when in planning and construction lime stabilization projects as oxidation of FeS_2 oxidation forms SO_4.

2.3.2 Glacial Till

Glacial activity scoured the existing surface material of nearly 2/3 of Ohio (Figure 3, ODNR 2014). As glaciers receded, rock, gravel, sand, silt and clay materials, also known as glacial till, were deposited. Sulfates have been identified in various types of glacial till in northern Ohio. Significant amounts of Celestine, $SrSO_4$, as well as calcium sulfates and pyrite have been found glacial soils of northwestern Ohio along the Findlay arch (Stueber

Figure 3 Glaciated Regions of Ohio (ODNR 2014)

et al., 1972). Ashtabula till near IR-90 in Euclid, east of Cleveland contained abundant gypsum crystal at depths of 4 meters (Szabo et al., 1988). Sulfates have been identified in lake or lacustrine deposit (Figure 4) in northeast Ohio (Wolfe 2001) such as the Cuyahoga Valley National Park (Szabo 1986). Fractures within glacial till have also been reported as a site for deposit of gypsum. Till fractures although under acknowledged in geologic literature of Ohio have been found in the majority of counties within glaciated zone (Brockman & Szabo 2006). The frequency of till fractures decreased with depth and are typically not found in soil at depths between 10-20 feet (Brockman & Szabo 2006). Composition of material within till fractures varies based on geochemistry of surrounding soils. Fractures have been found to be coated or filled with: calcite, Fe, Mg, gypsum, sand and silt (Brockman & Szabo 2006). Oxidation of Fe created stains along fractures making them more visible (Szabo 1988). Evidence of water movement through till fractures has been provided by formation of gypsum crystals 4 cm long at depths of 4 meters in Summit County (Szabo 2006).

2.3.3 Groundwater

Another potential source of natural sulfate is groundwater. Although groundwater movement could transport sulfates, the velocity of groundwater is very slow limiting the ability of sulfate migration. The physical characteristic like particle size and void space of the ground material controls the ability of soil to transmit water, which is measured as hydraulic conductivity, k (Table 3, Das 2010).

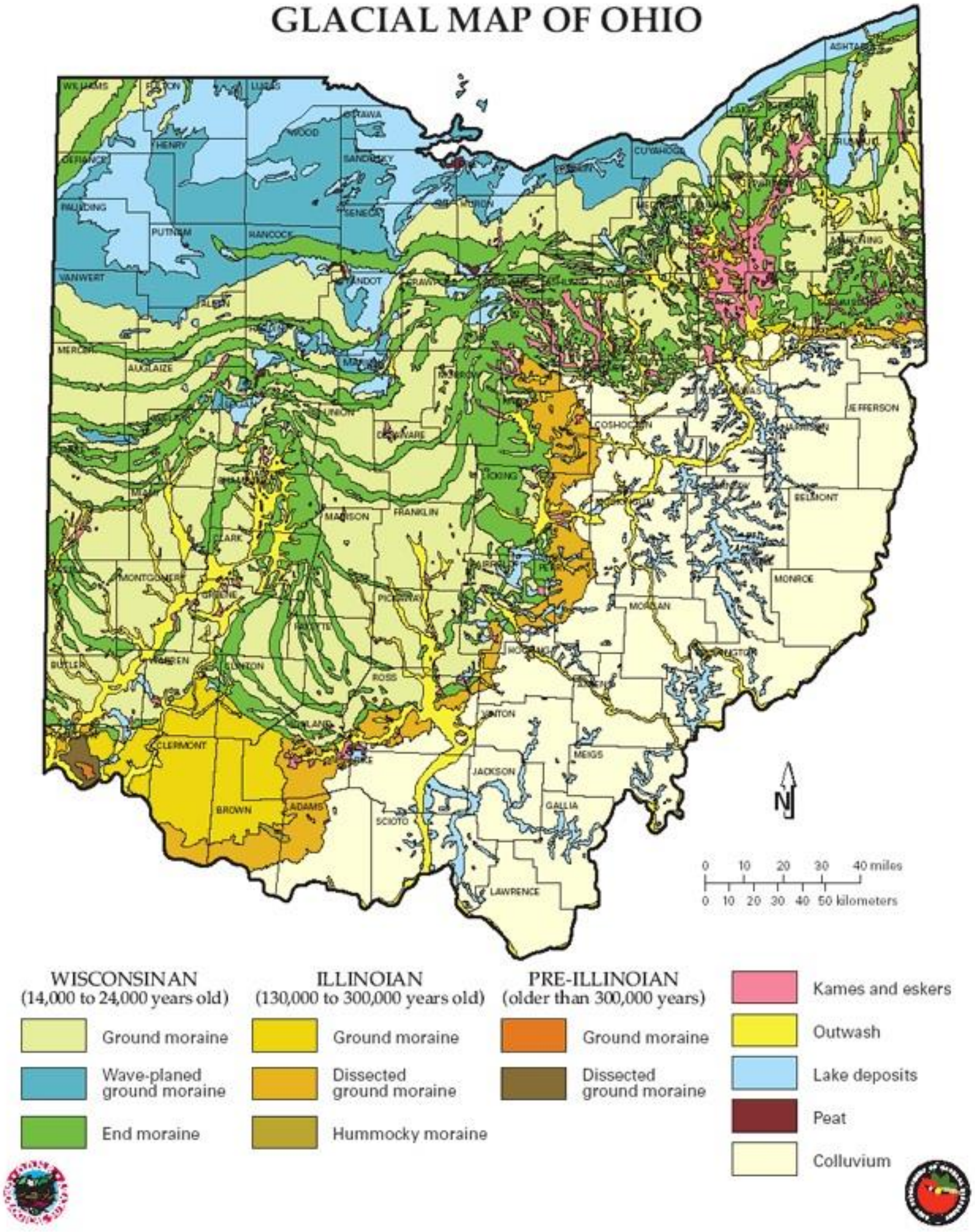
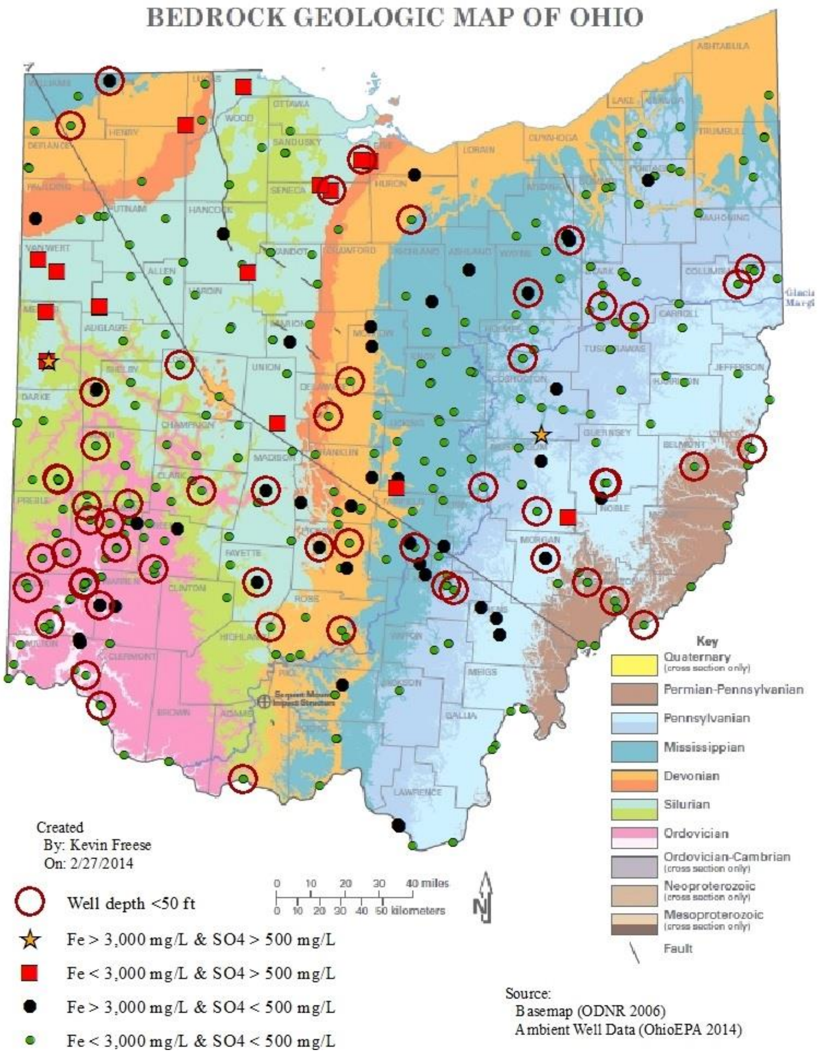


Figure 4 Glacial Map of Ohio (ODNR 2005)

Table 3 Typical Values of Hydraulic Conductivity for Saturated Soils (adapted from Das 2010)

	k	
Soil Type	cm/sec	ft/year
Clean gravel	100 - 1.0	100,000,000 - 1,000,000
Course sand	1.0 - 0.01	1,000,000 - 10,000
Fine Sand	0.01 - 0.001	10,000 - 1,000
Silty Clay	0.001 - 0.00001	1000 - 10
Clay	<0.000001	<1.0

Groundwater bedrock/soil contact allows sulfates to enter groundwater naturally via two chemical processes, dissolution and oxidation. The moderate solubility of gypsum at 2.58 g/L (Perry & Green 2008) allows for the dissolution of gypsum and release of both Ca and SO_4 ions into groundwater. Gypsum within an aquifer has been recognized as the primary source of increased down gradient sulfate concentration in groundwater (Rye 1981; Derring 1983). A survey of 100 fifty foot deep wells was conducted to analyze the groundwater geochemistry of northwest Ohio. Groundwater passing through regions of relatively pure dolomite contained Ca, Mg and bicarbonate. Whereas results showed sulfate concentrations of groundwater higher approaching Lake Erie and the greatest concentrations coincided with known gypsum, anhydrite and celestite deposits within the region (Deering 1983). The Ohio Environmental Protection agency (OEPA) provides access to ambient well chemical analysis. The distribution of most recent results for measured SO_4 and Fe from these wells was mapped using ArcGIS (Figure 5). Differences in SO_4 concentrations were divided into < 500 mg/L or > 500 mg/L and Fe was divided into <3,000 mg/L or >3,000 mg/L. The trends suggested by Deering appear to be present in current groundwater. Higher sulfate concentrations were recognized in northwest Ohio groundwater. Carbonate aquifers of northwest Ohio comprise the greatest number of public water systems categorized by the OEPA as on the watch list or impaired due to sulfate concentration (OhioEPA 2014). Again the source of sulfate cited is evaporate content in soil, namely the Salina formation. The second chemical method for sulfate to enter groundwater is the oxidation of pyrite. Investigation into the geochemical evolution of groundwater in the great lakes region found that oxygen rich groundwaters recharge confined aquifers and can cause the oxidation of soils containing pyrite (McIntosh & Walter 2006). The impact SO_4 rich groundwater has on elevation of SO_4 concentrations is


BEDROCK GEOLOGIC MAP OF OHIO

Created
By: Kevin Freese
On: 2/27/2014

Source:
Basemap (ODNR 2006)
Ambient Well Data (OhioEPA 2014)

Figure 5 Soluble SO4 and Fe Distribution in Ambient Wells limited and may only exist in regions where the groundwater table is at very shallow depths. Therefore well depth was indicated within the ambient well map (Figure 5) as either less than 25 feet (well symbols encircle) or greater than 25 feet (not encircled). Additionally groundwater of Ohio containing acidic H_2S (Kostelnick 1981; Schmidt 1982; Raab 1986), promote the dissolution of limestone which supplies Ca into the reaction with SO_4 forming gypsum (Harris et al., 2004).

2.4 Anthropogenic Sources of Sulfate in Ohio Surficial Soils

Many of the natural sources of sulfate in Ohio are well below surface which could limit their ability to create deposits of gypsum in surficial soils. There are several anthropogenic activities that introduce sulfate into soil. The effects of which have been noticed in increase sulfate concentrations of glacial cores (Weiss et al., 1975). Among the most significant sources in the Ohio Valley Region is sulfur dioxide (SO_2) emission from coal fired power plants. Sulfur is a common component of coal with standards for total sulfur content in coal ranging from 0.59-3.18% (Golighty et al., 1989) which when burned releases sulfur into the air as SO_2. The USEPA estimates 66% of SO_2 emissions are derived from coal fired power plants (Nemalapuri 2013). SO_2 emissions have the greatest concentration at altitudes less than 2000m (Hennigan et al., 2006) with emission migration controlled by wind direction (Husain et al., 1984) and other meteorological factors such as barometric pressure and clouds (Carmichael et al., 1990). According to the US Energy Information Administration (USEIA) Ohio is the 10th largest coal producing state, but the 3rd largest coal consuming state with 90% used for coal power plants (USEIA 2013). There are nearly 30 coal fired power plants in Ohio with the majority of plant located along the Ohio River and Lake Erie (Figure 6). Ohio has historically led the country in SO_2

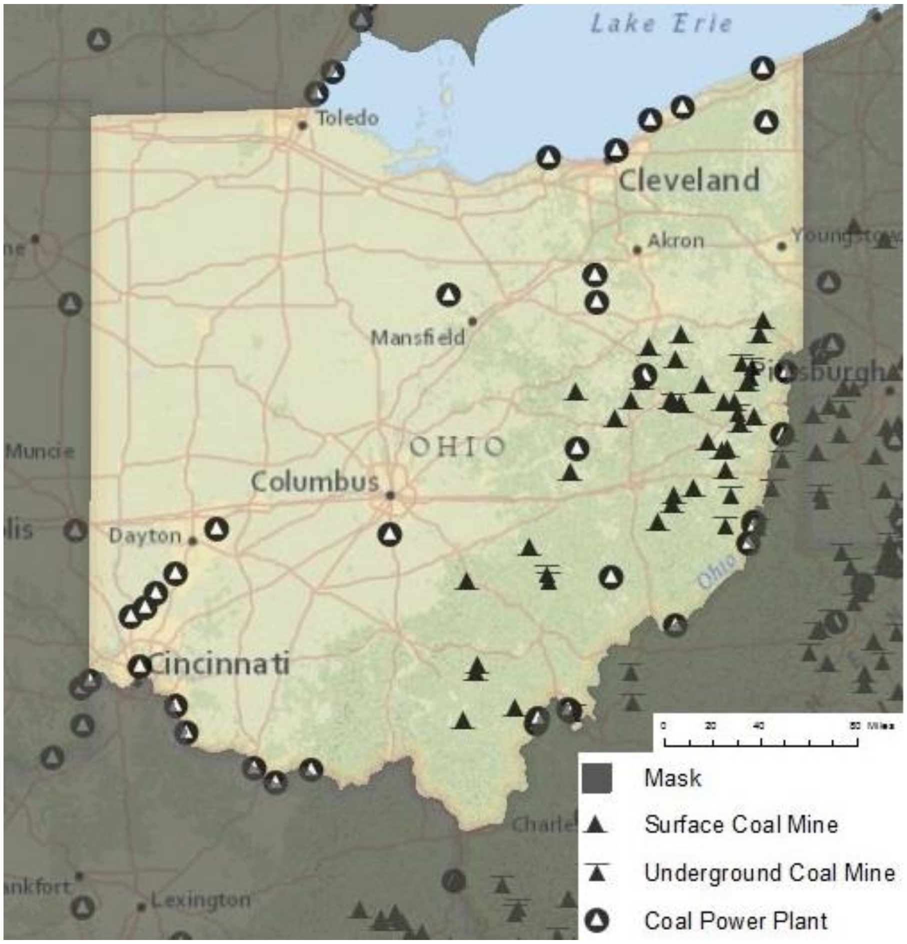


Figure 6 Location of Coal Fire Power Plant and Coal Mines in Ohio (EIA 2014)

emissions with 2.2 million tons released in 1990 (USEPA 2008). Regulations on the level of SO_2 emissions have reduced SO_2 levels in the US (Figure 7) (Stern 2006) and especially Ohio (Holland et al., 1998; Shannon 1999: Lynch et al., 2000). However as of 2010, Ohio was still the highest ranked state in SO_2 emissions at 610 thousand metric tons (USEIA 2012). The USEPA lists four sites in Ohio in non-attainment of SO_2 1-hour maximum emissions rate of 75 parts per billion (ppb): Lake County, Clermont County, Steubenville County and Washington & Morgan Counties. Emissions react with oxygen (O_2) and water

(H_2O) to form sulfuric acid (H_2SO_4) and falls to the ground as dry deposition in the form of dust, possibly forming gypsum (Mori et al., 1998), or smoke and wet deposition in wet climates as acid rain or snow (Stein & Lamb 2000; White et al., 2013). A 2006 study examined the effects of season, summer or winter, and demography, urban or rural, in the

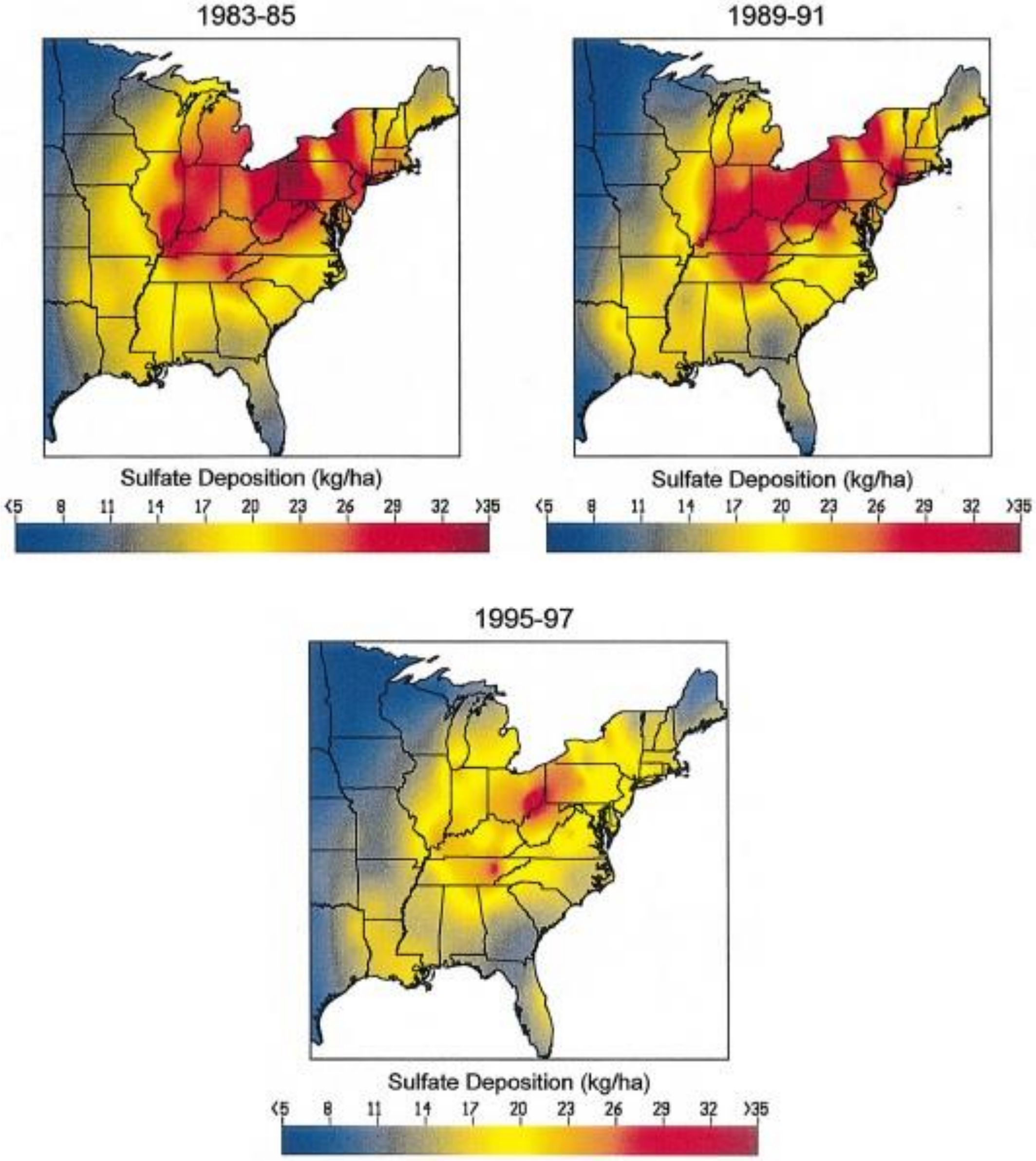


Figure 7 Ohio River Valley hotspot for SO2 emissions and reduction in SO2 emissions since CAAA of 1990 (Lynch et al., 2000)

upper Midwestern US on sulfate loading rates. Results of sulfate concentration for Cleveland, Ohio were reported at a year round average concentration of 4.9 $\mu g/m^3$ with average concentrations of 6.3 $\mu g/m^3$ and 3.8 $\mu g/m^3$ for the summer and winter respectively (Zhao et al., 2007).

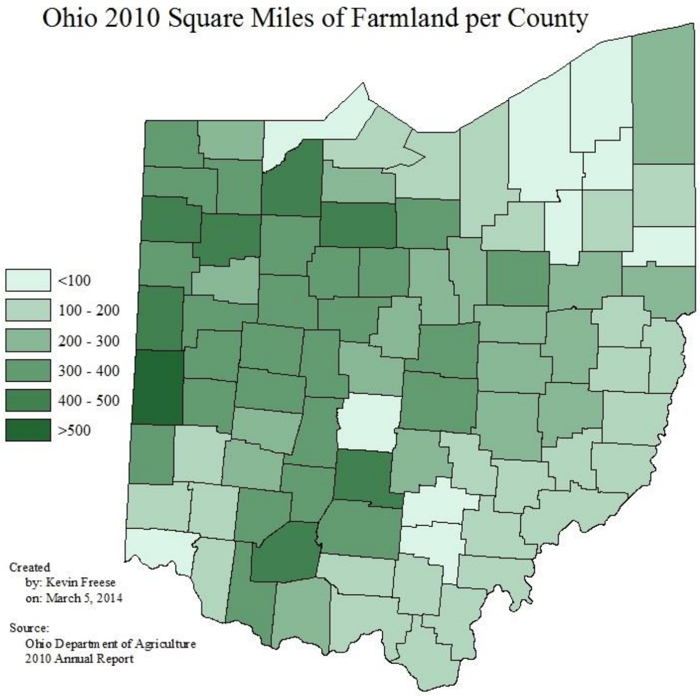
Sulfate bearing minerals have been applied directly to the soil as gypsum has several benefits to agriculture. Application provides both Ca and S, secondary plant nutrients, mitigates Al plant toxicity and improves water infiltration. FGD sources of gypsum have added benefits of greater $CaSO_4{\cdot}H_20$ purity (Lee et al., 2007), reduced grain size (Table 4), lower cost (Chen & Dick 2011) and potential for reduction in phosphorus (P) runoff (Clark et al., 2001). The reduction of SO_2 emissions resulting from the Clean Air Act reduced the amount of sulfur deposited onto farmland providing a desire for application of S-bearing fertilizers (Chen & Dick 2012). Farmlands in Ohio have been used as study areas for the effectiveness of FDG as a soil amendment. Crawford County

Table 4 Comparison of FGD and mined gypsum used as soil amendment (Chen & Dick 2012)

Property	Unit	FGD Gypsum	Mined Gypsum
Minerals Present		Gypsum, Quartz	Gypsum, Quartz, Dolomite
Water content	%	5.5	0.38
$CaSO_4{\cdot}2H_2O$	%	99.6	87.1
Insoluble residue	%	0.4	13
Particle size			
> 250 µm	%	0.14	100
150-250 µm	%	3.2	0
105-150 µm	%	33	0
74-105 µm	%	33	0
< 74 µm	%	31	0

test site Research site in Crawford County with doses of 1.1 and 2.2 Mg/hectacre (ha) applied to a soybean/corn crop rotated field. Researchers found FGD mitigated Al toxicity without mechanical mixing (Lee et al., 2007). FGD application was examined at an additional site in Ohio with a dose of 20 Mg/ha. This dosage was higher than typically recommended with researchers concluding FGD would not have significant impact on trace metals in soils when recommended dosages are used (Chen et al., 2014). Effects of FGD or mined gypsum application on sulfate concentration along farmland drainage areas could not be identified but could potentially be a source of higher SO_4 concentration along ditches into which agricultural runoff empties. Agricultural activities are greater in northwestern and midwestern Ohio (Figures 8 and 9). Additional agricultural sources of sulfate are decay of plant material and application of manure as a fertilizer (Zhao 2007).

In addition to burning, sulfur in coal can lead to increased sulfate concentration in soils through acid mine drainage (AMD) which occurs when sulfide bearing materials commonly pyrite, are exposed to oxygen and water (Akcil & Koldas 2006). Residual coal tailings and exposed bedrock adjacent to mined coal deposits contain pyrite. Mining activities expose pyrite to oxygen and water causing oxidation and formation of sulfuric acid (H_2S) which then seeps from mines into local stream and lakes (Sams & Beer 2000). The mining activities in southeastern Ohio have led to AMD contamination of numerous watersheds (Figure 10, ODNR 2002). One method of neutralizing the acidity of AMD is

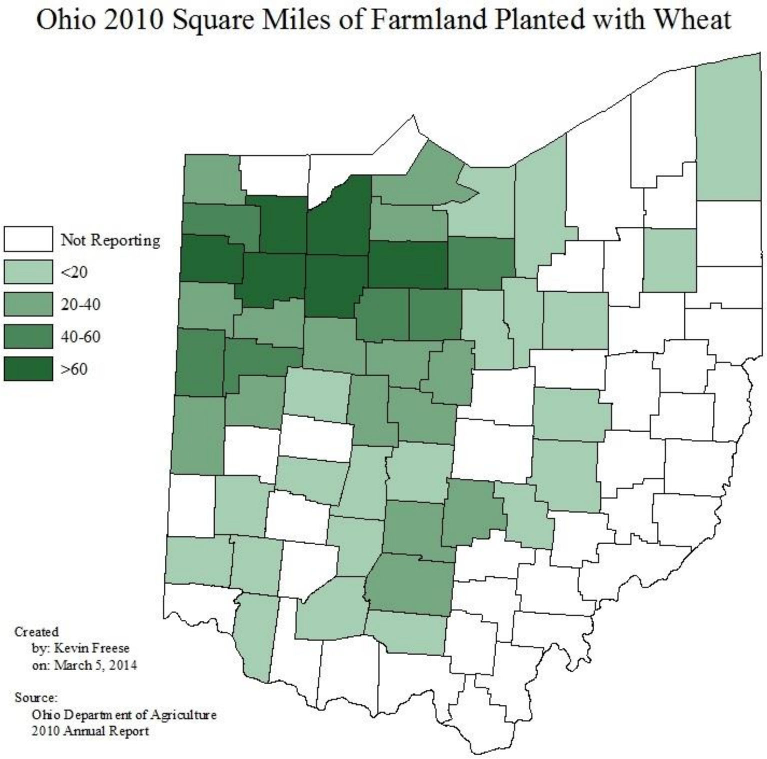


Ohio 2010 Square Miles of Farmland per County

Created
by: Kevin Freese
on: March 5, 2014

Source:
Ohio Department of Agriculture
2010 Annual Report

Figure 8 Increased agriculture in northwest and midwest Ohio.

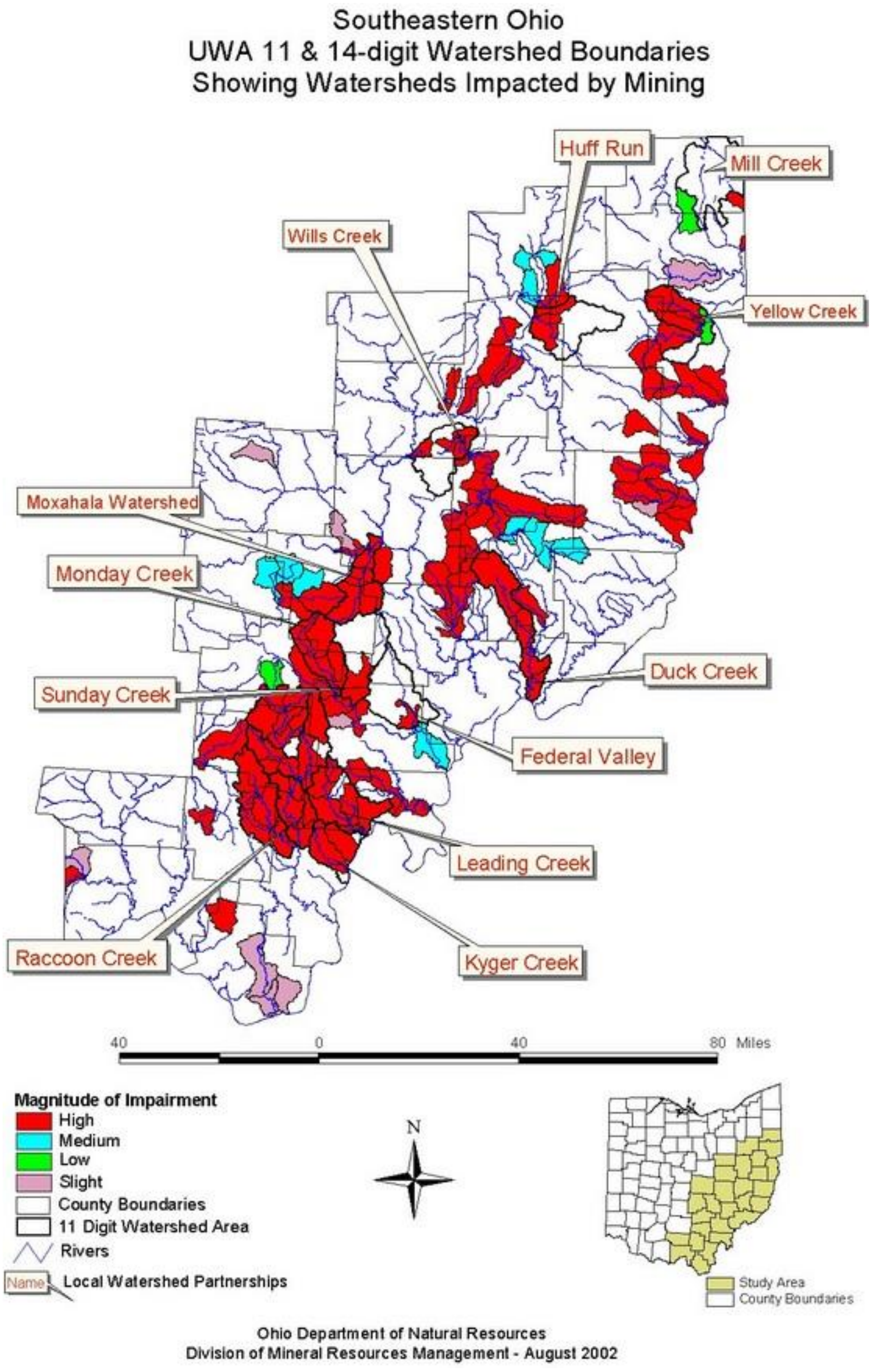


Ohio 2010 Square Miles of Farmland Planted with Wheat

Created
by: Kevin Freese
on: March 5, 2014

Source:
Ohio Department of Agriculture
2010 Annual Report

Figure 9 Ohio farms producing wheat concentrated in the northwest part of the state



Southeastern Ohio
UWA 11 & 14-digit Watershed Boundaries
Showing Watersheds Impacted by Mining

Ohio Department of Natural Resources
Division of Mineral Resources Management - August 2002

Figure 10 Mining impacted watersheds in southeast Ohio (ODNR 2002).

additions of limestone (Foos 1997) which could cause the formation of anhydrite (Yanful & Orlandea 2000).

$$\frac{1}{2}Fe_2(SO_4)_3 + CaCO_3 \rightarrow \frac{2}{3}Fe(OH)_3 + CO_2 + CaSO_4 \qquad \text{(eq. 8)}$$

Another concern with regards to AMD is higher potential levels of soluble sulfate. The levels of soluble sulfate from gypsum are limited by the solubility of gypsum at 2.58g/L. Soluble sulfate concentrations have been reported much high in AMD affected waters at 2.7 g/L (Yanful & Orlandea 2000). The use of calcium sulfite ($CaSO_3$) in the form of flue gas desulfurization (FGD) byproducts has also been studied as a treatment of coal mine spoils and was found to be ineffective after 13 weeks due to O_2 availability. Recommended modification was to bury the coal mine spoils and FGD containing $CaSO_3$ underground (Hao & Dick 2000) which would create higher concentrations of sulfate in soils. Additionally, others have reported the formation of ettringite in minespoil reclamation studies using FGD (Stehouwer et al., 1995).

The USEPA provides requires industry to report spills of toxic chemicals. The compilation of these reports is provided in the EPS's toxic release inventory (TRI). As of 2011, there were four sulfur bearing chemicals within the TRI for Ohio: sulfuric acid, carbon disulfide, carbonyl sulfide and dimethyl sulfate (USEPA 2012). TRI data from 2011 for Ohio show that sulfuric acid (Table 5) and carbonyl sulfide are the greatest S-bearing minerals released in Ohio (Table 6). Releases were greatest in Ashtabula accounting for over a quarter of the S-bearing minerals in the state. The vast majority, 99.2%, of these releases was in the form of carbonyl sulfide, over 2,400 tons released Cristal USA Inc. a titanium dioxide manufacturer. Twenty eight counties in Ohio had reported releases in the 2011 TRI with a total of nearly 9000 tons of S-bearing minerals released (Figure 11).

Table 5 2010 Toxic Release Inventory S-bearing minerals released

2011 Ohio TRI Data	Sulfuric Acid	Carbon Disulfide	Carbonyl Sulfide	Dimethyl Sulfate
Counties reported release	25	8	6	3
Total amount released (ton)	6,140	186	2,615	0.023
Percent of TRI S-bearing (%)	68.7%	2.1%	29.3%	0.00025%

Table 6 TRI reported top ten Ohio counties releasing Sulfuric Acid

County	Sulfuric Acid Released (Ton)	County	Sulfuric Acid Released (Ton)
Adams	915	Jefferson	780
Clermont	1,125	Lorain	122
Coshocton	240	Lucas	199
Gallia	992	Ross	160
Hamilton	788	Washington	497

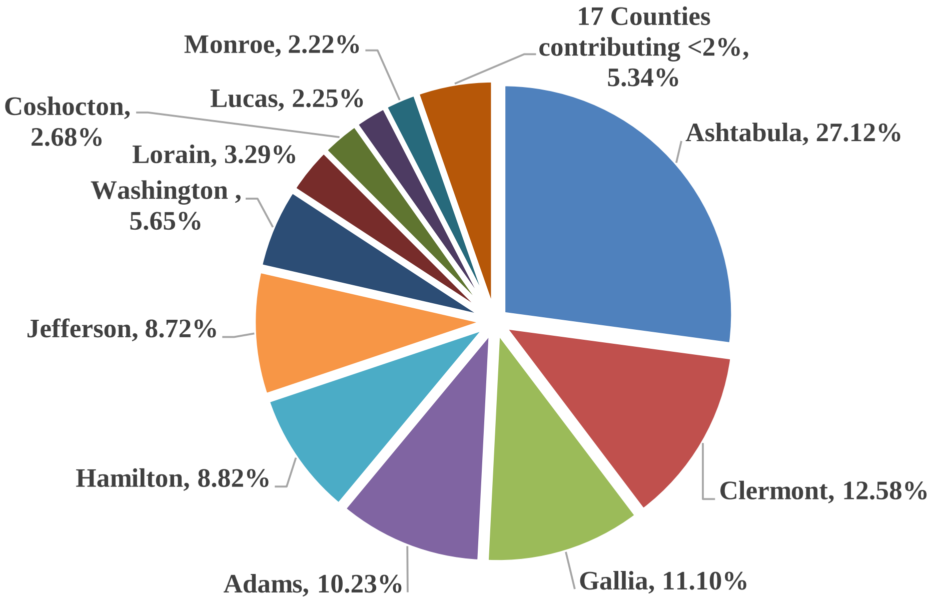


Figure 11 Distribution of total S-bearing TRI releases throughout the state of Ohio in 2011. 17 counties contributing <2% from highest to lowest % released are: Ross; Lake; Wayne; Trumbull; Butler; Wood; Montgomery; Pike; Allen;

Tuscarawas; Cuyahoga; Pickaway; Ottawa; Columbiana; Guernsey; Defiance; Stark.

Another potential anthropogenic source of SO_4 in Ohio soils, especially near roadways is the sodium chloride (NaCl) used as a deicing agent. Sulfate has been reported as the greatest impurity in sodium chloride road salt (Granato 1996). ODOT averages use of 300,000 to 900,000 tons of salt for deicing per year (ODOT 2011). Highest snowfall levels are within the Lake Erie Snowbelt in northeast Ohio (Figure 12).

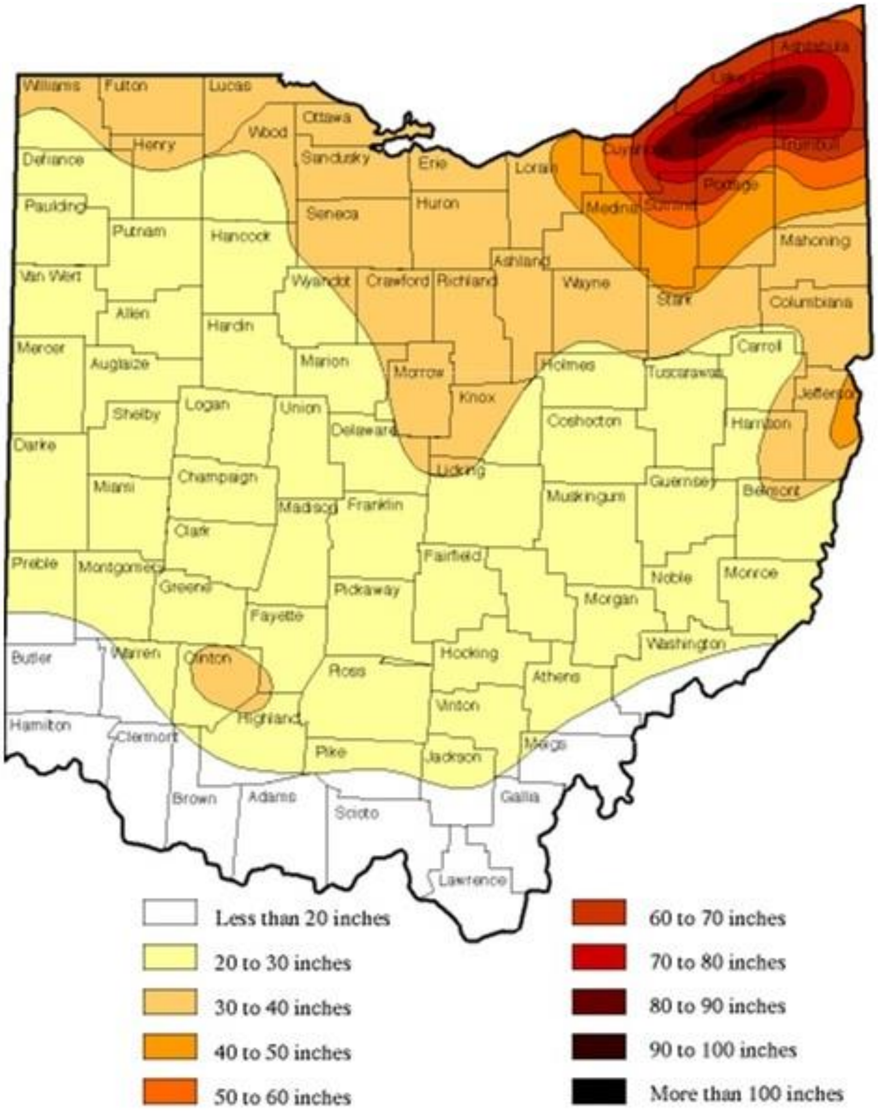


Figure 12 Annual snowfall levels in Ohio (ODOT 2011)

Chromite ore processing residue (COPR) is a carcinogenic byproduct of industrial chromium manufacturing. A high lime process of heating chromium ore in a rotary kiln at temperatures of approximately 1200ºC (Moon et al., 2007) has been used to extract chromate. Although this process has not been used in most of the western world since the late 1960's (Geelhoed et al., 2003) the residue, which contains 2-7% chromium (Burke et al., 1991) has been used as fill material (Dermatas et al., 2006). Many strategies for remediation of COPR involve addition of Sulfur (S) bearing minerals (Geelhoed et al., 2003; Dermatas et al., 2006; Graham et al., 2006; Wazne et al., 2007; Moon et al., 2008). The Diamond Shamrock Company in Lake County, Ohio was in operation in Painesville from 1912-1977 with the COPR landfilled on site (USEPA 2012). This material, due to its proximity to the SR-2 project in Lake County, was initially suspected as a SO_4 source in the region.

CHAPTER III

EXPERIMENTAL METHODS

3.1 Soil Preparation

Soils analyzed arrived in various forms. The majority of soil samples had already been tested for soluble SO_4 and therefore already ground. These samples were only subjected to passing a 425 μm (No. 40) sieve. However a number of samples (Paulding Franklin County cores and 2011/2012 soil borings) arrived as intact cores approximately 1.5 inches in diameter and of variable length ranging from ¾ of an inch to 3 inches. If there were numerous cores in a project, one could be crushed and ground for analysis. If there was only one core, or in some instances, only part of an intact core only XRD and post-XRD SO_4 analysis was conducted on these soils. The surface of these cores was scraped with a metal spatula until approximately 3 grams of soil was removed. This soil was then subjected to standard XRD and post XRD testing as described in sections 3.3 and 3.2.2 respectively. A few core samples from Paulding County contained visible crystals which were investigated for mineralogy. The crystals did not contain enough material for standard XRD analysis. The crystals were scraped ground and subjected to XRD analysis as described below in Section 3.3.2. Other samples arrived as bulk sample with no prior processing. These samples were allowed to dry overnight in an aluminum time and then crushed, ground and sieved (No. 40).

3.2 Soluble Sulfate Testing using TEX-145E

A HACH DR/890 handheld colorimeter was used to assess the sulfate concentration. A SulfaVer®4 sulfate reagent pillow purchased from HACH was used as the reactant. Sulfate concentrations were verified by duplicate analysis with a UV-Vis Spectrophotometer. Three 40 gram subsamples were measured to the nearest 0.1 gram. Twenty grams (to the nearest 0.1 gram) from each subsample was placed in a 500 ml bottle, 400 ml of distilled water was added and the bottle was shaken vigorously for one minute. The subsamples were incubated at room temperature for a minimum of 12 hours. After the specified waiting period, each subsample was shaken vigorously for one minute then vacuum filtered in a two stage process. The first step was a rough filtration using a Buchner funnel and Whatman No. 1 filter paper that would retain particles > 11 µm. The second filtration step was used 0.45 µm filter paper which removed turbidity remaining after the initial filtration step. Then 10 ml of the filtrate transferred to a clean sample vial.

After zeroing the calorimeter with the sample, the contents of the SulfaVer4 powder pillow (HACH chemical) was added to the sample vial, mixed and allowed to react for five minutes. After the reaction was complete, the sample vial was reinserted into the colorimeter chamber to read the soluble sulfate concentration. If the reading was above the colorimeter range (70 mg/l), additional filtrate was obtained and diluted with additional distilled water as needed until the sulfate reading was within range of the colorimeter.

3.2.1 Post-XRD soluble sulfate analysis

The XRD analysis utilized a set volume of soil for each analysis. As soil density varies by composition of clay and sand and other minerals, the mass of samples needed for each XRD analysis varied but was generally in the range of 1.5 to 2.0 grams. XRD is a non-destructive test thus the sulfate content would not have been altered. A post-soluble sulfate was conducted to correlate a specific sulfate level to the specific minerals identified. Modified TEX-145E post-XRD tests were conducted on 1.5±0.005 grams of soil. The distilled water to soil ratio was kept at 20:1. Therefore, 30 ml of distilled water was used for 1.5 g of soil. Some soils had a low density and if less than 1.5 grams of soil were available the soil was measured to the nearest 0.05 even gram, i.e., if only 1.367 grams of soil was used for XRD analysis, then 1.35±0.005 was measured and used for post-XRD testing with 27 ml of distilled water. After 24 hours of contact, the solution was mixed, filtered and then analyzed using the basic steps described in 4.1.1.

3.2.2 Verification of HACH DR 890 results via spectrophotometer

A Spectronic 20D+ Spectrophotometer (Thermo Scientific) was used as a secondary verification of the sulfate concentration obtained by the HACH DR 890. The Spectronic system is a traditional UV-visible spectrophotometer that operates in the 340-950 nm range. A calibration curve was made using a pure sulfate standard (1000 mg/l sulfate) diluted to 5 mg/l, 10 mg/l, 15 mg/l, and 20 mg/l of sulfate. The curve was then used to convert the absorbance units to mg/L SO_4.

3.2.3 Creation of User defined program for Colorimetric SO_4 concentration

HACH DR 890 procedures manual recommended creating a user-entered calibration curve to obtain most accurate results for SO_4 concentration (HACH 2013). Standards of 10 mg/l, 20 mg/l, 30 mg/l 40 mg/l, 50mg/l, 60 mg/l and 70 mg/l were created from a 1000 mg/l SO_4 standard. These standards and a blank sample of distilled water were used to create the user defined program 102 according to the method described in the HACH DR 890 instrument manual (HACH 2009).

3.3 XRD Analysis

Soil for XRD analysis was acquired from two sources: bulk soils or soil scraped directly from intact core samples. Samples were then ground using a ceramic mortar and pestle until the grain size was "flour-like". Samples were then packed into thin metal sample holders with outer diameter ~2.1", inner diameter of ~1.05" and depth of ~0.1" shown in Figure 13. Powdered soil samples were packed into disks using a small metal spatula, then compressed and excess soil removed using a glass slide. The glass slide was then placed over top of the soil sample and rotated with a slight amount of pressure to smooth the exposed soil sample surface (Figure 14).

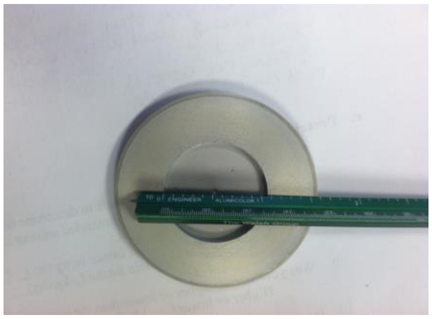


Figure 13 Metal XRD powder sample holder.

Figure 14 Packed XRD powder sample

Samples were then tested using an automated Phillips© XRG 3100 x-ray diffractometer equipped with a nickel filtered Cu Kα radiation at a generator tension of 40kV and generator current of 35mA. The angular range of tests was from 2.010° – 69.990° 2θ with a speed of 0.020° 2θ per second. Analysis of the resulting diffraction pattern was conducted using Phillips© PW Automated Powder Diffraction software version 3.6j. Diffractogram patterns were generated using the peak search program and likely minerals within samples were identified using the match pattern program within this software.

Each mineral has a pattern of intensity reading at particular angular degrees (2θ). The diffraction patterns for the sulfur/sulfate bearing minerals identified or investigated for this project are provided in Table 7. Specific minerals were identified by comparing diffractogram patterns for each sample with the mineral patterns of recommended minerals from the software match pattern. All samples were checked for gypsum as it is the most dominant sulfate-bearing mineral in natural soils. The most-probable minerals provided by the Phillips software were also compared to reference standards. The diffraction pattern of key minerals were also examined for certain samples even if the match pattern program failed to recommend these minerals. For example, ODOT officials asked that samples from the shoulder of MRW 71-3.17 be analyzed for the presence of halite due to concerns

Table 7. X-ray diffraction patterns of typical sulfate/sulfur bearing minerals

Gypsum		Anhydrite		Arcanite		Lanarkite		Pyrite		Ettringite	
2θ (°)	% Intensity	2θ (°)	% Intensity	2θ (°)	% Intensity	2θ (°)	% Intensity	2θ (°)	% Intensity	2θ (°)	% Intensity
20.82	100	25.47	100	30.82	100	26.67	100	28.74	100	9.09	100
11.72	88.21	25.47	98.76	29.84	72.12	30.15	75.56	56.75	84.74	15.78	46.33
29.29	73.3	31.37	60.16	31.04	63.39	31.4	35.64	37.38	69.33	18.88	24.87
31.25	52.99	40.83	38.88	29.77	32.66	44.13	24.34	47.82	67.94	32.26	24.06
33.59	36.27	38.66	33.96	43.54	28.5	30.21	23.43	41.1	27.8	22.92	20.93
16.61	26.11	48.75	27.77	37.17	27.41	20.03	18.42	64.84	20.27	22.92	16.9
36.38	23.16	55.79	27.63	21.37	26.49	31.19	17.69	33.31	17.96	34.99	15.94
43.5	17.65	36.33	13.95	23.8	17.83	14.31	16.77	59.52	11.74	40.85	14.87
48.22	17.29	43.41	12.23	40.53	15.95	13.91	16.66	50.92	9.62	34.99	14.21
23.56	15.37	41.33	12.21	40.94	14.56	36.27	15.29			25.62	13.52
50.61	15.27	52.31	10.57	26.35	12.58	49.27	15.17			17.83	11.76
48.72	13.69	52.33	10.25	21.27	12.48	39.93	15.02			40.85	11.59
36.03	12.46	62.28	9.86	48.22	12.35	36.97	14.07			27.52	10.32
23.57	12.01	45.46	9.02	37.94	11.5	55.12	12.93			24.7	8.41
51.6	10.6	22.94	8.87	35.96	11.31	24.04	12.58			41.94	8.22
36.74	7.16	46.87	6.36	55.08	10.56	53.08	11.82			9.98	7.81

about road salt contributing to sulfate. X-ray diffractogram patterns of post-stabilized soils from Lake and Paulding/Defiance Counties were specifically analyzed for ettringite.

3.3.1 Sample modification for analysis of intact cores crystals

The crystals in some cores were investigated for mineralogy by scraping off 0.1-0.3 grams of crystalline material. This material was then ground to a flour like grain size and placed onto a circular glass slide. Three to five drops acetone was applied to the slide to create a mud-like solution that was spread evenly across the surface. The acetone was allowed to evaporate, leaving a dry sample, followed by XRD analysis.

3.3.2 Acid wash procedure

Kota et al., (1996) reported difficulty in identifying ettringite when using XRD due to masking from calcite. They proposed acid washing soils samples prior to XRD scan to mitigate the masking effect. Four of the PAU-DEF Heave samples that tested highest in SO_4 were subjected to an acid wash prior to XRD analysis. Two grams off soil were placed to a 50 ml centrifuge test tube containing 40 ml of 2.1 M HCl. The solution was agitated gently for 15 minutes in a Lab-line Environmental Shaker. Then the solution was then centrifuged at 2500 rpm for another 15 minutes. The aqueous solution was decanted from the tube and the soil was allowed to dry over night at room temperature. After drying, the samples were ground to a flour like consistency and subjected to XRD analysis as described in section 4.2.1

3.3.3 Approach to XRD comparisons

The majority of the samples contained more than 3,000 mg/kg SO_4 were analyzed using XRD. An additional soil within each project that was well below 3,000 mg/kg SO_4

was tested using XRD. Comparison of x-ray diffractogram patterns between the soils with high and low SO_4 concentrations assisted to further identify potential sulfate sources.

3.4 Assessment of Total Metal Content in Soils

The soil metal concentrations were determined by the EPA 3050b acid digestion procedure (USEPA 1989) followed by analysis via ICP-OES. Two grams of air-dried soil was mixed with ten ml of 1:1 HNO_3 and the solution heated at 95^{o}C for 15 minutes. Five ml concentrated HNO_3 was then added to the solution and the mixture was refluxed for 30 minutes at 95^{o}C. The final volume was brought up to approximately five ml. Once the solution cooled, 25 ml of 30% H_2O_2 was added to the solution in one ml increments. Once the peroxide reaction was completed, five ml of concentrated HCL was added to the solution and the solution was refluxed for 15 minutes. Once cool, the solution was filtered through a Whatman NO.42 filter paper and diluted with DI water to make the total volume to 50 ml. The final solution was labeled and kept in the refrigerator until analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). The specific ICP-OES system used in this study was a Perkin Elmer Plasma400 ICP emission spectrometer, located in the Geochemistry Lab at the University of Akron Department of Geology and Environmental Sciences. It was operated following the user's manual. Standard solutions were prepared to calibrate ICP-OES using pure element solutions (~1000 µg target element/ml). Serial dilutions in distilled water were used to make mixed standard solutions that contained 5 mg/L, 10 mg/L or 20 mg/L each of Al, Cr, and Fe. The standard curves were used to convert the intensity to mg/L. The minimum detection limits of ICP-OES were 0.028 mg/L for Al, 0.015 mg/L for Fe, and 0.0071 mg/L for Cr.

3.5 Analysis of Herrick Road stabilized core sample mineralogy using scanning electron microscope and energy dispersive atomic X-ray spectrometry (EDAX)

Stabilized cores were processed and examined per ODOT technical liaison's recommendations. Upon delivery, the stabilized core samples contained visible amount of moisture. These soils were dried in an oven at approximately 125° Fahrenheit over a three day period. After samples were dry, approximately 3" was removed from the top of each core using a concrete saw. These three inch cylinders were then cut in half in the axial direction. The half cylinder core pieces were returned to the oven to dry for approximately 2 hours (Figure 15). Then the samples were inspected for white streaks in cracks along the cut surface. No streaks were found nor were cracks easily identified. White precipitate was collected from the top of cores 4 and 5 and transferred to glass jars for examination

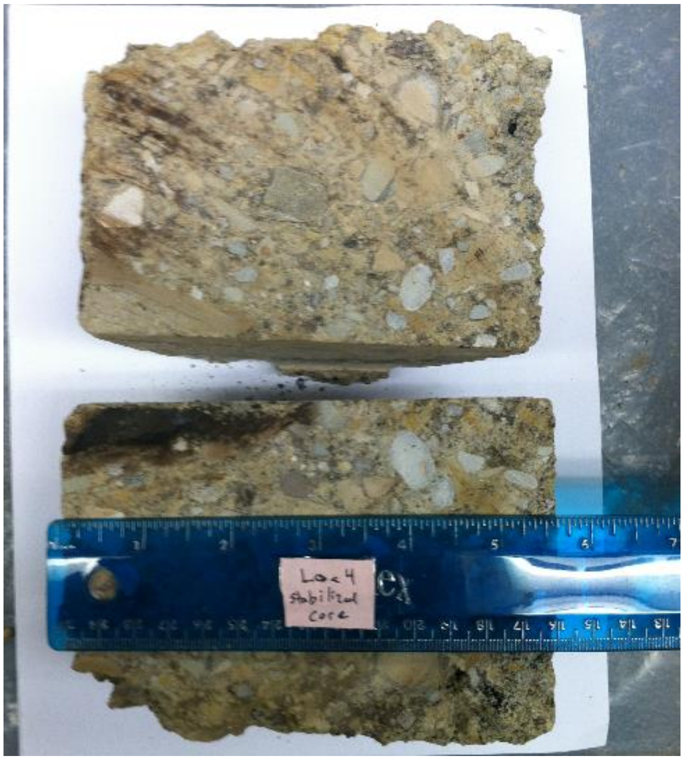


Figure 15 Inside Surface of Loc 4 Stabilized Core Inspected for White Precipitate.

with the scanning electron microscope (SEM) to determine if the precipitate could be ettringite. One of the half cut cylinder cores from each location was then smashed, ground and sieved for soluble sulfate, total metal and XRD testing. While handling the smashed pieces from Loc 3 stabilized core, white samples were selectively collected from the natural breaks, a likely location of ettringite formation, and also tested on the SEM. A FEI (formerly Philips) Quanta 200 Environmental Scanning Electron Microscope and attached EDS program were used.

3.6 Analysis of Quarry groundwater samples

A potential source of sulfate in the lime stabilization process was identified as potable water used during stabilization. Two 400 ml groundwater samples were collected by ODOT from Auglaize and Scott Quarries for analysis of SO_4 concentration and dissolved minerals. Sulfate analysis was conducted via colorimetry the same day water samples arrived. Approximately 50 ml of the solution was vacuum filtered through a 0.45 µm filter paper to remove any turbidity. Three separate 10 ml samples of the filtrate were measured, placed in a clean sample vials and used to zero calibrate the HACH DR 890 colorimeter. Then a SulfaVer®4 sulfate reagent pillow was added, the vial was capped and mixed by inverting the sample vial several times and the sample. After the 5 minute reaction time the SO_4 concentration was read. If the measured SO_4 concentration was above the manufacturer’s specified upper range for sulfate analysis of 75 mg/L, the sample was diluted by addition of equal amount of DI water and water sample. This process was repeated until the measured concentration was within range. The actual sulfate concentration for each sample was calculated as the product of the measured sulfate concentration and the dilution factor, 2^n, where n is the number of times the sample was diluted. The final average SO_4 concentration was recorded as the average of each actual SO_4 concentration for each sample. Approximately 210 ml of groundwater sample was placed into a 400 ml glass beaker. The sample was then heated at a gentle boil until completely evaporated, 3-4 hours leaving a white precipitate in the beaker. The beakers were allowed to cool overnight and the next day the precipitate was scraped out of the beaker using a metal spatula. The precipitate was then ground with a mortar and pestle and analyzed for mineralogy in a manner similar to section 3.2.2.

3.7 Methods for Investigation into Process Variable Affecting Measured Soluble Sulfate Concentration (SCC) using TEX-145E

The experiment was designed to determine if differences in SO_4 source, contact time, and solution extraction method lead to variability in detectable soil SO_4, and the degree of these differences. Oxidation of pyrite (FeS_2), present in Ohio bedrocks (Hoover 1960; Schieber & Riciputi 2004), results in the formation of both $FeSO_4 \cdot 7H_2O$ (Hu et al., 2006) and $CaSO_4 \cdot 2H_2O$ (Little & Nair 2009). Additionally, both $FeSO_4 \cdot 7H_2O$ (Dermatas et al., 2006) and $CaSO_4 \cdot 2H_2O$ (Wild et al., 1999) have been associated with ettringite formation and subsequent soil swell. For this study, technical grade crystalline $FeSO_4 \cdot 7H_2O$ and >99% pure powdered $CaSO_4 \cdot 2H_2O$ (Fisher Scientific, New Jersey, USA) were selected as the two SO_4 sources.

3.7.1 Soil Source, Characteristics and Spiking Method

The soil used was representative of a Northeastern Ohio soil. The bulk soil material was analyzed for texture (72% sand, 11.1% clay), pH (6.16±0.02), water content at field capacity (25.31± 1.63 cm^3/cm^3), cation exchange capacity (CEC, 9.18 meq/100 g), and organic matter content (1.84%) (Hwang & Cutright 2002). In addition, using three replications, equivalent to 20 g of oven-dried soil were analyzed by Tex145E method and yielded a background SSC of 80±30 mg/kg.

The soil material was air dried, crushed and passed through a 425-µm (No. 40) sieve. After thoroughly mixing the soil, six 500-g samples were weighed and assigned to different sulfate sources. One sample was spiked with 0.434 g and another with 4.34 g of $FeSO_4 \cdot 7H_2O$ to obtain sulfate concentrations of 300 and 3,000 mg/kg (equivalent to 0.15 and 1.5 g/500 g soil), respectively. The other four samples were spiked with 0.269, 2.688, 5.377, and 10.754 g of $CaSO_4 \cdot 2H_2O$ to obtain sulfate concentrations of 300, 3,000, 6,000 and 12,000 mg/kg (equivalent to 0.15, 1.5, 3.0, and 6.0 g/500 g soil), respectively.

Instead of adding theses amount of sulfate directly to the bulk soil material, a more homogeneous distribution was created by first mixing sulfates with water. Two soil materials were spiked 300 and 3,000 mg/kg sulfate by adding 0.434 and 4.34 g of $FeSO_4 \cdot 7H_2O$, respectively into 100 mL of DI water. After ten minutes of mixing the solution was then added to the 500-g bulk soil materials and mixed thoroughly with a metal spatula. The sample process was used for the bulk soil material spiked to 300 mg/kg sulfate by adding 0.269 g of $CaSO_4 \cdot 2H_2O$. However, the limited solubility of $CaSO_4 \cdot 2H_2O$, at 2.58 g/L (Perry & Green 2008), required extensive and impractical volumes of water: ~1, ~2 and ~4 L for complete dissolution of 2.688, 5.377 and 10.574 g of $CaSO_4 \cdot 2H_2O$, respectively. Therefore these amounts of $CaSO_4 \cdot 2H_2O$ were added to 200 mL of DI which after mixing was added to the 500-g bulk soil materials and thoroughly mixed with a metal spatula. Approximately 100 mL of DI was added the next day to each 500-g spiked soil, remixed with a metal spatula and allowed to dry (one to three days). After the mixing was complete and the samples had dried, they were ground using a mortar and pestle until the entire sample passed a 425-µm (No. 40) sieve.

3.7.2 Contact Times and Solution Extraction Methods Evaluated

Each sulfate source and concentration combination was investigated for soil to water contact times of 12, 15, 18, 21 and 24-h. Four different soil solution extraction methods were investigated for each contact time based on literature as well as feedback from field consultants. The first two methods did not mix the soil suspension for extraction after the specified contact time. For the first two methods, 25 mL of liquid from the top of the soil in the sample jar was collected directly by a pipet without disturbing the mixture and transferred to a 50-mL glass beaker. This solution was turbid, especially in test samples spiked to 300 mg/kg sulfate. Then, for the first method, two 10-mL subsamples were transferred to testing vials, one as the zero calibration sample and the other as the test sample. For the second method, the 25 mL of solution extract removed by pipet was filtered (0.45 µm) and two 10-mL samples, clear of turbidity, were transferred to test vials for analysis. The third and fourth methods remixed the soil suspension followed by partial filtration (~100 mL) where the fourth method filtered the entire (400 mL) of water. Here, filtration was completed in a two-step process. The first step was a rough filtration using a Buchner funnel and Whatman No. 1 filter paper that would retain particles > 11 µm, followed by filtration using a Milipore funnel and 0.45-µm filter paper. Filtrate from both full and partial filtration was clear of turbidity.

3.7.3 Statistical Analysis of Effects of Treatments

To ensure valid statistical and experimental methods triplicate measurements of each treatment combination were taken. Triplicate samples used in this experiment were three separate, randomly selected 20-g soil material samples for each treatment combination, i.e., spiked sulfate concentration and contact time. Results were analyzed individually (i.e., one sulfate level and source) with one-way general linear ANOVA model using the Minitab statistical package (Minitab 16). Tukey's pairwise comparison was used to assess differences between specific sulfate source, contact time and/or separation methods at a 95% confidence interval.

3.8 Statistical Analysis

Statistical analysis was conducted using Minitab® 16 statistical software package. Statistical significances, α, was set at 0.05. Microsoft 2013 Excel was used in analysis of regression. Due to the variability of the number of project set and soil factors per county, statistical models varied and details of the models are provided within the statistical analysis of each county.

CHAPTER IV

RESULTS FOR TEX-145E PROCESS VARIABLE ANALYSIS

Analysis of the process variable affecting measured soluble sulfate concentration (SSC) were examined as described in section 3.7. Solution extraction method was the dominant, statistically significant ($p\text{-value} < 0.05$) factor affecting the accuracy of colorimetric measured soluble SO_4 concentration for soils spiked to 300 and 3,000 mg/kg SO_4. (Figure 16 a & b) As anticipated, partial filtration and full filtration solution extraction methods yielded the most accurate soluble SO_4 concentration measurements. Directly pipetting samples after the specified contact times produced samples that were moderately to slightly turbid, which would adversely impact the ability of the colorimeter to provide an accurate measure of soluble SO_4 concentration. This was more pronounced with 300 mg/kg SO_4 samples (Figure 16 a)which remained very turbid after the specified contact time. Lower than expected soluble SO_4 concentrations were obtained using the method of pipet then filter method even when the samples were clear of turbidity. This could be due to the solution not being remixed again after the specified contact time.

As shown in Figure 16, separation methods that included direct pipetting and pipetting followed by filtration significantly ($p<0.05$) underestimated the SSC regardless of the specified contact time. For example, the measured SSC of the soil spiked with 300 mg/kg SO_4 as $FeSO_4{\cdot}7H_2O$ with a 12 h contact time was 80±28 mg/kg for direct pipet, 233±33 mg/kg for pipet then filter, 293±18 mg/kg for partial filtration and 286±19 mg/kg

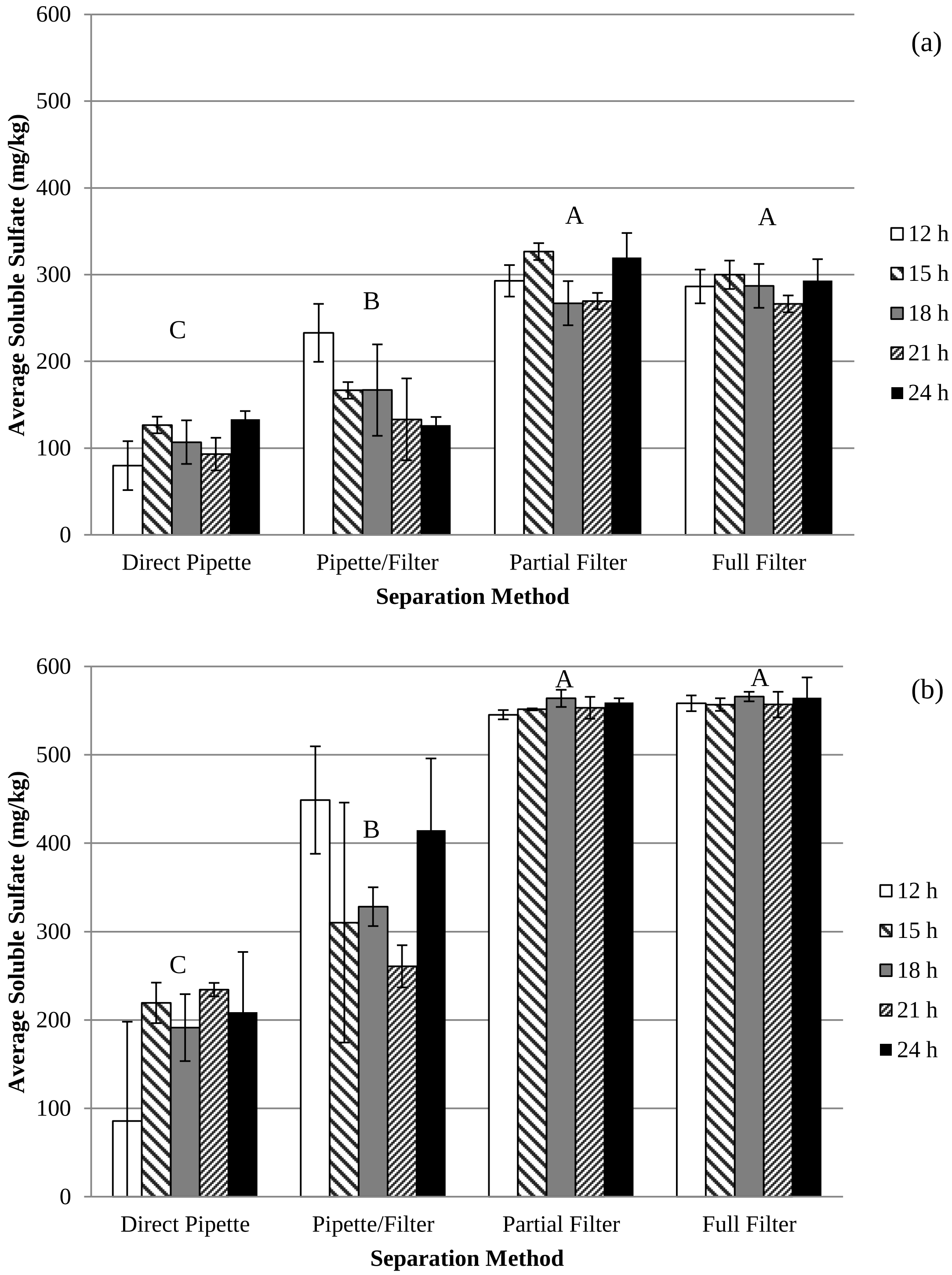
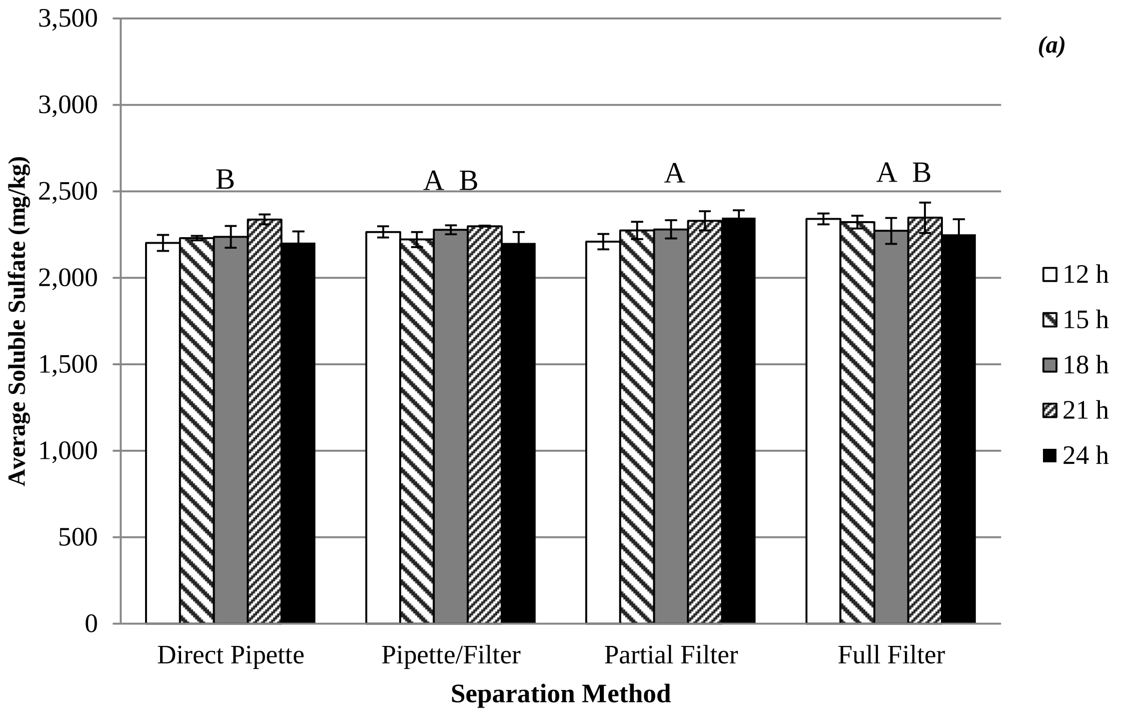


Figure 16 Comparison of average measured soluble sulfate concentration of 300 mg/kg spiked soils spiked with (a) FeSO4•7H2O or with (b) CaSO4•2H2O for different separation methods and contact times. n=3 replicates. Different letters (A, B, C) represent means that are statistically different at $p<0.05$.

for full filtration (Figure 16(*a*)). Soils spiked with $CaSO_4{\cdot}2H_2O$ to 300 mg/kg SO_4 followed the same pattern. However the results were less precise. At a 15 h contact time the measured SSC of the soil spiked with 300 mg/kg SO_4 as $CaSO_4{\cdot}2H_2O$ was 219±136 mg/kg for direct pipet, 310±23 mg/kg for pipet then filter, 551±1 mg/kg for partial filtration and 557±7 mg/kg for full filtration (Figure 16(*b*)). Differences between 300 mg/kg $FeSO_4{\cdot}7H_2O$ and $CaSO_4{\cdot}2H_2O$ were attributed to localized low SO_4 levels during spiking. The solubility of $FeSO_4{\cdot}7H_2O$ is higher at, 480 g/L than $CaSO_4{\cdot}2H_2O$ at 2.58 g/L, at 20° C (Perry & Green 2008). Other researchers have reported substantial variations when SO_4 was added at low concentrations. For instance, Harris et al., (2011) reported inaccuracies of SO_4 measurements as high as 37.9% when SO_4 was amended at 280-760 mg/kg.

There was less difference in measured and theoretical SSC due to separation method for soils spiked to 3,000 mg/kg with $FeSO_4{\cdot}7H_2O$ across all five contact times. Partial filtration, full filtration and pipet followed by filtration showed no statistical difference in mean measured SSC ($p>0.05$). For example, the measured SSC of the 3,000 mg/kg SO_4 as $FeSO_4{\cdot}7H_2O$ with a 21 h contact time was 2,337±29 mg/kg for direct pipet, 2,298±3 mg/kg for pipet then filter, 2,329±55 mg/kg for partial filtration and 2,347±88 mg/kg for full filtration (Figure 17(*a*)). Results for the 3,000 mg/kg $CaSO_4{\cdot}2H_2O$ depicted a statistical difference between each separation method, with full filtration being the most accurate. At a 24 h contact time the measured SSC of the 3,000 mg/kg soil spiked with $CaSO_4{\cdot}2H_2O$ was 1,889±98 mg/kg for direct pipet, 2,162±189 mg/kg for pipet then filter, 2,767±39 mg/kg for partial filtration and 2,989±36 mg/kg for full filtration (Figure 17(*b*)).



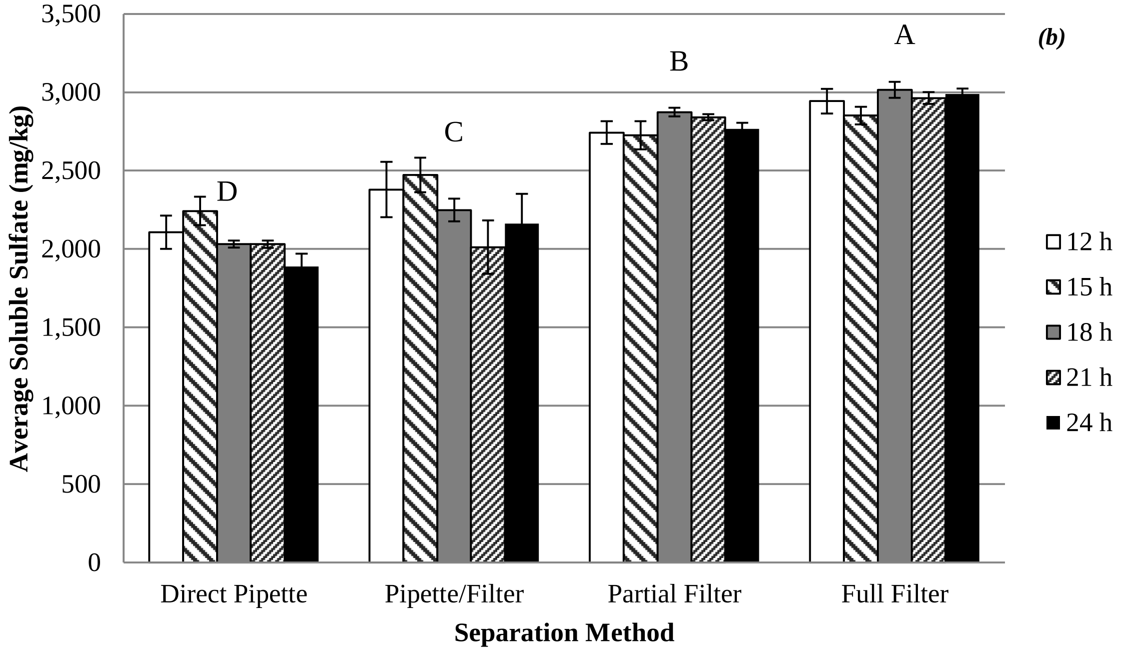


Figure 17 Comparison of average measured soluble sulfate concentration of 3,000 mg/kg soils spiked with (a) $FeSO_4 \cdot 7H_2O$ or with (b) $CaSO_4 \cdot 2H_2O$ for different separation methods and contact times. n=3 replicates. Different letters (A, B, C, D) represent means that are statistically different at $p<0.05$.

Across all separation methods, the spiked SO_4 concentrations and sources yielded very little statistical difference ($p>0.05$) in SSC measured after variable soil to water contact time. As shown in Figure 18(*a*), soils spiked with 300 mg/kg $FeSO_4{\cdot}7H_2O$ did indicate a statistical difference in average SSC at 12 and 15 h compared to 21 h. At 3,000 mg/kg SO_4 as $FeSO_4{\cdot}7H_2O$, there was only a significant difference between 21 h and 24 h. $CaSO_4{\cdot}2H_2O$ spiked soils indicated no statistical difference in average SSC for all five contact times, regardless of the concentration of SO_4 added (Figure 18(*b*)).

An additional test was conducted with $CaSO_4{\cdot}2H_2O$ at 6,000 mg/kg and 12,000 mg/kg to ascertain the impact of its limited solubility on accurate SO_4 measurement, as it is often the dominant SO_4 source associated with heave. Based on our earlier results the experiment was conducted with the partial filtration as the sole separation method. As shown in Figure 19, colorimetric testing of soluble SO_4 was accurate up to 6,000 mg/kg using partial filtration. The ability to accurately assess SSC up to this level was important as some states have acceptable risk thresholds 5,000-6,000 mg/kg (Little & Nair 2009). However the colorimetric method underestimated the SO_4 level when $CaSO_4{\cdot}2H_2O$ was spiked at 12,000 mg/kg. Other researchers have reported the overestimation of SSC with soils spiked with 10,000 mg/kg sodium sulfate ($NaSO_4$) (Talluri et al., 2012). The difference between overestimation of soil spiked with $NaSO_4$ and underestimation of soil spiked with $CaSO_4{\cdot}2H_2O$ in this study could be due to difference in solubility of Na_2SO_4 and $CaSO_4{\cdot}2H_2O$. Na_2SO_4 is more soluble at 407 g/L compared to $CaSO_4{\cdot}2H_2O$ at 2.58 g/L (Perry & Green 2008). $CaSO_4{\cdot}2H_2O$ is only partial soluble in water which may lead to soluble SO_4 measurements lower than actual SO_4 concentration (Oldecop & Alonso 2012; Visconti et al., 2010). Additionally, several successive dilutions were needed to

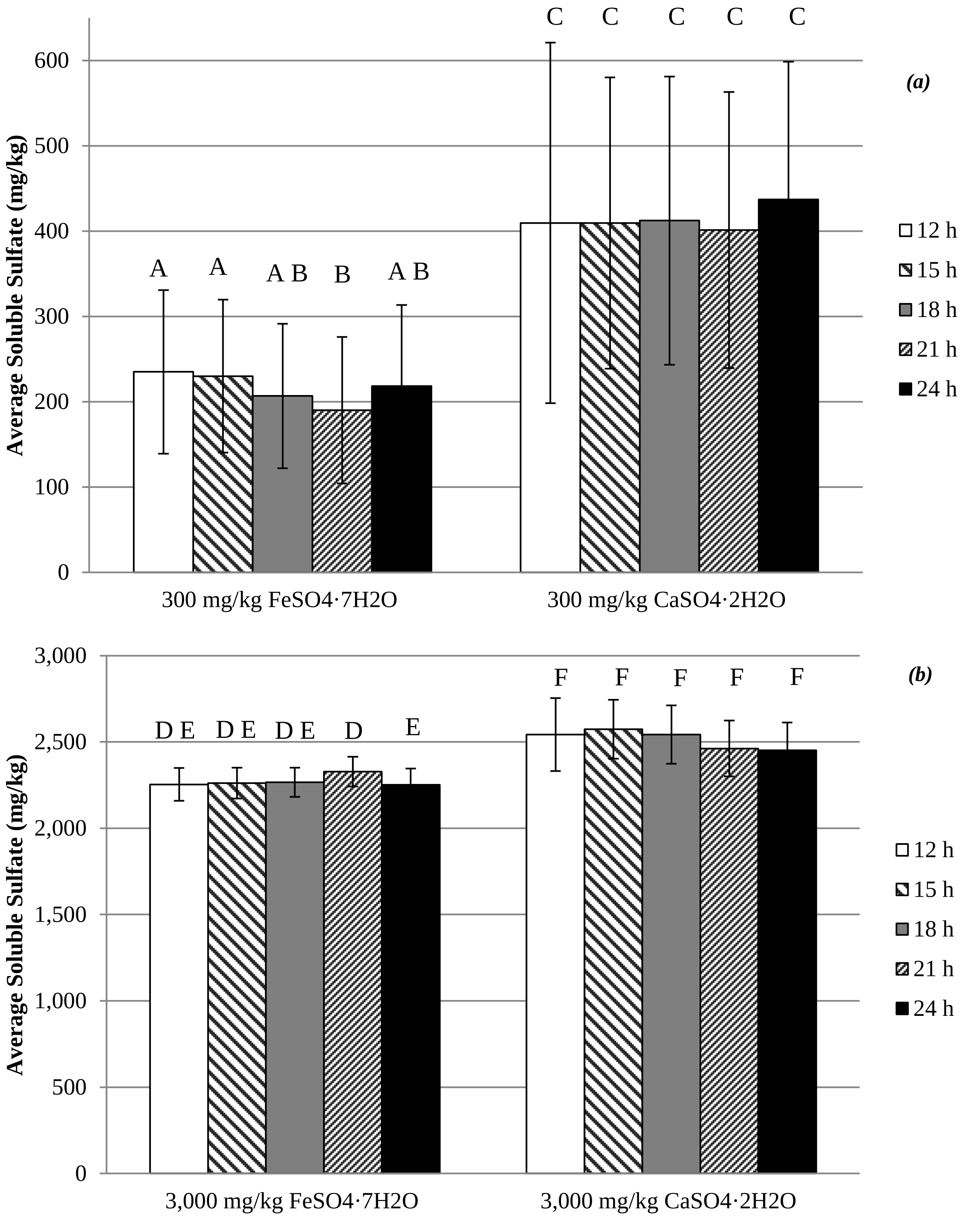


Figure 18 Comparison of differences in average measured soluble sulfate concentration of all 300 mg/kg spiked soil (a) and 3,000 mg/kg (b) spiked soil due to contact time. n=12 replicates. Different letters (A, B, C, D, E, F) represent means that are statistically different within each experimental unit at $p<0.05$

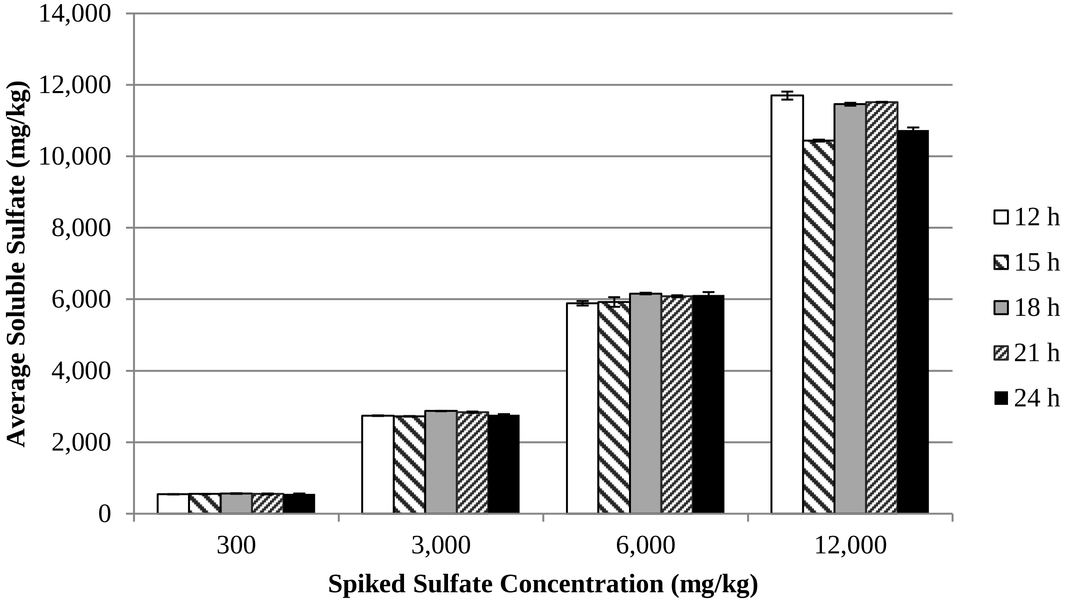


Figure 19 Comparison measured soluble sulfate concentration for increasing sulfate as gypsum concentrations using partial filtration as the separation method for different contact times. n=3 replicates.

measure the 12,000 mg/kg. The use of successive serial dilutions has been shown to lead to error (Pandya et al., 2010; Liao & Duan 2006). Over estimating the 300 mg/kg $CaSO_4 \cdot 2H_2O$ was not critical since it was still significantly below the recommended low level of risk (i.e., 3,000 mg/kg). The overestimation was partially attributed to the 80 mg/kg SO_4 that was naturally present in the clean soil.

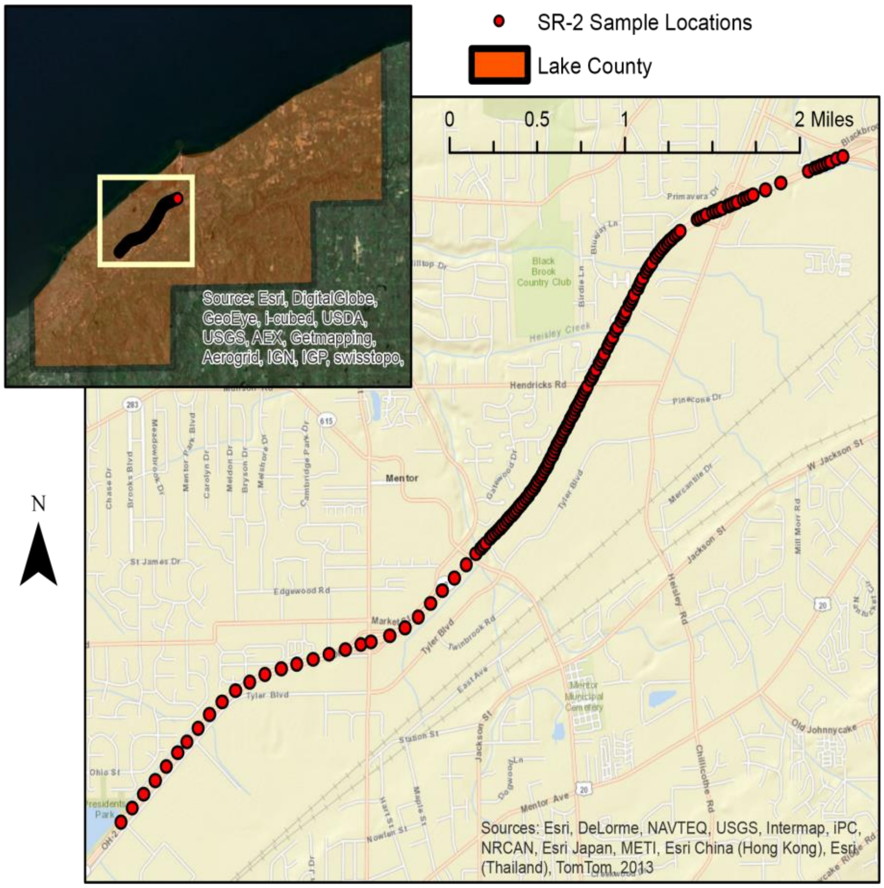
Sulfate source did have an effect on measured SSC. The soils spiked with $FeSO_4 \cdot 7H_2O$ measured lower than soils spiked with $CaSO_4 \cdot 2H_2O$ even though the solubility of $FeSO_4 \cdot 7H_2O$ is higher at 480 g/L at 20˚ C (Perry & Green 2008) compared to $CaSO_4 \cdot 2H_2O$ at 2.58 g/L. One difference could be attributed to the dissolution of $FeSO_4 \cdot 7H_2O$ thus allowing for the oxidation of Fe^{2+} ions. This is highly probable as rusty orange residue was observed. Variability of SO_4 level could be greater in $FeSO_4 \cdot 7H_2O$ than $CaSO_4 \cdot 2H_2O$.

CHAPTER V

LAKE COUNTY, STATE ROUTE 2

5.1 Summary of Lake County Soil Analysis

Soils analysis of SR 2 samples from Lake County (Figure 20) were given a high priority because sulfate induced heave has been observed by ODOT. Soluble sulfate



Source: Ohio Department of Transportation, Jeff Wigdahl
Created by: Kevin Freese

Figure 20 Location of SR-2 soil samples within Lake County concentrations of natural and stabilized soils as well as base material were tested by three consultants using the TEX-145E soluble sulfate test method. A summary of consultant measured soluble SO_4 concentrations is provided in Table 8. This table depicts the number of sample with results for soluble sulfate concentration within the ranges of: <3,000 mg/kg, 3,000-5,000 mg/kg, 5,000-8,000 mg/kg and >8,000 mg/kg. A total of 400 samples were tested, of which 29% tested above the limit of 3,000 mg/kg which is the upper limit of low risk for sulfate heave (Little and Nair 2009). According to results from PSI the base material was most saturated with sulfate with 29 out of 30 samples testing above 8,000 mg/kg. At this time it is unclear whether the base material tested was pre or post stabilization. If the base material in question is pre stabilization then this material could have introduced excessive levels of sulfate which may have contributed significantly to ettringite formation. Stabilized subgrades also tested by PSI were repeatedly high in soluble sulfate with all but two of the 30 samples testing above the 3,000 mg/kg limit. Even within the natural subgrades tested, nearly 75% of the samples tested above 3,000 mg/kg in soluble sulfate. The testing PSI conducted on the boring samples were markedly lower

Table 8 Summary of ODOT provided consultant results for TEX-145E soluble sulfate for SR-2 samples

Consultant	Soil Description	<3,000 (mg/kg)	3,000-5,000 (mg/kg)	5,000-8,000 (mg/kg)	>8,000 (mg/kg)	Total
CTL/ SME	East Bound	137	6	3	0	146
	West Bound	127	11	6	2	146
PSI	Borings	10	4	3	1	18
PSI	Base	0	0	1	29	30
	Stabilized Subgrade	2	1	5	22	30
	Natural Subgrade	8	8	3	11	30
Total		284	30	21	65	400

in soluble sulfate concentration with only approximately 40% of the boring sample testing above the 3,000 mg/kg limit. Testing conducted by CTL and SME on samples indicated the lowest levels of soluble sulfates. Within these sample there were slightly more samples testing above the 3,000 limit for the west bound sample compared to east bound; 13.0% vs. 6.2% respectively.

ODOT provided the University of Akron with 64 soil samples from SR 2 projects; 53 of these samples were natural (non stabilized) and 11 stabilized soils. The natural soils type could be distinguished by labeling and consisted of base (1 sample), borings (22 samples), natural subgrade (8 samples), top powder (4 samples), top middle powder (4 samples), bottom middle (3 samples) and rock fragment of these powder samples (11 samples).

5.2 Results for Lake County Soluble SO_4 Analysis

Soluble sulfate testing was conducted on all samples excluding the rock fragment and stabilized subgrade samples within a laboratory at the University of Akron following the TEX-145E method. The results for soluble sulfate are given in Table 9 and are based on triplicate or duplicate testing of soil samples. The summary of number of soils with soluble sulfate concentrations within the ranges of <3,000 mg/kg, 3,000-5,000 mg/kg, 5,000-8,000 mg/kg and >8,000 mg/kg are provided in Table 10.

5.2.1 Statistical Analysis of Average Soluble SO_4 Concentration in Lake County Soils

Statistical analysis of mean soluble sulfate concentration was conducted using a one way ANOVA model. Two models where created to determine the statistical difference in mean soluble sulfate concentration; Model SO_4A was based on the 42 individual samples

Table 9 Results for TEX-145E soluble sulfate for SR-2 samples. Bold font for SO4 >3,000 mg/kg (n=2 or 3).

Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)
28	416±122	45	1588±340
29	610±76	B1 base	956±33
33	428±105	B1 natural subgrade	2383±144
36	**7803±68**	B2 natural subgrade	2855±95
42	**4958±433**	B3 natural subgrade	**7546±251**
46	1332±110	B4 natural subgrade	2533±315
47	557±3	B5 bottom mid	2144±219
49	1867±4	B5 top mid	2410±102
30	**8460±266**	B5 top	**3722±120**
40	248±52	B6 bottom mid	1215±91
48	923±140	B6 top mid	2321±81
50	115±1	B6 top	1758±18
29	600±29	B7 bottom mid	2158±74
31	**4755±242**	B7 top mid	**4636±57**
32	**5459±209**	B7 top	1983±5
34	1373±62	B8 top mid	**3956±111**
35	624±2	B8 top	**5209±51**
37	2121±110	B9 natural subgrade	604±48
38	**4619±420**	B10 natural subgrade	514±10
39	113±160	B11 natural subgrade	644±46
43	2073±246	B12 natural subgrade	439±87

Table 10 Summary of number of soils with soluble sulfate concentration within ranges based on soil type

Soil Type	<3,000 (mg/kg)	3,000-5,000 (mg/kg)	5,000-8,000 (mg/kg)	>8,000 (mg/kg)	Total
Borings	16	3	2	1	22
Base	1	0	0	0	1
Natural Subgrade	7	0	1	0	8
Top Powder	2	1	1	0	4
Top Mid Powder	2	2	0	0	4
Bottom Mid Powder	3	0	0	0	3
Total	31	6	4	1	42

(including replicate results) and Model SO_4B was based on the soil type, i.e., natural subgrade, bottom middle, base, etc. The one way ANOVA analysis for Model SO_4A showed there was statistical difference in mean soluble sulfate concentration as a function of the actual sample with a p-value<0.001. Tukey's pairwise comparisons were conducted additionally within Model SO_4A to show which sample were statistically different (Figure 21). These results confirm that soils are very heterogeneous and soluble sulfate concentration is a factor of actual sampling location within this Lake County project. Model SO_4B, with p-value=0.618, showed that there is no evidence for statistical difference in mean soluble sulfate concentration based on soil type.

5.3 Results for Lake County Total Metal Analysis

The total metal concentration of Fe, Al and Cr of soils from the SR-2 project were determined for the 11 samples testing above 3,000 mg/kg soluble sulfate and 13 randomly selected soils testing less than 3,000 mg/kg sulfate. Samples tested were from all soil types provided within the SR-2 project with the exception of bottom middle samples, including: 11 boring, 1 base, 6 natural subgrade, 4 top middle and 2 top samples. The total Fe concentration within these soils (Table 11) ranged from a high of 57,567±22,466 mg/kg in the B-12 natural subgrade to a low of 5,503±1,587 mg/kg in the B-1 base sample. This lower range could be considered 20,192±2,163 mg of Fe/kg of soil from boring sample 47 as the base is assumed to be an external base (limestone) material. The total Al concentration within these soils ranged from 26,750±14,673 mg of Al/kg of soil in the B-11 natural subgrade to a low of 6,088±4,953 mg of Al/kg of soil in the B-1 base sample. Again this lower range came from the assumed foreign base sample so the lower range could be considered 9,842±1,942 mg of Al/kg of soil from boring sample 47 (Table 11).

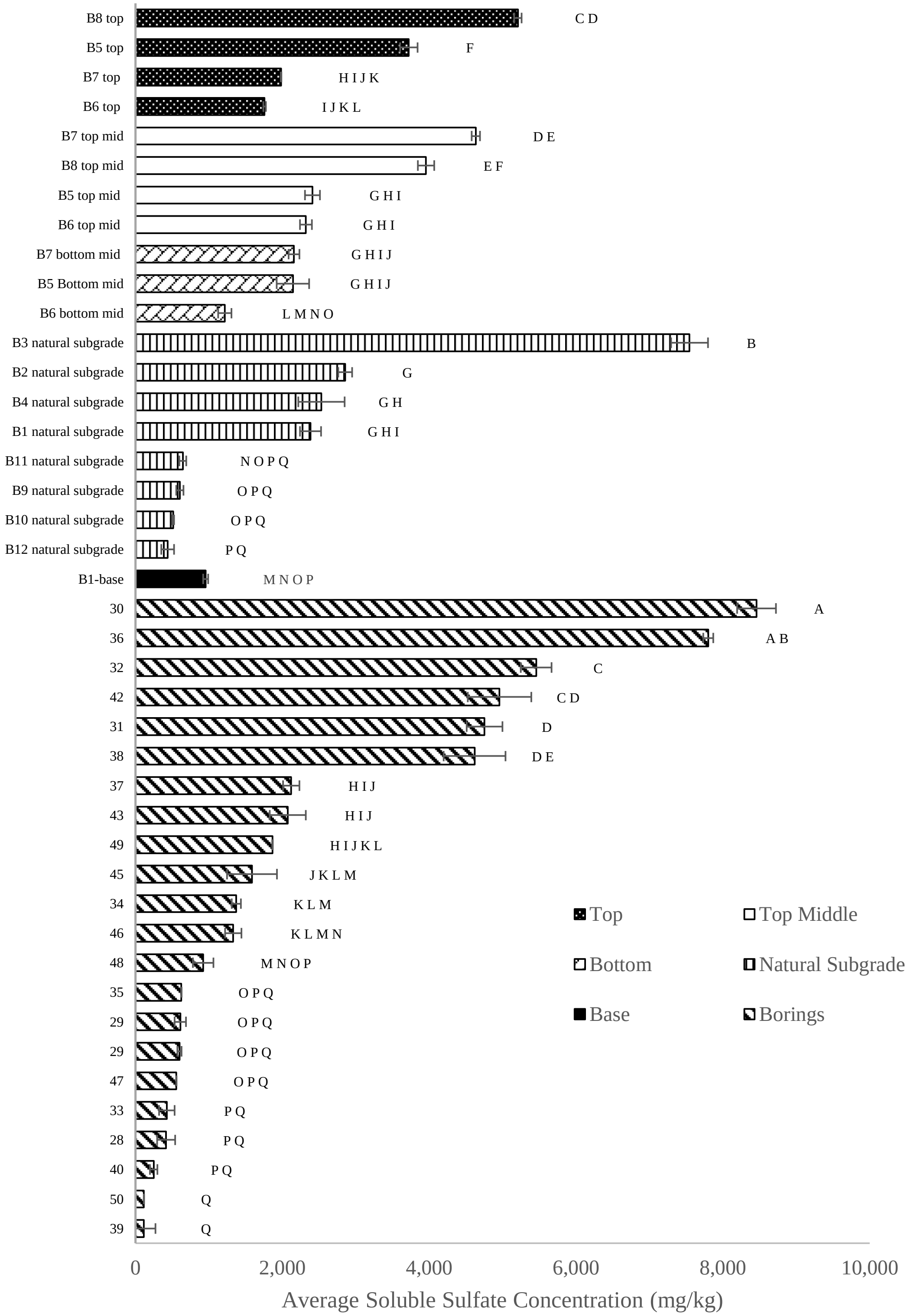


Figure 21 Model SO4A statistical analysis showing no significant difference in SO4 concentration due to sample location indicating heterogeneous distribution of SO4 in soils. N=42, n=2 or 3, P-value <0.001, Different letters (A-Q) represent means that are statistically different at p<0.05.

Table 11 Total Fe, Al & Cr Results for Lake County SR-2 Soils (n=3)

Soil Identification	Soluble SO_4 Average (mg/kg)	Fe Average (mg/kg)	Al Average (mg/kg)	Cr Average (mg/kg)
29	610±76	30,275±6,078	15,392±3,013	8.3±2.0
30	8,460±266	27,183±2,108	13,342±2,231	9.5±0.3
31	4,755±242	26,525±2,112	13,433±1,531	10.8±2.9
32	5,459±209	22,083±5,387	11,158±2,467	8.8±1.4
34	1,373±62	22,633±2,715	13,792±392	9.0±0.3
36	7,803±68	34,642±5,064	16,483±2,344	9.3±0.4
37	2,121±110	25,042±1,035	15,258±396	9.4±0.4
38	4,619±420	23,108±4,236	10,800±1,737	7.8±0.9
40	248±52	32,583±2,814	16,808±2,340	9.4±0.1
42	4,958±433	34,633±5,468	16,108±3,181	9.6±0.1
47	557±3	20,192±2,163	9,842±1,942	6.2±1.5
B1Base	956±33	5,503±1,587	6,088±4,953	3.3±0.4
B2NS	2,855±95	40,738±4,402	14,025±1,379	3.5±0.0
B3NS	7,546±251	33,250±2,722	12,438±1,290	2.4±0.9
B4NS	2,533±315	23,458±1,889	11,875±898	13.3±0.8
B5T	3,722±120	27,358±1,573	12,833±891	12.9±0.4
B5TM	2,410±102	29,642±3,435	13,858±2,098	3.3±0.7
B6TM	2,321±81	28,733±1,663	13,542±925	4.5±0.3
B7TM	4,636±57	32,313±2,245	11,400±1,167	3.3±0.4
B8T	5,209±51	32,646±7,725	12,875±1,084	11.8±4.3
B8TM	3,956±111	33,175±4,501	14,217±1,963	4.1±0.8
B10NS	514±10	51,842±12,311	22,242±4,736	5.1±0.1
B11NS	644±46	50,967±28,001	26,750±14,673	7.1±0.4
B12NS	439±87	57,567±22,466	25,867±10,103	7.3±0.5

The total Cr concentration within these soils ranged from a high of 13.3±0.8 mg of Cr/kg of soil in the B-4 natural subgrade to a low of 2.4±0.9 mg of Cr/kg of soil in the B-3 natural subgrade soil. These measured Cr concentrations are lower than, but on the same magnitude as reported values of Cr for ten samples measured at Euclid Creek Reservation in the adjacent county of Cuyahoga which range from 11.6 – 14 mg/kg (OhioEPA 2013).

5.3.1 Statistical Analysis of Total Fe, Al & Cr in Lake County Soils

The results for Fe, Al and Cr concentrations of 23 of the samples (excluding the base because of variability and it is not assumed to be a native soil) were used for statistical analysis. Analysis of the effect of soil type on average measured total Fe, Al and Cr concentrations were planned using a one way ANOVA. However, it was necessary to first create a two way ANOVA using a general linear model to determine if sulfate range also had a main effect on the total metal (Fe, Al or Cr) concentration. Three GLM (two way ANOVA) models was created $\alpha=0.05$ with response variable as average Fe, Al and Cr concentration respectively and treatment factor of soil type and sulfate range. Due to variability in sulfate range and limited numbers of test samples for comparison from the T, TM and BM soil types the levels of the treatments were selected as: <3,000 mg/kg (11 soils) and >3,000 mg/kg (12 soils) for sulfate range (2 levels) and Bor (11 boring samples), NS (6 natural subgrade) and T (2 top and 4 top middle) for soil type (3 level).

Results of the Fe GLM showed sulfate range was found to have neither a main effect (p-value 0.524) nor interactive effect (p-value 0.358). Therefore, the sulfate range factor was removed from the model and a one-way ANOVA for soil type was created. The one-way ANOVA model for Fe concentration showed there is a statistically significant effect on Fe concentration due to soil type (p-value 0.002) with the mean Fe concentration of 42,970 mg/kg for the natural subgrade soil samples statistically significantly higher than the mean Fe concentration of 27,173 mg/kg and 30,644 mg/kg for boring and T/TM soil samples respectively (Figure 22).

The Al GLM also indicated that sulfate range had neither a statistically significant main effect (p-value 0.130) nor interactive effect (p-value 0.338) on Al concentration.

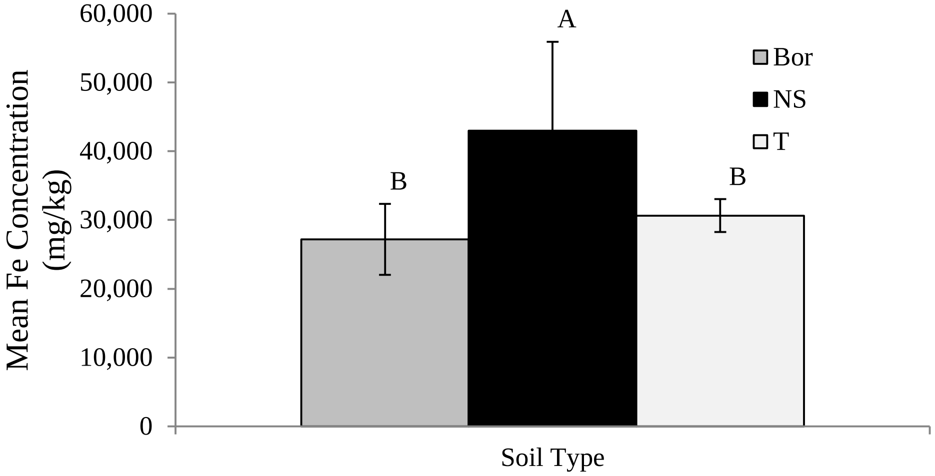


Figure 22 Comparison of the statistically significant effect of soil type on: average measured total Fe concentration. n=11 for Bor, n=6 for NS, n=6 for T. Different letters (A & B) represent means that are statistically different at p<0.05.

Again the factor was eliminated from the model and a one-way ANOVA model for Al concentration was created which showed there is a statistically significant effect on Al concentration due to soil type (p-value 0.030). The mean Fe concentration of 18,866 mg/kg for the natural subgrade soil samples was statistically significantly higher than the mean Al concentration of 13,856 mg/kg and 13,121 mg/kg for boring and T/TM soil samples respectively (Figure 23).

The Cr GLM indicated that sulfate range had neither a statistically significant main effect (p-value 0.982) nor interactive effect (p-value 0.117) thus a one-way ANOVA model was created for Cr concentration to determine if soil type had a significant effect. There was no significant effect on Cr concentration due to soil type within the one-way ANOVA (p-value 0.208). Therefore there is no statistical evidence for difference in the mean of the Cr concentrations: 6.451 mg/kg, 8.917 mg/kg and 6.635 mg/kg for the natural subgrade, boring and T/TM samples respectively.

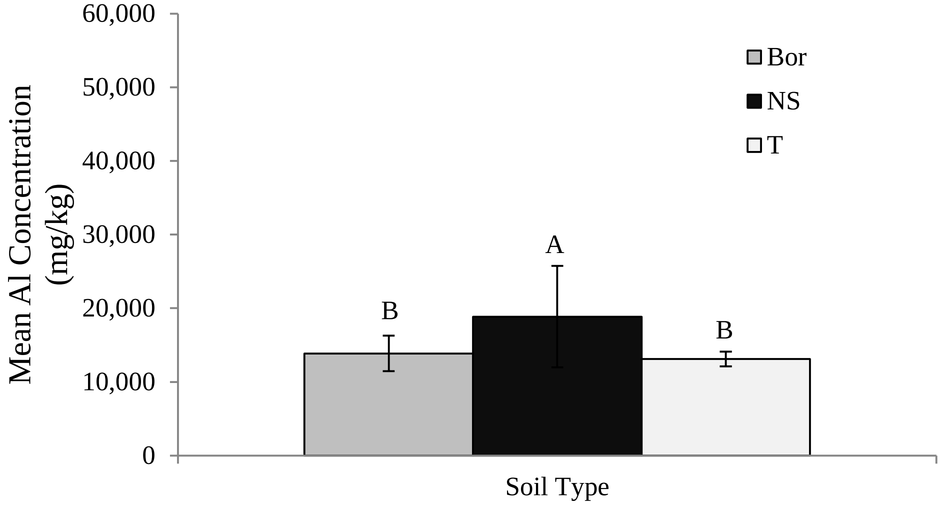


Figure 23 Comparison of the statistically significant effect of soil type on average measured total Al concentration. n=11 for Bor, n=6 for NS, n=6 for T. Different letters (A & B) represent means that are statistically different at $p<0.05$.

5.4 Results for Lake County XRD Analysis

The primary objective of this research was to identify SO_4 sources and origins in Ohio soils. XRD analysis was used to identify minerals present within soils. Twenty-two samples from the Lake County SR-2 project were tested using XRD and the distribution of sample testing is provided in Table 12. Duplicate or triplicate tests of the 22 soils were conducted for a total of 56 XRD tests of the Lake SR-2 soils. Analysis of the diffractograms of samples indicated dominant minerals within Lake county soils were Quartz, (SiO_2) in 56 out of 56 test samples, Dolomite ($Ca\,Mg(CO_3)_2$) in 47 samples, Calcite ($CaCO_3$) in 33 samples. The primary sulfate sources were calcium sulfate as gypsum ($CaSO_4{\cdot}2H_2O$) both natural in 22 samples and synthetic in 14 samples and anhydrite ($CaSO_4$) in 19 samples. There were also two secondary sulfate sources: Arcanite (K_2SO_4) in 6 samples and Lanarkite ($Pb_2(SO_4)O$) in 6 samples. Although the bedrock source under

Table 12 Distribution of XRD testing and mineral identification of Lake County soils.

Soil Type	Soils Tested	Number of Soils <3000 mg/kg sulfate	Number of Soils >3000 mg/kg sulfate	Total Replicates	Number of replicates <3000 mg/kg sulfate	Number of replicates >3000 mg/kg sulfate
Boring	9	3	6	26	9	17
Base	1	1	0	2	2	0
Natural Subgrade	6	5	1	14	11	3
Top	2	0	2	5	0	5
Top Middle	4	2	3	9	4	5
Bottom Middle	0	0	0	0	0	0
Totals	22	11	12	56	26	30

the SR-2 project is Devonian Shale, known to contain pyrite (Hoover 1960), none of the samples tested indicated the presence of pyrite. This could be due to the oxidation of pyrite which alters the sulfur (S) within pyrite from sulfide (S^{2-}) to sulfate (SO_4^{2-}). Gypsum was the dominant sulfate source in soils tested at greater that 4,000 mg/kg soluble sulfate (Table 13). Comparison of diffractograms for soils with high sulfate and low sulfate are provided in Figures 24-26. The XRD test 30-1 of boring sample 30 with 8,460 mg/kg soluble sulfate clearly shows the presence of gypsum (Figure 24(a)). While the XRD test 47-1of boring sample 47 with 557 mg/kg soluble sulfate did not indicate the presence of any sulfur bearing minerals (Figure 24(b)). Similar comparison are provided in Figure 25 and Figure 26 for comparison of natural subgrade and T/TM soils.

Table 13 XRD identified sulfate mineral source for Lake County soil samples.

Sample Name	Average Sulfate Concentration (mg/kg)	Replicate Number	Gypsum	Gypsum, syn	Anhydrite	Arcanite	Lanarkite
29	610	1			x		
		2			x		
		3			x		
30	8460	1	x				
		2	x				x
		3	x	x			x
31	4755	1	x		x		
		2	x			x	
		3			x	x	
32	5459	1	x			x	
		2	x	x			
		3	x	x			x
36	7803	1	x	x			
		2	x	x		x	
		3	x	x			x
38	4619	1	x	x			
		2	x				
40	248	1					
		2			x		
		3			x		
42	4958	1	x	x			
		2	x				
		3	x				
47	557	1					
		2					
		3					
B1Base	956	1					
		2					
B2NS	2855	1					
		2					
		3					
B3NS	7546	1					
		2	x	x			
		3	x				
B4NS	2533	1			x		
		2					
B10NS	514	1			x		
		2			x		
B11NS	644	1			x		
		2			x		
B12NS	439	1					
		2			x		
B5T	3722	1					
		2					
B5TM	2410	1			x		
		2			x		
B6TM	2321	1			x		
		2			x		
B7TM	4636	1	x	x			
		2	x	x			
		3	x	x			
B8T	5209	1					
		2		x		x	
		3		x			
B8TM	3956	1			x	x	x
		2		x		x	

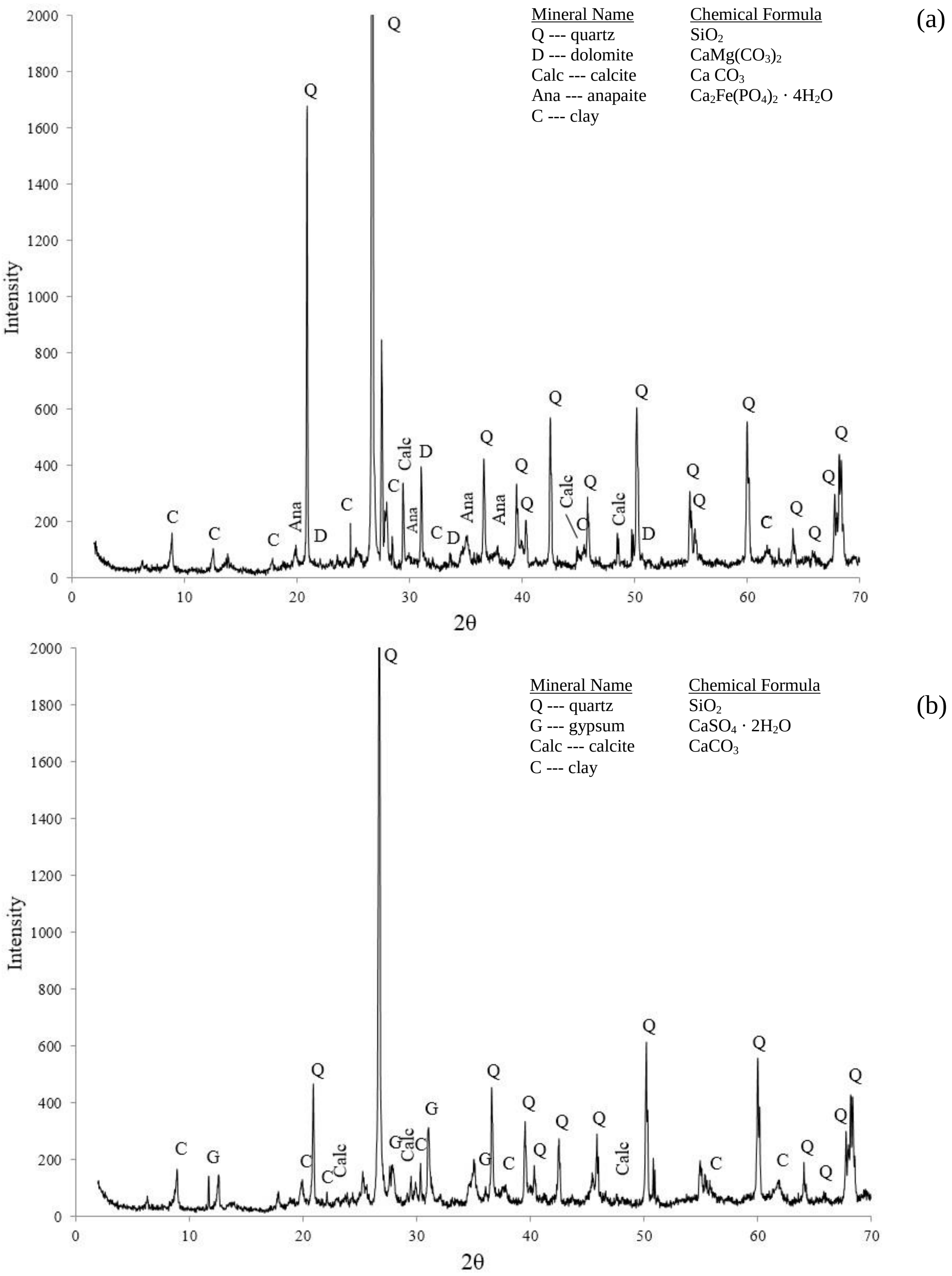


Figure 24 XRD Diffractogram for Lake County boring samples (a) 47-1 soil low soluble sulfate (557 mg/kg) and (b) 30-1 with high soluble sulfate (8460 mg/kg).

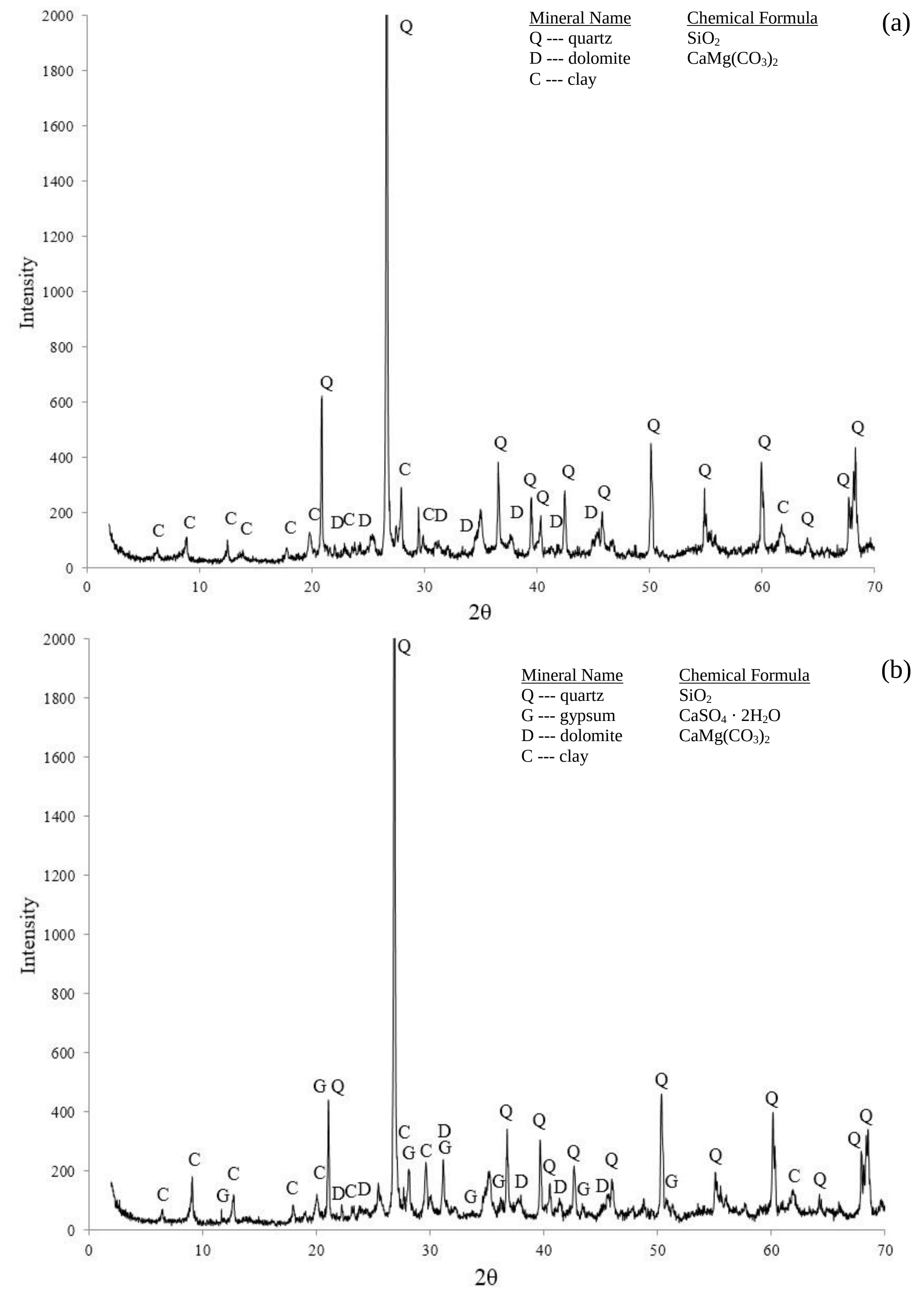


Figure 25 XRD Diffractogram for Lake County (a) B12NS-1 with low soluble sulfate (439 mg/kg) and (b) B3NS-2 with high soluble sulfate (7546 mg/kg).

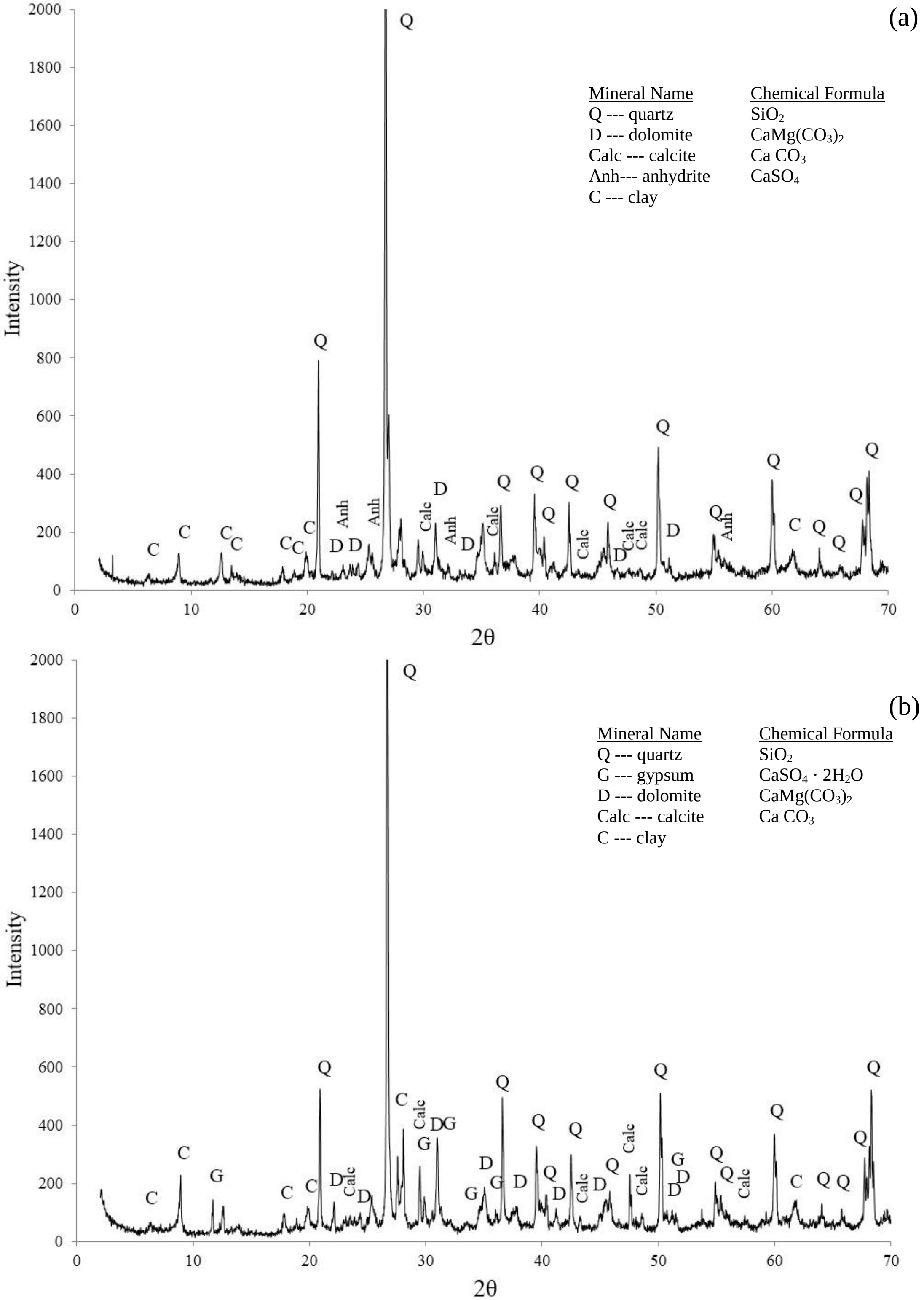


Figure 26 XRD Diffractogram for Lake County (a) B6TM-1 soil low soluble sulfate (2321 mg/kg) and (b) B8T-3 with high soluble sulfate (5209 mg/kg).

5.5 Discussion of Lake County Soil Testing Results and Potential SO_4 Sources

The results of soil analysis for Lake County, SR-2 soils depicted sufficient quantities of SO_4 for the formation of ettringite. XRD analysis indicated the primary sources of SO_4 are calcium sulfates, gypsum and anhydrite. Researchers at Bowling Green State University (BGSU) conducted XRD analysis on a separate set of 22 soils collected from SR-2 and also found gypsum and anhydrite present in 57% of samples (Farver et al., 2014). Additionally, preliminary investigations conducted by ODOT revealed multiple gypsum crystals up to half an inch in length (Narsavage 2011). Calcium sulfates are clearly the source of SO_4 in the Lake County SR-2 soils. However, due to natural occurring reactions with calcium bearing minerals such as dolomite or calcite and sulfate, the origin of SO_4 in Lake County soils is difficult to pinpoint. The surface soils of much of Lake County are form glacial lake deposits (Figure 4) known to contain gypsum and anhydrite (Wolfe 2001; Szabo 1986). The bedrock through the SR-2 region is Devonian shale which contains FeS_2 (Hoover 1960; Kane et al., 1990; Schieber & Riciputi 2004; Rimmer et al., 2004; Angle et al., 2005; Leventhal & Hosterman 1982). Glacial till within this region has also been shown to have fractures where evaporates and Fe oxides accumulate (Szabo 2006). Both dry and wet atmospheric deposition of emitted sulfur dioxide may contribute to sulfate in soil as Lake County is one of four regions in Ohio listed by the EPA as non-attainment for SO_2 emissions (USEPA 2013). Total Cr concentrations measured lower than background levels reported at 21.1 mg/kg for soils in Cuyahoga County, adjacent to the west of Lake (OEPA 2013). Therefore even though the fill material may have been used during the construction of SR-2, COPR nor remediation with $FeSO_4$ is likely a source of higher sulfate concentrations along SR-2 in Lake County.

CHAPTER VI

PAULDING AND DEFIANCE COUNTIES SOILS

6.1 Summary of Paulding and Defiance County Soil Analysis

ODOT provided four sets of soils from Paulding/Defiance Counties. Three sets of these soil samples were taken along United State Route (US) 24 throughout both counties prior to stabilization and the final set of soil samples was taken from heave damaged stabilized subgrades along US-24. ODOT provided two sets of soil samples, ground bulk samples (BS) and intact cores, from Project PAU/DEF-24-12.30. There were a total of 24 BS taken at 12 different boring locations at depths of 1.5-3.0’ or 3.0-4.5’and 21 of the corresponding cores samples. ODOT additionally provided another set of 14 subgrade core samples from PAU/DEF 24-4.51 from three different boring locations and at a variety of 1.5’ incremental depths ranging from 0-10.5’. Finally, in the summer of 2013, ODOT provided 41 heave damaged stabilized subgrade bulk soils samples. BS soils from PAU/DEF 24-12.30 and the PAU/DEF Heave contained enough sample mass to preform: standard TEX-145E testing for soluble sulfate; total Fe, Al and Cr and XRD testing. The core samples provided were much smaller in mass and ODOT requested these soil samples be left intact if possible. Due to these limitations, only XRD testing was conducted with the modified TEX-145E, post-XRD soluble sulfate as described in section 4.1.2. The US-24-12.30 project spanned from Crane Township in northern Paulding County east into

Defiance County (Figure 27). Soil testing schedule for Paulding and Defiance County soils is provided in Table 14.

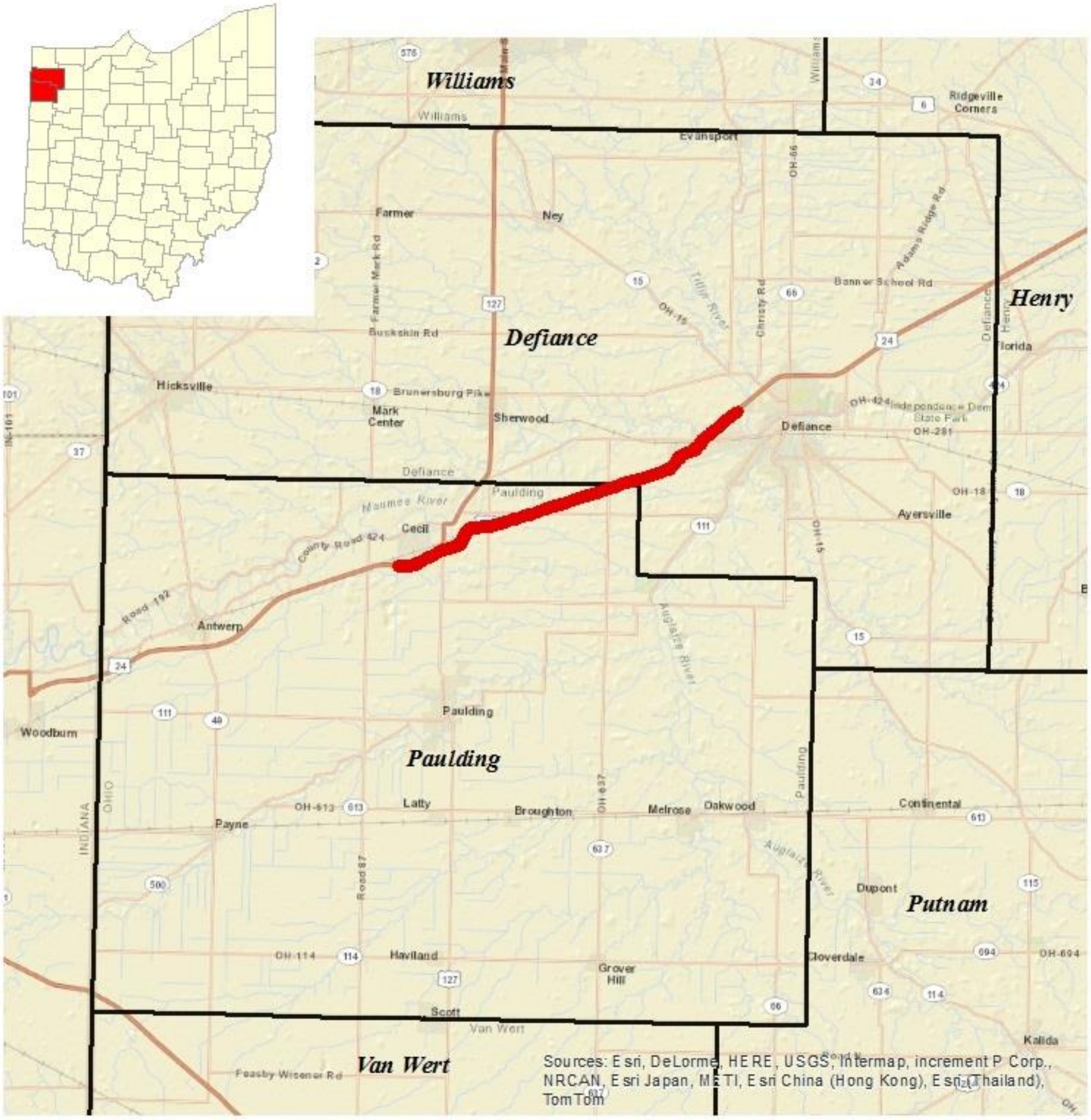


Figure 27 US-24 Project Location in Northern Paulding County and Southern Defiance County

Table 14 Summary of Paulding and Defiance Counties soils tested

Project	Number of Soil Samples	Number of TEX-145E Tested Soils	Number of Post-XRD SO_4 Tested Soils	Number of Total Fe Tested Soils	Number of Total Al Tested Soils	Number of Total Cr Tested Soils	Number of XRD Tested Soils
PAU/DEF 24-12.30 BS	24	24	11	17	13	0	11
PAU/DEF 24-12.30 Cores	21	0	6	0	0	0	6
PAU/DEF 24-4.51 Cores	14	0	12	0	0	0	12
PAU/DEF Heave BS	41	41	36	41	41	41	36

6.2 Results for Paulding and Defiance counties Soluble SO_4 Analysis

As outlined in Table 14, TEX-145E tests for soluble sulfate were conducted on all BS samples from Paulding/Defiance Counties provided by the Central Office. Soil samples from PAU/DEF 24-12.30 contained soil samples at depths of 1.5-3’ and 3-4.5’ for each boring (Table 14). The 3,000 mg/kg limit was exceed in 7/12 borings at either depth. The sample highest in soluble sulfate was 29845 (B-2, depth 3-4.5’) at 10,016 mg/kg (Table 15). As mentioned above the core samples from PAU/DEF 24-12.30 and PAU/DEF 24-

Table 15 Soluble Sulfate Results for PAU/DEF 24-12.30 BS. Bold font for SO4 >3,000 mg/kg (n=1).

Soil Identification	Boring	Depth	Soluble Sulfate (mg/kg)	Soil Identification	Boring	Depth	Soluble Sulfate (mg/kg)
29820	B-6	1.5-3'	1,102	29844	B-2	1.5-3'	**9,408**
29821	B-6	3-4.5'	570	29845	B-2	3-4.5'	**10,016**
29824	B-8	1.5-3'	2,504	29848	B-3	1.5-3'	344
29825	B-8	3-4.5'	**4,010**	29849	B-3	3-4.5'	15
29828	B-9	1.5-3'	**4,317**	29852	B-4	1.5-3'	1,534
29829	B-9	3-4.5'	**4,910**	29853	B-6	3-4.5'	254
29832	B-11	1.5-3'	**5,240**	29856	B-5	1.5-3'	1,126
29833	B-11	3-4.5'	**5,647**	29857	B-5	3-4.5'	173
29836	B-12	1.5-3'	2,690	29860	B-7	1.5-3'	1,858
29837	B-12	3-4.5'	**3,929**	29861	B-7	3-4.5'	592
29840	B-1	1.5-3'	**3,462**	29864	B-10	1.5-3'	**5,314**
29841	B-1	3-4.5'	1,934	29865	B-10	3-4.5'	**6,135**

4.51 were texted for SO$_4$ concentration using the post-XRD method because these samples did not contained enough soil for traditional TEX-145E soluble sulfate analysis. This testing was particularly critical for samples from PAU/DEF 24-4.51 because no corresponding bulk samples for this project provided by central office. Six core samples from PAU/DEF 23-12.30 (Table 16) and 12 cores from PAU/DEF 24-4.51 (Table 17) were analyzed with 4/6 and 12/12 testing above the 3,000 mg/kg limit respectively. Depth nor corresponding soil identification was provided for the core samples from PAU/DEF 24-12.30. However, with the exception of B-2 the values of post-XRD testing of these cores was similar to the results for TEX-145E testing of the BS samples. PAU/DEF 24-4.51 cores were very high in SO$_4$ as only one of the twelve tested below 10,000 mg/kg and B1-1-S15

Table 16 Post XRD Soluble Sulfate Results for PAU/DEF 24-12.30 Cores. Bold font for SO$_4$. >3,000 mg/kg (n=2).

Soil Identification	Boring	Depth (feet)	Soluble Sulfate (mg/kg)
29845	B-2	3-4.5'	**23,106±1,592**
29861	B-7	3-4.5'	1,958±10
29824	B-8	1.5-3'	2,108±161
29828	B-9	1.5-3'	**4,390±225**
29865	B-10	3-4.5'	**6,188±245**
29833	B-11	3-4.5'	**5,458±359**

Table 17 Post XRD Soluble Sulfate Results for PAU/DEF 24-4.51 cores. Bold font for SO$_4$ >3,000 mg/kg (n=2 or 3).

Soil Identification	Boring	Depth	Soluble Sulfate (mg/kg)	Soil Identification	Boring	Depth	Soluble Sulfate (mg/kg)
B1-0-S7	B1-0	NA	**9,288±251**	B1-1-S17	B1-1	6-7.5	16,820±576
B1-0-S9A	B1-0	4-5.5	**19,098±932**	B1-1-S19	B1-1	9-10.5	29,677±1,245
B1-0-11	B1-0	7-8.5	**22,339±2,399**	B2-0-S2B	B-2-0	2.5-4	21,240±3,727
B1-1-S13	B1-1	0-1.5	**20,590±935**	B2-0-S3	B-2-0	4-5.5	7,741±106
B1-1-S15	B1-1	3-4.5	**32,902±1,195**	B2-0-S5	B-2-0	7-8.5	24,926±2,772
B1-1-S16	B1-1	4.5-6	**21,555±1,466**	B2-0-S6	B-2-0	8.5-10	19,154±812

contained the highest SO_4 concentration measured of all ODOT soils tested at 32,902±1,195 mg/kg. It should be noted however that soil samples for XRD are required to be ground to a very small (flour-like) grain size. The reduction in grain size increases the surface area and may cause higher SO_4 results (Cerato et al., 2011). PAU/DEF Heave BS samples contained very high concentrations of SO_4, with 34 of the 41 samples having SO_4 concentrations above 3,000 mg/kg and nearly half of the samples above 10,000 mg/kg (Table 18).

Table 18 Soluble Sulfate Results for PAU/DEF 24-Heave. Bold font for SO4 >3,000 mg/kg (n=3).

Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)
S-1	**6,710±130**	S-15	**14,539±695**	S-29	**4,650±80**
S-2	**13,374±984**	S-16	**11,326±226**	S-30	**7,027±446**
S-3	**7,358±744**	S-17	**15,310±387**	S-31	**4,714±118**
S-4	**5,802±412**	S-18	**15,968±978**	S-32	**14,192±959**
S-5	**15,230±410**	S-19	**5,629±12**	S-33	**8,509±509**
S-6	**17,000±414**	S-20	**17,331±226**	S-34	**6,254±1028**
S-7	**20,592±2,358**	S-21	**18,067±199**	S-35	**4,820±243**
S-8	**6,886±376**	S-22	**17,134±464**	S-36	2,042±28
S-9	**11,811±23**	S-23	**8,665±279**	S-37	893±620
S-10	**4,798±109**	S-24	**13,427±380**	S-38	2,342±63
S-11	**5,509±200**	S-25	**19,192±744**	S-39	1,337±179
S-12	**15,226±358**	S-26	**10,706±287**	S-40	2,557±286
S-13	**11,987±41**	S-27	2,788±1,060	S-41	1,561±218
S-14	**11,582±33**	S-28	**8,314±972**		

6.2.1 Statistical Analysis of Average Soluble SO_4 Concentration in Paulding and Defiance Counties Soils

Statistical comparison of average sulfate concentration of PAU/DEF 24-12.30 and PAU/DEF Heave was conducted using a one way ANOVA with the project being the treatment factor. Post-XRD results for PAU/DEF 24-12.30 and PAU/DEF 24-4.51 cores were not included in this statistical analysis because the method for measuring sulfate from post XRD analysis, i.e., quantities of 1.5 – 1.25 grams of soil and 30 – 25 ml of distilled water, was different than the standard TEX-145E method used for PAU/DEF 24-12.30 and PAU/DEF Heave. The result of the one-way ANOVA ($\alpha=0.05$) indicated PAU/DEF Heave (N=41) had statistically significant higher SO_4 concentrations with a mean of 9,589±5,664 mg/kg than PAU/DEF 24-12.30 (N=24) with a mean SO_4 concentrations of 3,212±2,791 mg/kg (p-value <0.001). One-way ANOVA analysis was additionally conducted on sulfate concentration of PAU/DEF 24-12.30 samples to determine the statistical significance of depth or boring location. Depth of sample 1.5-3’ or 3-4.5’ did not have a statistically significant effect on SO_4 concentration of these samples (p-value=0.96). However, there was a statistical significance between borings and the mean SO_4 concentrations of boring B-2 was statistically higher than all other borings at 9,712±430 mg/kg. The significant effect of boring location is not surprising and supports the belief that SO_4 concentrations within soils is heterogeneous (Jefferis 2011).

6.3 Results for Paulding and Defiance County Total Metal Analysis

The overview of the number of samples tested for each project in Paulding and Defiance Counties soil samples was provided in Table 14. Only the bulk samples from PAU/DEF 24-12.30 (Table 19) and PAU/DEF Heave (Table 20) were analyzed for total metal content. The majority of the soils that were above the 3,000 mg/kg soluble sulfate limit were subjected to acid digestion and ICP analysis to ascertain the total Fe, Al and Cr. Total metal testing was also conducted on random samples that were below 3,000 mg/kg from these projects in order to assess if the concentration of these metals correlated with sulfate concentrations reported in Tables 15 & 18.

The mean Fe and Al concentrations were slightly higher in the soils tested from PAU/DEF 24-12.30 at 23,326±3,229 mg/kg and 18,591±3,217 mg/kg respectively, compared to all 41 soils from PAU/DEF 24 Heave at 22,487±3,218 mg/kg and 17,507±4,416 mg/kg for Fe and Al respectively. However, the maximum levels of Fe and Al concentration within a PAU/DEF sample was found in the highly variable PAU/DEF Heave sample S35 at 31,675±9,920 mg/kg and 27,883±10,244 mg/kg respectively. Mean chromium levels were higher slightly higher in soils from PAU/DEF Heave at 11.59±3.18 mg/kg compared to 10.83±6.37 mg/kg in soils from PAU/DEF 24-12.30. Cr concentrations in PAU/DEF 12.30 samples were highly variable with a maximum of 24.25±12.37 mg/kg from sample 29824 and minimum of 0.25 mg/kg from samples 29853, both of which were highest and lowest Cr concentrations measured for all PAU/DEF soils.

Table 19 Total Fe, Al & Cr Results for PAU/DEF 24-12.30 (n=3)

Soil Identification	Soluble SO_4 (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)	Average Cr (mg/kg)
29849	15	24,108±1,566	19,883±1,638	9
29857	173	29,475±2,299	23,575	19.5
29853	254	28,300±3,926	20,475	0.25
29848	344	24,469±3,808	14,700	11.5
29821	570	26,613±2,104	20,250	15.25
29861	592	24,675±5,441	23,367±4,875	-
29824	2,504	22,584±1,393	19,625	24.25±12.37
29840	3,462	21,567±7,563	16,325±4,369	-
29837	3,929	22,783±10,389	17,475±5,353	-
29828	4,317	23,950±5,355	-	9.42±0.72
29832	5,240	21,575±5,594	18,675	-
29864	5,314	24,788±10,578	-	5.97±0.95
29833	5,647	20,800±1,658	-	5.48±1.13
29865	6,135	21,650±1,136	14,492±1,195	11.75±0.90
29844	9,408	16,825±1,046	-	6.38±0.68
29845	10,016	19,048±3,635	14,250	8±3.51

Table 20 Total Fe, Al & Cr Results for PAU/DEF 24 Heave (n=3)

Soil Identification	Soluble SO_4 (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)	Average Cr (mg/kg)
S37	893±620	19,108±1,580	17,483±1,157	13.17±0.95
S39	1,337±179	25,458±923	25,017±3,414	14.67±0.52
S41	1,561±218	27,433±1,982	22,667±2,033	17.75±0.25
S36	2,042±28	31,150±8,826	26,775±7,310	16.75±0.87
S38	2,342±63	22,358±2,195	19,817±1,553	14.50±0.25
S40	2,557±286	24,625±2,610	20,450±1,644	15.83±0.63
S27	2,788±1,060	24,292±1,152	21,592±88	17.58±0.63
S29	4,650±80	22,000±3,156	14,267±1,397	10.33±1.28
S31	4,714±118	25,775±581	23,192±705	17.25±1.52
S10	4,798±109	26,283±3,200	21,892±1,990	14.00±1.52
S35	4,820±243	31,675±9,920	27,883±10,244	13.17±4.72
S11	5,509±200	24,325±1,735	23,783±2,354	13.67±1.18
S19	5,629±12	23,500±1,303	15,942±1,365	10.00±1.32
S4	5,802±412	21,817±1,158	17,642±846	9.83±0.76
S34	6,254±1,028	24,783±13,263	18,525±9,952	12.83±0.29
S1	6,710±130	21,108±2,224	14,358±1,454	6.83±0.38
S8	6,886±376	22,158±1,504	13,650±1,476	7.83±1.01
S30	7,027±446	22,200±3,539	14,608±3,457	10.75±0.43
S3	7,358±744	20,375±229	15,208±1,097	9.00±0.43
S28	8,314±972	19,033±1,591	12,225±1,143	10.17±1.01
S33	8,509±509	20,992±2,413	19,333±1,765	14.25±0.66
S23	8,665±279	19,600±890	13,908±543	11.08±0.38
S26	10,706±287	20,692±345	14,550±1,282	11.17±0.80
S16	11,326±226	19,333±1,245	13,100±697	8.08±1.13
S14	11,582±33	18,892±1,150	12,817±426	8.17±0.29
S9	11,811±23	27,692±4,488	24,217±3,969	15.33±1.38
S13	11,987±41	26,025±545	22,667±388	16.75±0.43
S2	13,374±984	21,525±1,243	19,833±1,280	10.42±0.63
S24	13,427±380	18,792±726	11,458±354	8.75±0.43
S32	14,192±959	21,800±1,056	17,358±4,343	10.92±0.63
S15	14,539±695	19,725±513	12,800±1,371	7.00±0.25
S12	15,226±358	22,867±1,234	19,442±1,449	12.08±0.63
S5	15,230±410	19,500±975	12,550±254	7.83±0.63
S17	15,310±387	21,208±864	15,317±1,906	10.42±0.80
S18	15,968±978	21,033±3,390	14,767±2,281	8.25±0.75
S6	17,000±414	21,842±1,410	14,650±1,129	9.67±0.14
S22	17,134±464	21,383±903	15,467±615	11.50±0.90
S20	17,331±226	18,925±1,720	14,442±2,122	7.83±0.38
S21	18,067±199	18,800±979	14,358±1,388	9.92±0.14
S25	19,192±744	19,600±1,027	14,508±1,179	12.00±0.25
S7	20,592±2,358	22,292±787	13,250±844	7.83±0.38

6.3.2 Statistical analysis of total metal content for Paulding and Defiance Counties

Statistics was also used to assess if there was any correlation between the specific metal concentration and soluble sulfate. Scatter plots of the resulting sulfate concentration on the x-axis and average Fe and Al concentrations on the y-axis (Figure 28) showed there could be possible correlation between both Fe and Al concentration and SO_4 concentrations. Regression analysis, performed in Minitab concluded the trends in Fe and Al versus SO_4 was statistically significant with the highest p-values of 0.018 within these four regressions and generally showed a trend for decrease in Fe and Al concentration as SO_4 increased. The variability within these Fe and Al trends directly related to SO_4 concentrations is given by the R^2 values. For example, 70.6% of the variation in Fe concentrations in PAU/DEF 24-13.30 can be explain SO_4 concentrations. Even though the p-values for these tests are well under $\alpha=0.05$, the trend equations should not be used as an estimator of either Fe, Al or SO_4 concentrations due to moderate R^2 values, the limited number of samples tested and the high degree of heterogeneity of soils. Regression analysis was additionally conducted on chromium concentrations versus SO_4 concentration in PAU/DEF 24-12.30 and PAU/DEF 24-Heave soils (Figure 29). Results showed significant trend in Cr versus SO_4 in PAU/DEF 24-Heave (p-value < 0.001), but no significant trend could be identified in PAU/DEF 24-12.30 (p-value =0.354) due to the high level of variability and limited number of soils tested.

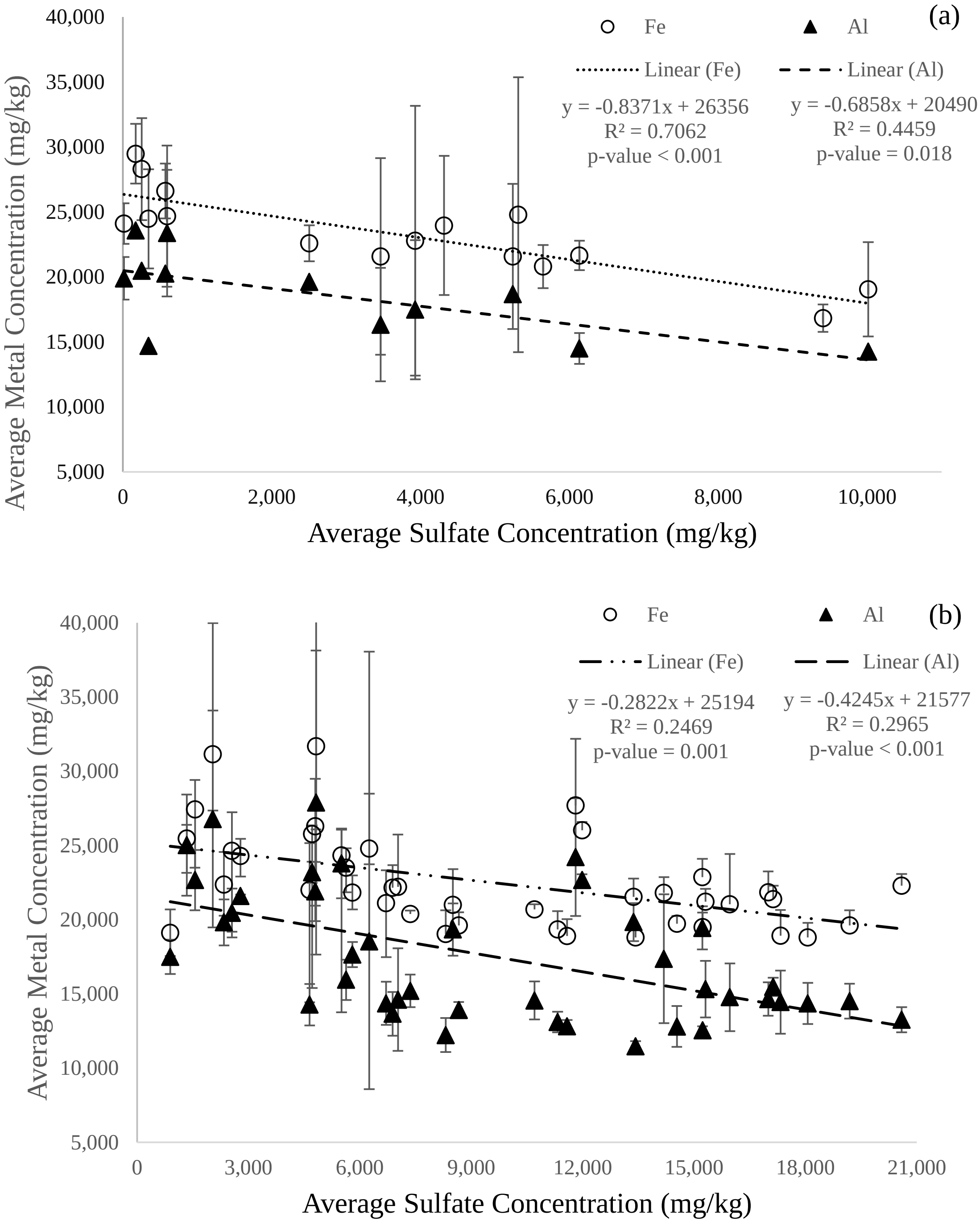


Figure 28 Scatter plot depicting strong trend between both Fe ($p<0.001$) and Al ($p=0.018$) compared to SO_4 concentration in (a) PAU/DEF 24-12.30 and both Fe ($p=0.001$) and Al ($p<0.001$) compared to SO_4 concentration in (b) PAU/DEF 24-heave

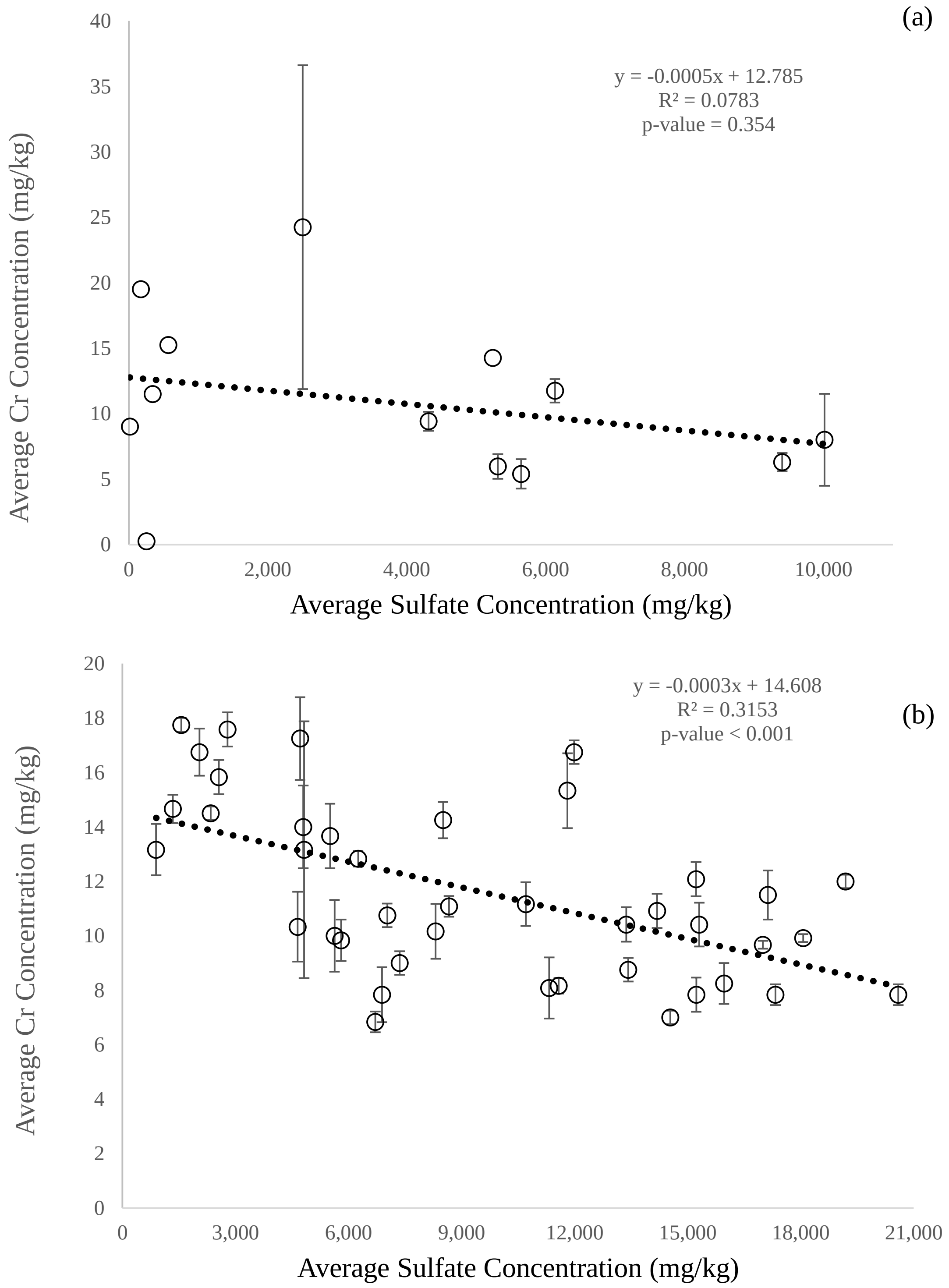


Figure 29 Scatter plot depicting (a) no significant trend between Cr (p=0.354) and SO4 concentration in PAU/DEF 24-12.30 and (b) significant trend between Cr (p<=.001) compared to SO4 concentration in PAU/DEF 24-heave.

6.4 Results for Paulding and Defiance County XRD Analysis

XRD analyses were conducted on samples from all four projects. Triplicate tests were conducted on the 11 selected samples from 24-12.30 including 6 which tested >3,000 mg/kg SO_4. Duplicate tests were conducted on five of the core samples from 12.30 with quadruplicate testing on B-11 for a total of six cores analyzed. Duplicates of ten and triplicates of two cores were also tested from the twelve 4.51 core samples. Finally, duplicate and triplicate tests were randomly assigned and conducted on the 35 of the PAU/DEF 24-Heave samples. The most dominant minerals present throughout PAU/DEF samples were quartz, dolomite, calcite and corundum. The presence of corundum (Al_2O_3) in a number of these samples is noteworthy because this mineral may have been a source of the aluminum required for ettringite formation contributing to the sulfate-induced heave which occurred along SR 24. Additionally, eskolaite, Cr_2O_3, was identified in 2/33, 3/14, 6/26 and 15/56 test samples from 12.30 ground, 12.30 cores, 4.51 cores and Heave projects, respectively, potentially explaining higher concentrations of total Cr measured in PAU/DEF samples. The primary sulfate bearing mineral identified in the PAU/DEF soils was gypsum (Table 21). Four of the top five angular peak locations, 2θs, in typical gypsum diffraction patterns, are in close proximity to angular location in diffraction patterns of quartz, dolomite and calcite (Table 22). As mentioned above these are among the most dominant minerals within PAU/DEF soils. Identifying the presence of peaks at ~11.7 2θ mitigated the masking effects of these shared angular locations on gypsum identification. Even though 6 soils from the 24-12.30 ground project tested for mineralogy had SO_4 concentrations above 3,000 mg/kg, gypsum was only identified in the three replicate test

Table 21 Dominant sulfate minerals identified in Paulding and Defiance Counties Soils Tested.

Project	Gypsum $CaSO_4 \cdot 2H_2O$	Anhydrite $CaSO_4$	Arcanite K_2SO_4	Lanarkite $Pb_2(SO_4)O$	Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
24 Ground	3/33	1/33	1/33	1/33	0/33
24 Cores	2/14	0/14	0/14	0/14	0/14
PAU 24-4.51 Cores	24/26	5/26	0/26	0/26	0/26
DEF Heave	74/90	0/90	0/90	0/90	3/90
DEF Heave Acid Wash	0/4	1/4	0/4	0/4	0/4

Table 22 Gypsum's shared angular peak locations (Bold font highlights non-shared angular location at 11.72 2θ).

Gypsum Pattern Locations		Shared Pattern Locations		
2θ	% Intensity	2θ	% Intensity	Mineral
20.82	100	20.87	19.93	Quartz
11.72	**88.21**		Not Shared	
29.29	73.3	29.43	100	Calcite
31.25	52.99	31	100	Dolomite
33.59	36.27	33.38	5.64	Dolomite

samples of 29845 containing an average 10,016 mg/kg SO_4 (3 replicates) (Figure 30(a)). Gypsum, surprisingly was not identified in sample 29844 collected from the same boring, but at a depth of 1.5-3' and containing a similar concentration of SO_4 at 9,408 mg/kg (Figure 30(b)). The same was true for 12.30 cores as the only sample indicating the presence of gypsum was core sample B-2 (2 replicates) also collected from the same boring as 29844 & 29845. Gypsum was easily identified in all but one 24-4.51 core sample, replicate tests of core B1-0-S7. A number of the diffractograms from these sample contain very high peak intensities for gypsum (Figure 31). Initial analysis of PAU/DEF 24-Heave

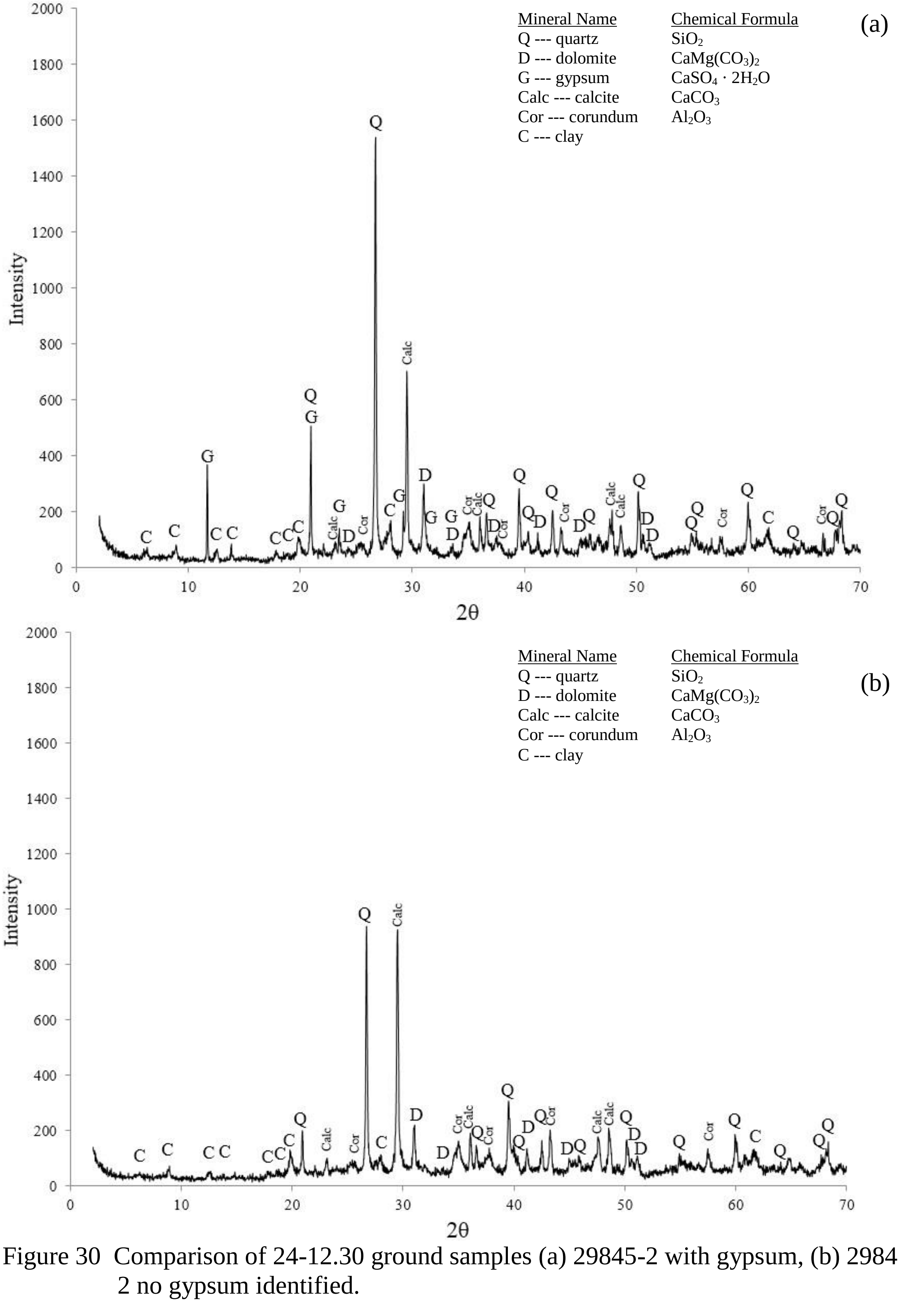


Figure 30 Comparison of 24-12.30 ground samples (a) 29845-2 with gypsum, (b) 29844-2 no gypsum identified.

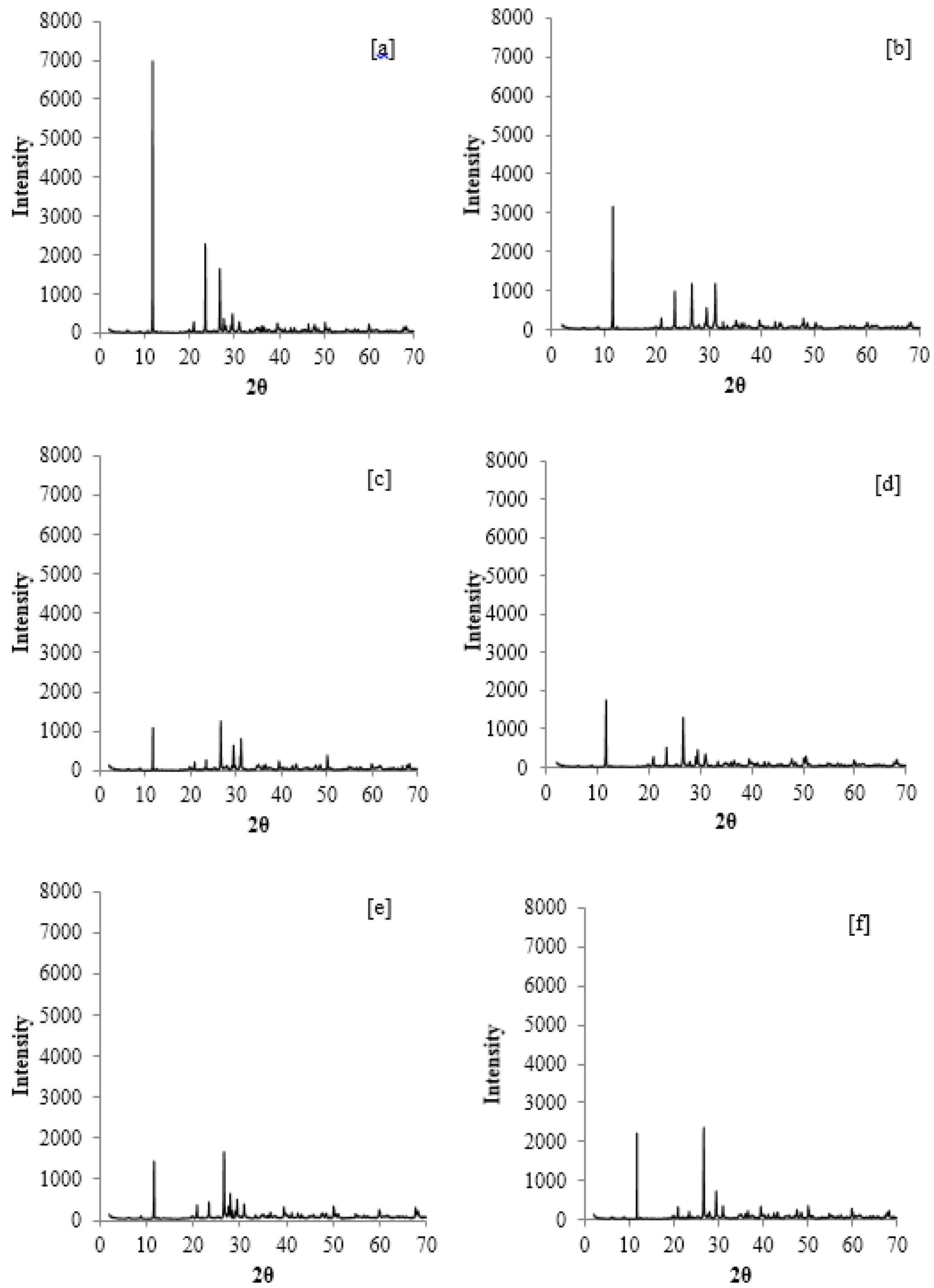


Figure 31 X-ray diffractograms depicting high intensity at 11.7 2θ indicating presence of gypsum in [a] B1-0-11-2, [b] B2-0-S2B-2, [c] B1-1-S13-1, [d] B1-1-S19-1, [e] B2-0-S5-1, and [f] B2-0S3-2.

XRD samples was focused on identifying the presence of ettringite because formation of this mineral is believed to be the mechanism which caused heave of US-24 were these soil samples were collected. Diffractogram analysis for identification of ettringite was conducted on six random samples as an initial inspections. None of these selected test samples indicated the presence of ettringite. However, others have indicated failure to identify ettringite through XRD testing could be due to: expansive material can be lost in subsampling or sample preparation; ettringite may not compose more than 10% of the sample used for XRD testing and calcite can mask the ettringite in XRD analysis (Kota et al., 1996). They recommend acid washing the samples to remove calcite. The four samples with the highest soluble SO_4 concentration were subjected to acid wash as described in section 3.3.3, dried and XRD tests were conducted. Again, although calcite was removed, (Figure 32) ettringite was still not identifiable in these samples. Subsequent analysis of additional samples from PAU/DEF 24-Heave did identify ettringite in 3 (S-9, replicate 1 (Figure 33(a)), S-13 replicate 2 (Figure 33(b)) and S-39 replicate 2) of the 90 samples. Both of the S-9 and S-13 samples had similar concentration of SO_4, ~11,000 mg/kg, and total Al 22,667±388 mg/kg for S-9 and 24,217±3,969 for S-13 (Table 19). Further tests on soils from 24-Heave should be conducted including scanning electron microscope (SEM) to more accurately verify the presence of ettringite.

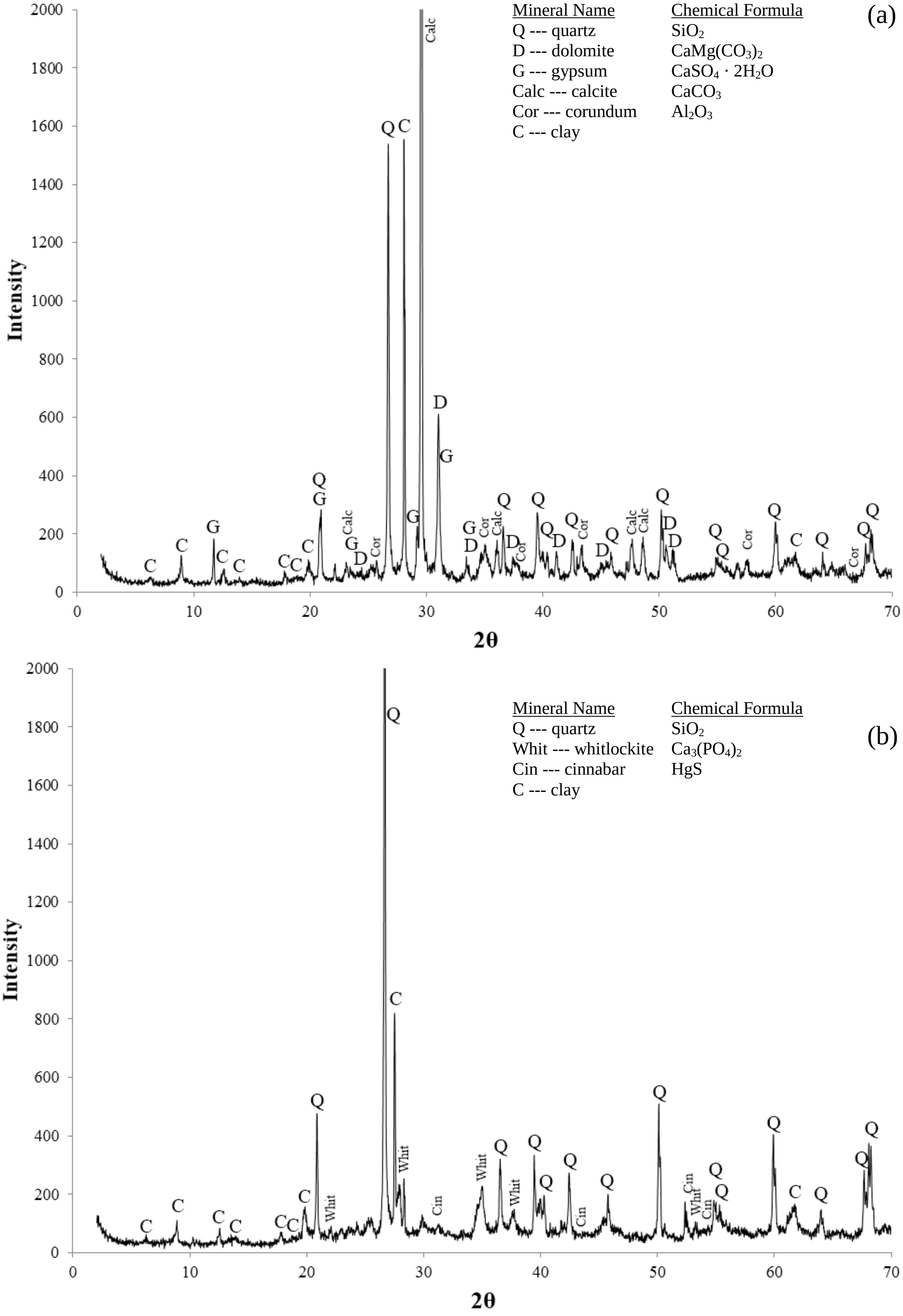


Figure 32 Comparison of PAU/DEF 24-Heave sample S-7 (a) without acid wash, (b) with acid wash. Neither indicate the presence of ettringite.

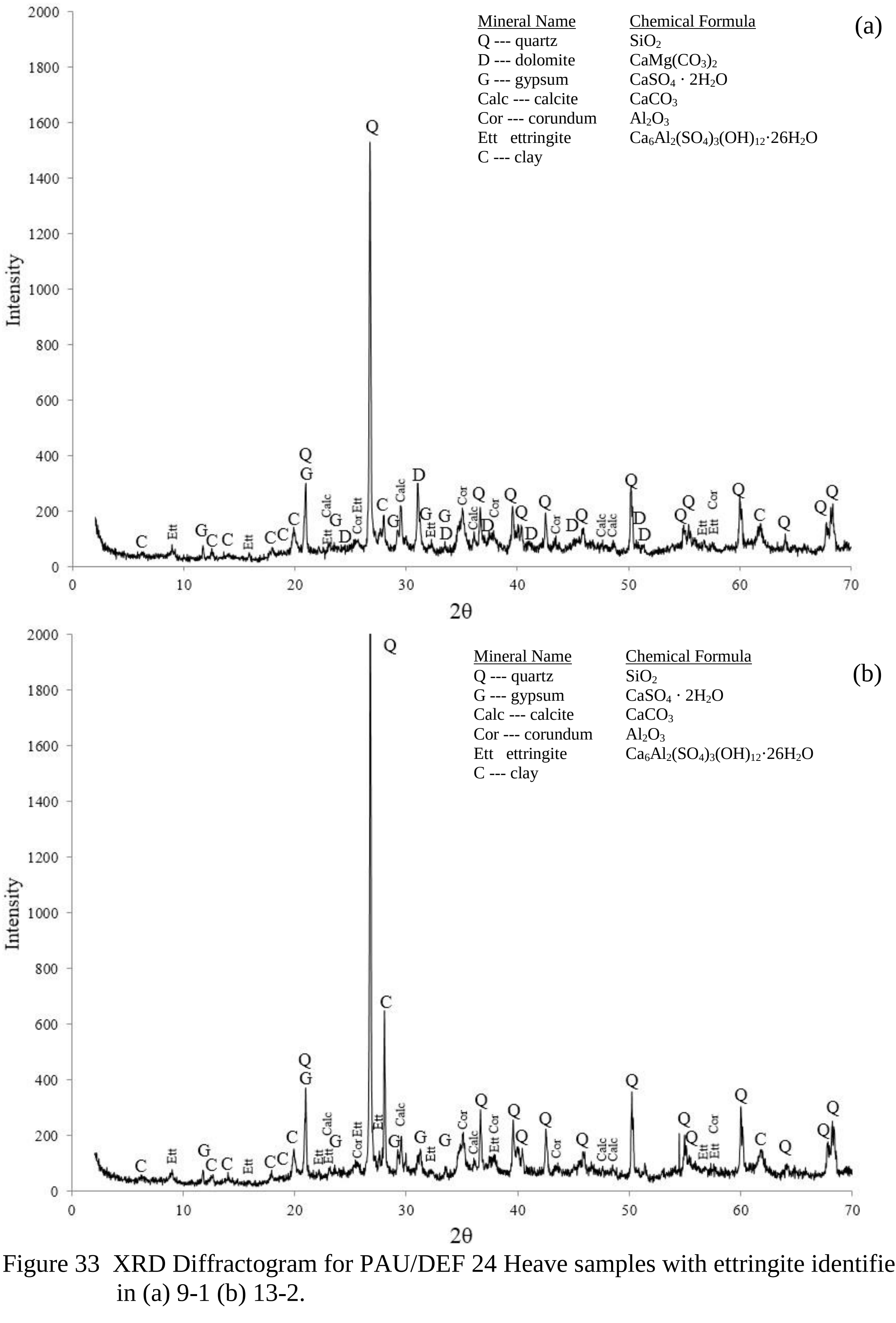


Figure 33 XRD Diffractogram for PAU/DEF 24 Heave samples with ettringite identified in (a) 9-1 (b) 13-2.

6.5 Discussion of Paulding and Defiance County Soil Testing Results and Potential SO_4 Sources

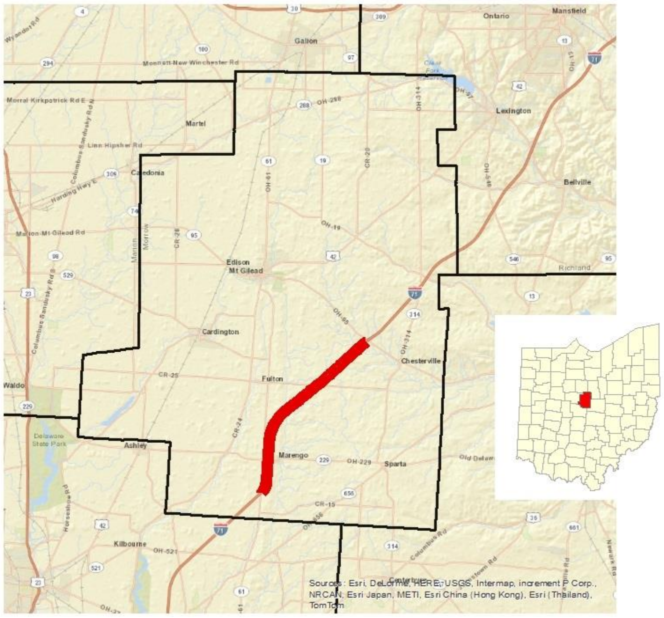
Soils along the Paulding-Defiance SR-24 project swelled resulting in distress pavement cracking in 2013. Initial soluble SO_4 testing of bulk and core samples from 24-12.30 caused concern as a number of samples tested >3,000 mg/kg SO_4. These concerns were heightened when soluble SO_4 results for cores from 4.51 were all measured in excess of 7,000 mg/kg SO_4 and many much higher (Table 17). ODOT officials were notified immediately in attempt to mitigate potential problems with heave. Unfortunately lime stabilization of these soils had already been completed. Later in 2013, damage to pavement surfaced was noticed and subsequent testing identified ettringite within the stabilized subgrade. Analysis of all the Paulding-Defiance soils tested, shows over 80% of the soils from this area measured >3,000 mg/kg, and many >10,000 mg/kg. These high average soluble sulfate concentration indicate high risk for sulfate induced heave and that SO_4 did not likely limit ettringite growth. Origin of Paulding and Defiance County surface soils, like Lake SR-2 soils, are lacustrine deposits (Figure 4 in section 2.3.2). Additionally, similar to Lake County samples, XRD analysis indicated the primary sources of SO_4 are calcium sulfates, gypsum and anhydrite which have been found in northwest Ohio (Stueber 1972) and in Ohioan lacustrine deposits (Wolfe 2001; Szabo 1986). Total Fe concentration were lower than those found in Lake and other regions within the state. The bedrock under the surface soils is Devonian, which contains the Fe bearing pyrite, however groundwater well records indicate the bedrock is covered by a clay layer approximately 50 feet thick (ODRN 1990; ODNR 2002). The depth of bedrock below ground surface and low hydraulic conductivity of clay soils limit the oxidation potential pyrite within bedrock shale. Total Al concentrations were higher in Paulding and Defiance soils and these higher levels are likely due to the soil being dominantly clay, known to contain higher Al concentrations than silt, loams and sand (Mirasol 1920). The soil type identified by the USGS soil survey is Paulding Clay (Soil Survey Staff 2014). Groundwater, although high in sulfur content (Raab 1986; Schmidt 1982) again is limited by the highly impermeable clay layer. Agricultural activities are high in Paulding and Defiance counties (Figure 8 and 9 in section 2.4) with 258,000 and 232,000 acres of farmland respectively reported in 2010 and Paulding ranking 6th of all counties in the state in wheat production (ODA 2010). The realignment of US-24 required the acquisition 1582 acres of farmland for road right of way. This affected 214 farm operations and within agriculture districts, eight properties and 178.1 acres (FWA 2012). No reports of gypsum amendment to farmland were identified, however, the conditions of the soil would likely benefit from gypsum application. Industrial activity is minimal and no coal-fired power plants are located in Paulding or Defiance counties. Therefore dry and wet deposition of H_2S could be considered at normal background levels for the region. Finally, toxic release inventory data showed neither Paulding nor Defiance counties had a repeated history of S-bearing releases.

CHAPTER VII

MORROW COUNTY SOILS

7.1 Summary of Morrow County Soil Analysis

Lime stabilization was also selected by ODOT for three projects along Interstate-71 in Morrow County, Ohio: MRW 71-11.50, MRW 71-12.19 and MRW 71-3.17. Samples from MRW 71-11.50 and MRW 71-12.19 were provided to the University of Akron lab by ODOT in August of 2012 and tested for soluble sulfate concentration. Additional soil samples from MRW 71-3.17, collected by consultants, were provided by ODOT for testing after several of the samples tested high in soluble sulfate. Initially, ODOT collected boring samples for the MRW 71-3.17 project at 122 locations and conducted TEX-145E tests finding three locations with soluble sulfate concentration in excess of 3,000 mg/kg. After award of project construction, consultants collected additional bulk samples per ODOT specifications (ODOT Supplemental Specification 1120) one every 5000 ft^2, for a total of 70 samples. These initial bulk samples were collected in the unpaved area 8’ offset from the inside or outside shoulder. Consultants conducted TEX-145E tests on these 70 bulk samples finding 18 out of 70 in excess of the 3,000 mg/kg limit and 14 of these 18 samples having soluble sulfate concentrations $\geq$ 8,000 mg/kg. An additional 21 soil samples were collected 32’ left of the centerline of the road to further delineate high sulfate areas. Seven samples at 50’ increments along Interstate 71 were taken at three separate areas. These soil samples were tested solely for soluble sulfate using TEX-145E with only one of the 21 above the 3,000mg/kg limit. Finally, five boring samples from underneath the shoulder pavement one foot from the edge of pavement where collect from the same locations where sample in the first 70 collected by the consultants tested above 8,000 mg/kg. This sampling strategy was conducted based on the theory that high sulfate levels in the median could be due to water run-off or deicing chemicals. All five of these pavement samples tested by the consultants were below 3,000 mg/kg with a high of 1,187 mg/kg for boring BS-15P. Fourteen of the 18 soils testing above 3,000 mg/kg sulfate and the five corresponding pavement soil samples were provided to the University of Akron lab for testing. The high variability in sulfate concentration level and consistency caused ODOT to collect an addition 24 bulk soil samples along the MRW 71-3.17 project. These samples also were sent to the University of Akron lab for testing and assigned a project number of MRW 71-3.22. Approximate plan location is provided in Figure 34 and a summary of Morrow County soil testing is given below in Table 23.



Sources: Esri, DeLorme, HERE, USGS, Intermap, increment P Corp., NRCAN, Esri Japan, METI, Esri China (Hong Kong), Esri (Thailand), TomTom

Figure 344 IR-71 Project Location in Southern Morrow County

Table 23 Summary of Morrow County Soil Testing Schedule

Project	Number of Soil Samples	Number of TEX-145E Tested Soils	Number of Total Fe Tested Soils	Number of Total Al Tested Soils	Number of Total Cr Tested Soils	Number of XRD Tested Soils
MRW 71-12.19	8	8	3	1	0	3
MRW 71-11.50	45	45	7	7	7	7
MRW 71-3.17	19	19	19	19	19	19
MRW 71-3.22	36	36	28	28	28	8

7.2 Results for Morrow County Soluble SO_4 Analysis

As described in Table 23, TEX-145E tests for soluble sulfate were conducted on all soil samples from Morrow County provided by ODOT and the results are provided in Tables 24– 27. Soil samples from MRW 71-12.19 contained both coarse and fine ground soils. Soil sample S-18f with a soluble sulfate concentration of 4,921±149 mg/kg was the only sample out of the eight above the 3,000 mg/kg limit (Table 24). Additionally, samples from MRW 71-11.50 were comprised of coarse and fine ground soils. A total of six of the 45 soils measured above the 3,000 mg/kg limit and soil sample 14f measured the highest at 12,099 mg/kg (Table 25). There were a total of 19 soils tested from MRW 71-3.17; 14 of which had tested above 3,000 mg/kg soluble sulfate by consultants after award of the

Table 24 Soluble Sulfate Results for MRW 71-12.19. Bold font for SO4 >3,000 mg/kg (n=3)

Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg))
S-15c	560±23	S-17c	421±69
S-15f	1380±46	S-17f	612±10
S-16c	525±12	S-18c	2180±138
S-16f	686±28	S-18f	**4921±149**

Table 25 Soluble Sulfate Results for MRW 71-11.50. Bold font for SO4 >3,000 mg/kg (n=1,2 or 3)

Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)
2	**8804±479**	28	113±19	24f	194
3	691	29	1064	26f	187±17
4	**9719±326**	30	531±12	27f	80±16
6	847	33	138±34	31f	73±126
8	2286±8	38	184±26	32f	244±20
10	0	41	424±69	35f	87±3
11	177.4	42	322	36f	547±17
12	**3882±408**	44	131±19	37f	126
13	1373±90	45	195±32	39f	360
16	**4591±117**	13f	1,468±5	40f	874±44
18	796	14f	**12,099±254**	43f	180±156
20	0±0	15f	**8,192±244**	47f	317
22	13±23	17f	1480	5f	479
23	1741±37	19f	0	7f	328
25	0	21f	0	9f	312

construction bid. ODOT provided 14 of the 17 soil samples collected and tested above 3,000 mg/kg soluble sulfate by consultants after award of the construction bid. The other five samples were the corresponding pavement cores collected adjacent to five of the sample locations which tested above 3,000 mg/kg soluble sulfate. All of the pavement cores tested below 3,000 mg/kg with a high in soil sample BS-24P of 1,097±42. Ten out of the 14 shoulder soil sample tested above 3,000 mg/kg with a high of 8,221±391 mg/kg soluble sulfate (Table 26). Finally, TEX-145E tests were conducted on 36 bulk soil samples collected by ODOT from MRW 71-3.22. Sample 5, testing at 4,902±406 mg/kg, was the only one of the 36 samples that tested above the 3,000 mg/kg soluble sulfate limit (Table 27).

Table 26 Soluble Sulfate Results for MRW 71-3.17. Bold font for SO4 >3,000 mg/kg (n=3)

Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)
BS-10	**4919±272**	BS-46	**7093±497**	BS-10P	439±62
BS-15	**8221±391**	BS-48	1802±102	BS-15P	1051±97
BS-23	**3890±189**	BS-49	**4250±263**	BS-23P	293±56
BS-24	**6462±720**	BS-50	**5564±405**	BS-24P	1097±42
BS-27	2319±65	BS-51	**5980±150**	BS-27P	940±22
BS-37	1155±25	BS-56	**4427±483**		
BS-38	**4529±169**	BS-66	2543±78		

Table 27 Soluble Sulfate Results for MRW 71-3.22. Bold font for SO4 >3,000 mg/kg (n=3)

Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)	Soil Identification	Soluble Sulfate (mg/kg)
1	524±33	13	252±13	25	146±23
2	116±36	14	92±28	26	316±180
3	195±44	15	340±46	27	348±136
4	724±73	16	201±22	28	216±28
5	**4902±406**	17	581±19	29	1320±157
6	518±3	18	516±4	30	57±60
7	112±41	19	107±5	31	644±25
8	3±5	20	124±15	32	1079±18
9	305±31	21	82±17	37	70±20
10	342±9	22	281±219	38	233±20
11	222±32	23	143±32	39	100±7
12	265±22	24	86±149	40	574±14

7.2.1 Statistical Analysis of Average Soluble SO_4 Concentration in Morrow County Soils

Statistical comparison of average sulfate concentration of MRW 71-12.19, MRW71-11.50 and MRW 71-3.17 was conducted using a one way ANOVA with the project being the treatment factor. MRW 71-3.22 sulfate results were not included in this statistical analysis because these samples were not randomly selected, rather 14 of the 19 soils within samples from this project provided by ODOT previously tested above the 3,000 mg/kg sulfate limit. The one-way ANOVA for the three projects listed above failed to show a statistical difference in mean soluble sulfate level between the projects at $\alpha=0.05$ as the p-value was 0.096. The mean sulfate concentrations for these projects are: 1403±1536 mg/kg, 1459±2804 mg/kg and 448±815 mg/kg for MRW 71-12.19 (N=8), MWR 71-11.50 (N=45) and MRW 71-3.17 (N=36) respectively. The ten corresponding pavement and shoulder samples from Project MRW 71-3.22 were analyzed first with a two-way ANOVA which showed no statistical significance based on sample locations. The soluble sulfate results for these 10 samples were then analyzed using a one-way ANOVA with whether the samples were shoulder samples or pavement samples as the treatment factor. The shoulder samples were statistically significantly higher (p-value – 0.003) in soluble sulfate than the pavement samples with means of 5,162±2,281 mg/kg and 764±371 mg/kg, respectively.

7.3 Results for Morrow County Total Metal Analysis

The total metal testing schedule for Morrow County soil samples is provided in Table XX. Soils tested above the 3,000 mg/kg soluble sulfate limit using TEX-145E where subjected to acid digestion (EPA 3050B) and subsequent ICP analysis for total Fe, Al and Additionally, for MRW 71-11.50 and MRW 71-12.19 at least one soil testing below 3,000 concentration of these metals correlated with sulfate concentration (Table 28-31).

Table 28 Average ICP measured total Fe and Al concentration using EPA acid digestion method 3050B for select MRW 71-12.19 soils (n=3).

Soil Identification	Soluble SO_4 (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)
16f	686±28	21,658±1,925	9,300±451
17f	612±10	22,667±838	
18f	4,921±149	30,875±2,676	

Table 29 Average ICP measured total Fe, Al & Cr concentration using EPA acid digestion method 3050B for select MRW 71-11.50 soils (n=3).

Soil Identification	Soluble SO_4 (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)	Average Cr (mg/kg)
2	8,804±479	25,917±3,595	9,758±1,185	7.4±0.8
4	9,719±326	24,075±3,454	7,817±1,216	10.0±1.6
11	177	24,608±508	9,625±601	9.3±1.2
12	3,882±408	29,333±1,734	15,567±4,070	9.9±0.1
16	4,591±117	26,325±677	11,333±1,275	8.7±0.7
14f	12,099±254	23,150±3,659	8,908±1,055	6.8±0.7
15f	8,192±244	25,267±791	10,392±288	7.8±0.8

Table 30 Average ICP measured total Fe, Al & Cr concentration using EPA acid digestion method 3050B for select MRW 71-3.17 soils (n=3).

Soil Identification	Soluble SO_4 (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)	Average Cr (mg/kg)
BS-10	4,919±272	30,658±6,810	12,283±2,722	6.5±1.3
BS-10P	439±62	28,508±1,050	11,275±929	3.6±0.5
BS-15	8,221±391	38,800±16,401	8,475±3,781	5.8±0.5
BS-15P	1,051±97	27,883±6,665	8,958±2,009	5.7±0.8
BS-23	3,890±189	29,567±4,041	11,500±1,300	7.0±0.0
BS-23P	293±56	26,233±2,056	12,375±1,385	10.7±1.0
BS-24	6,462±720	27,142±3,099	8,483±1,094	2.8±0.6
BS-24P	1,097±42	30,733±3,675	9,817±1,416	7.3±0.8
BS-27	2,319±65	29,500±3,328	10,258±1,380	4.8±0.4
BS-27P	940±22	27,792±938	11,167±1,028	6.9±1.4
BS-37	1,155±25	31,150±4,120	12,575±2,252	13.6±0.9
BS-38	4,529±169	24,917±945	10,092±491	7.7±0.4
BS-46	7,093±497	26,133±1,563	10,867±795	9.7±0.4
BS-48	1,802±102	71,142±2,952	25,025±2,101	10.2±0.7
BS-49	4,250±263	35,892±9,190	12,817±3,455	10.8±0.9
BS-50	5,564±405	28,858±1,406	11,775±346	7.5±0.9
BS-51	5,980±150	25,767±1,821	8,592±600	8.2±0.8
BS-56	4,427±483	27,917±744	9,217±265	7.7±0.4
BS-66	2,543±78	32,983±3,043	12,750±663	10.3±1.7

Table 31 Average ICP measured total Fe, Al & Cr concentration using EPA acid digestion method 3050B for select MRW 71-3.22 soils (n=3).

Soil Identification	Soluble SO_4 (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)	Average Cr (mg/kg)
5	4,902±406	39,775±3,642	11,967±1,068	4.8±0.7
10	342±9	34,558±3,426	8,958±734	2.2±0.5
11	222±32	37,592±1,079	10,967±669	2.7±0.8
12	265±22	33,617±3,590	8,883±1,451	1.2±0.6
13	252±13	34,967±1,943	9,925±1,819	1.3±0.3
14	92±28	29,583±1,005	9,483±359	1.7±0.4
15	340±46	29,958±3,165	10,392±1,632	2.0±0.4
16	201±22	24,308±1,667	6,933±213	0.1±0.1
17	581±19	35,725±3,141	11,758±966	3.0±0.3
18	516±4	27,492±2,191	9,892±2,183	3.1±0.4
19	107±5	25,167±1,017	7,558±554	4.3±1.1
20	124±15	26,242±3,519	8,092±1,104	5.1±0.4
21	82±17	23,425±1,386	5,008±1,075	0.0±0.0
22	281±219	26,975±4,385	8,783±1,858	3.6±0.4
23	143±32	24,592±1,151	9,683±1,429	4.8±0.1
24	86±149	23,675±3,748	8,225±1,089	2.6±0.1
25	146±23	25,150±463	13,000±915	15.9±0.6
26	316±180	28,067±3,740	10,542±1,755	13.0±1.1
27	348±136	25,175±1,203	10,017±1,849	12.8±0.5
28	216±28	21,792±2,482	7,442±1,059	14.3±0.5
29	1,320±157	24,233±1,809	9,467±802	11.7±0.1
30	57±60	26,617±2,311	8,658±625	12.1±0.1
31	644±25	25,458±1,188	8,742±430	13.0±0.4
32	1,079±18	27,208±2,030	7,967±1,234	2.3±0.5
37	70±20	24,058±1,960	8,633±3,134	2.3±0.1
38	233±20	20,225±5,295	10,425±2,438	14.1±0.5
39	100±7	22,767±5,753	9,525±2,972	11.4±0.5
40	574±14	25,667±3,541	10,450±1,721	9.1±5.7

7.3.1 *Total Metal Statistical Analysis*

Scatter plots of the resulting sulfate concentration on the x-axis and average Fe and Al concentrations on the y-axis (Figure 35) showed there was no significant correlation between sulfate concentration and either Fe ($R^2 = 0.0011$) or Al ($R^2 = 0.0019$) concentration throughout the Morrow County soils. This was confirmed for Fe concentration by statistical analysis of average Fe concentration using a general linear model with sulfate range (either below or above 3,000 mg/kg) and project number as treatments. Neither the sulfate range (p-value – 0.194) nor the project number (p-value – 0.243) treatments had a

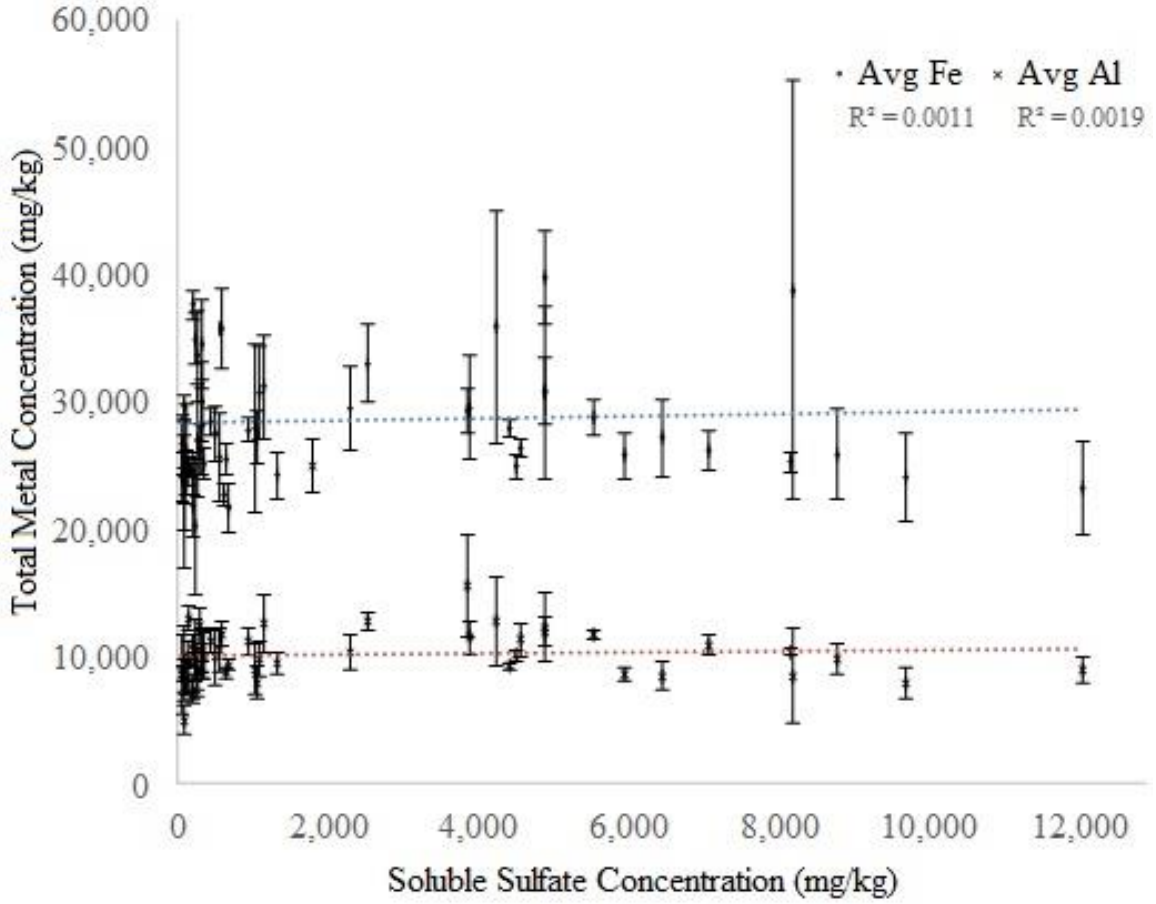


Figure 35 Scatter plot depicting no correlation between Fe (R2=0.0011) or Al (R2=0.0019) concentration and soluble sulfate concentration.

main effect or interactive effect (p-value – 0.114) on the Fe concentration. The statistical analysis for Al concentration was conducted on projects MRW 71-11.50, MRW 71-3.22 and MRW 71-3.17 (MRW 71-12.19 was omitted from statistical analysis because Al concentration was tested on only one soil from this project.). Similarly, the GLM for average Al concentration showed sulfate range had neither a main nor interactive effect on Al concentration. However, there was statistical evidence for the effect of project number (p-value – 0.026) on Al concentration using a one-way ANOVA with MRW. Samples from MRW 71-3.17 had statistically significant higher mean Al concentrations at 11,489±3,607 mg/kg than MRW 71-3.22 at 9,335±1,645 mg/kg. There was no statistical difference in the mean Al concentration of MRW 71-11.50 at 10,486±2,489 mg/kg compared to results from the two other locations. This is somewhat surprising because samples from MRW 71-3.22 and MRW 71-3.17 were collected along the similar sample location along Interstate 71. The higher results for Al in the MRW 71-3.17 project could be due to the fact that 14 out of 19 of the samples were collected from the road shoulder. However, subsequent one-way ANOVA analysis of the both Fe and Al concentrations indicated that whether the sample was collected from the shoulder or pavement did not have a statistically significant effect on mean Fe concentration at 28,230±1,631 mg/kg for pavement samples and 31,133±4,474 mg/kg for shoulder samples (p-value – 0.210) or mean Al concentration at 10,718±1,338 mg/kg for pavement samples and 10,200±1729 mg/kg for shoulder samples (p-value – 0.610).

7.4 Results for Morrow County XRD Analysis

XRD analysis were conducted on samples from all four projects. Triplicate tests were conducted on all 14 shoulder and 5 pavement samples from 71-3.17 as well as soils above 3,000 mg/kg and at least one soil below 3,000 mg/kg from 71-11.50, 77-15.19. XRD tests were also conducted on 8 soil samples from MRW 71-3.22, including duplicates of sample 5, the only soil from this project testing above 3,000 mg/kg. The most dominant sulfate source for Morrow County soils was gypsum (Table 32), present in 29/42 samples from 71-3.17 shoulder, 17/21 samples from 71-12.19 and 4/9 samples from 71-11.50. Gypsum was not identified in any samples from 71-3.22 or 71-3.17 pavements. This is expected due to the low soluble SO_4 results for these soils, with the exception of the two test samples from soils samples 5 in 71-3.22, all measured under 3,000 mg/kg. Pyrite was identified in 7/15 samples tested from pavement samples of 71-3.17 and soil sample number 4 from 71-12.19. Devonian shale, known to contain pyrite (Hoover 1960; Schieber & Riciputi 2004), is the parent bedrock for part of Morrow County (Figure 5 in section 2.4). Identification of pyrite within the 71-3.17 pavement samples could explain the difference in soluble sulfate levels between pavement and shoulder samples within this project. The samples in the shoulder have greater oxidation potential as they are not directly under the pavement and possible subject to increased construction activities which exposed pyrite to the oxygen (Harris et al., 2004). A comparison of diffraction pattern between shoulder (24S) and pavement sample (24P) is provided in Figure 36. Another

Table 32 Dominant sulfate minerals identified Morrow County Soils Tested.

Project	Gypsum $CaSO_4{\cdot}2H_2O$	Anhydrite, syn $CaSO_4$	Arcanite, syn K_2SO_4	Lanarkite, syn $Pb_2(SO_4)O$	Pyrite FeS_2
71-3.22	0/9	0/9	0/9	0/9	0/9
71-3.17 Shldr	29/42	0/42	4/42	6/42	0/42
71-3.17 Pave	0/15	3/15	2/15	0/15	7/15
71-12.19	17/21	0/21	1/21	4/21	2/21
71-11.50	4/9	0/9	0/9	1/9	0/9

theory for higher sulfate concentrations in the shoulder samples is sulfate contamination from de-icing media. As mention above, ODOT collected 122 soil samples in this project area in August of 2011 and only 3 soil samples tested above 3,000 mg/kg soluble sulfate. The shoulder samples collected in March and April of 2013 were adjacent to, or in the same location as the samples collected in 2011. Sulfate has been identified as the greatest impurity in sodium chloride road salts (Granato 1996). Per ODOT request shoulder samples diffractograms were also analyzed for halite the dominant mineral in de-icing media. Halite was not able to be identified as present in the XRD diffractograms of shoulder or pavement samples (Figure 37). This however could be due to the greater mobility of sodium chloride, 359 g/L in cold water (Perry & Green 2008) causing it to migrate off site through run-off (Green et al., 2008).

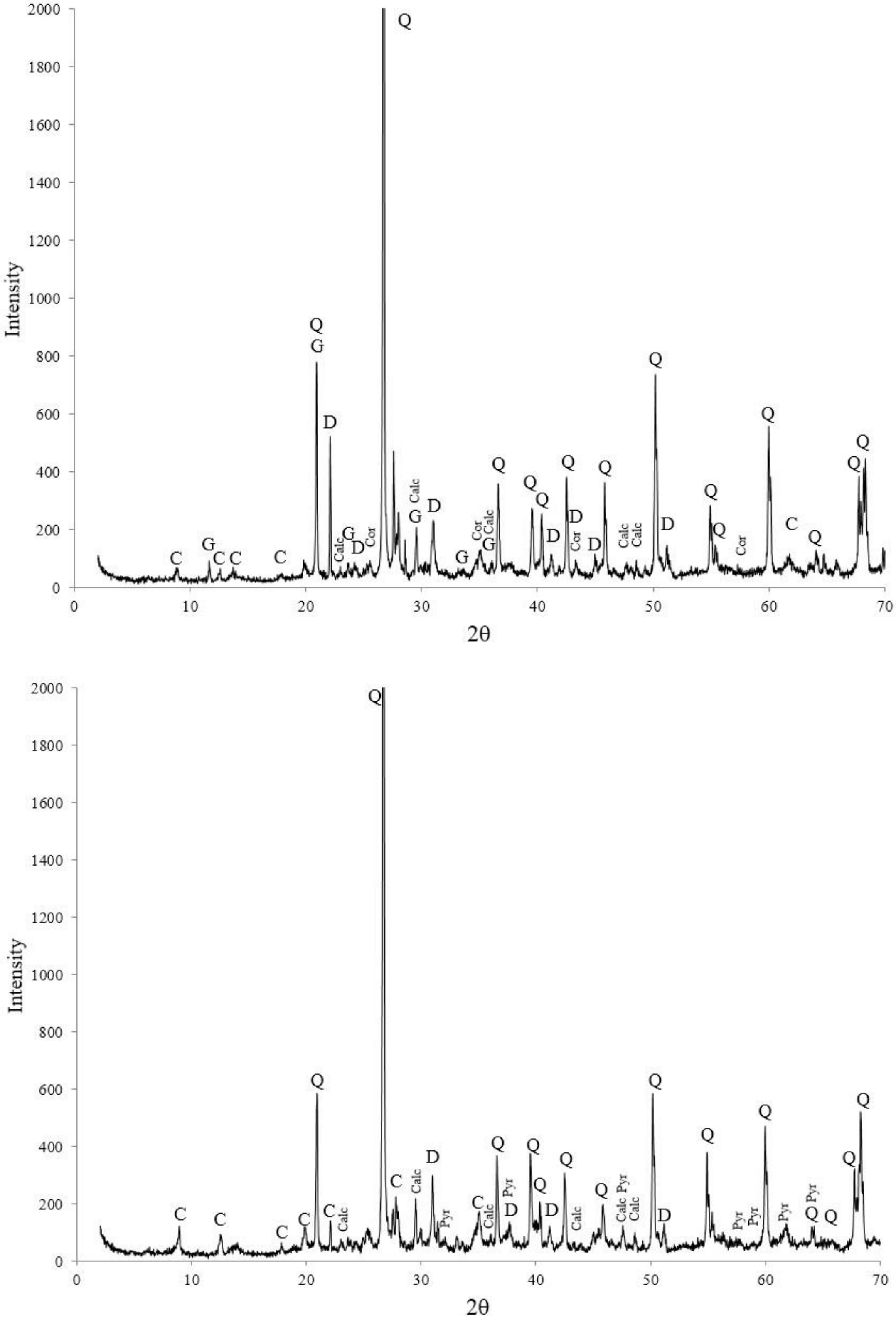


Figure 36 Comparison of MRW 71-3.17 (a) B24S, shoulder sample with gypsum and, (b) B24P pavement sample with pyrite.

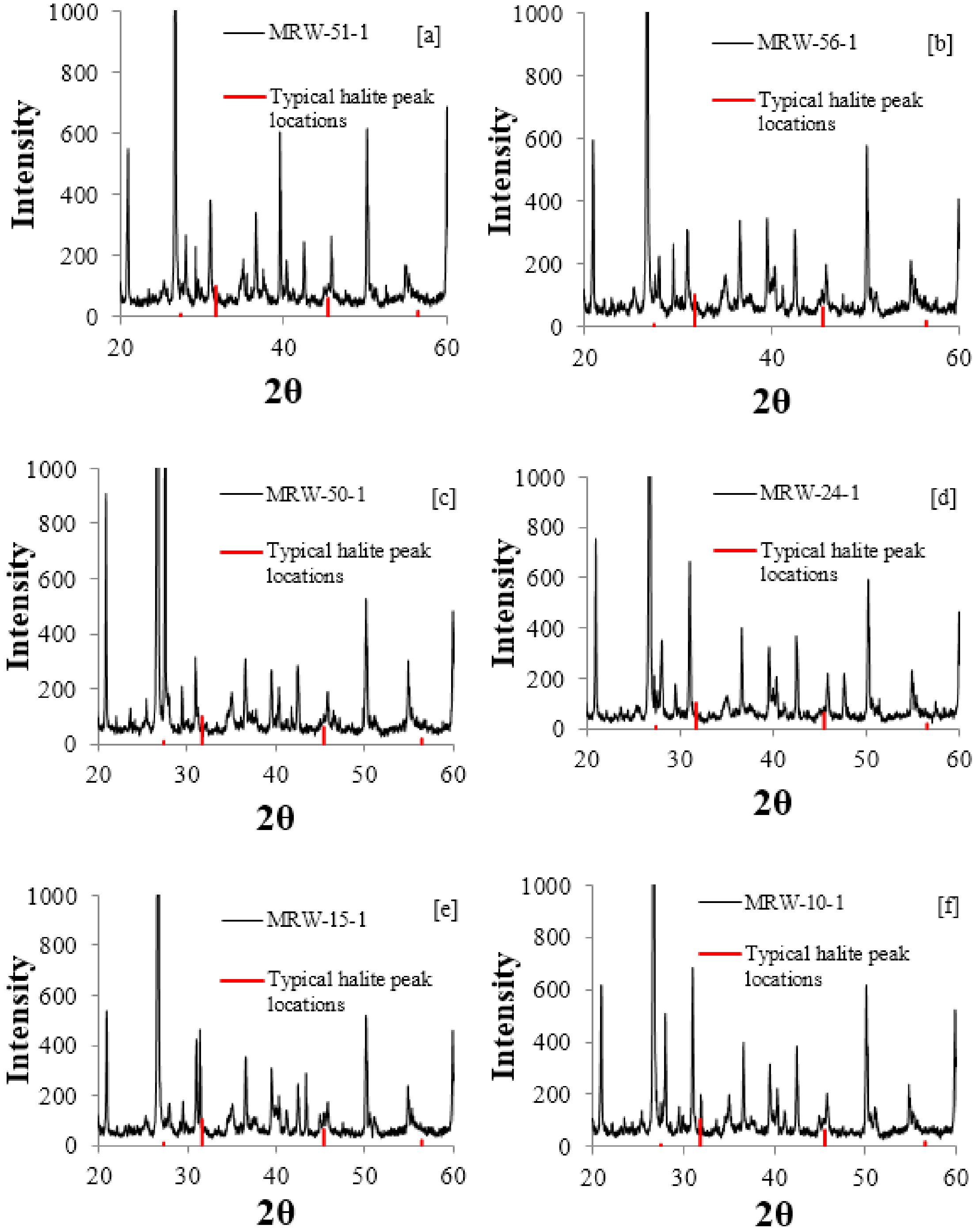


Figure 37 Halite not identified in XRD diffraction patterns of several MRW 71-3.17 samples.

7.5 Discussion of Morrow Soil Testing and Potential Sulfate Sources

Sulfate concentrations varied throughout the different projects and even in similar location, but collected a season apart, as was the case with 71-3.17 and 71-3.22. From the 108 soils tested, 83% measured under 3,000 mg/kg SO_4 yet there were eight samples with SO_4 measured greater than 5,000 mg/kg. Total Fe concentrations were higher compared to soils from Lake and Paulding/Defiance counties and averaged 28,588±7,227 mg/kg. These higher Fe concentrations verify the presence of pyrite in the soils tested. Pyrite identified within the surface soil is a concern as exposure of pyritic soil to the atmosphere during construction activities can lead to oxidation and subsequent release of sulfate into soils (Kota et al., 1996).

Total Al concentrations measured lower than Paulding/Defiance soil which is not surprising as the Morrow County Soil Survey indicates the primary soil type throughout these projects is a silty loam, Centerburg Silt Loam, compared to clay in Paulding and Defiance (Mirasol 1920). The primary natural source of sulfate is the Devonian bedrock which underlays the western half of the county (ODGS 2006). Pyrite was identified in samples with measure SO_4 concentrations <3,000 mg/kg and even in samples above 3,000 mg/kg (sample 4 in MRW 71-12.19). Again pyrite is a known constituent in Devonian shale (Hoover 1960) and Devonian bedrock in Delaware County, immediately south of Morrow is rich in pyrite (Angle et al., 2005). Ground water in these project areas in can contain H2S and depth to ground water varies and ground water well record ground water depths as high as 0.7 ft from the surface (ODNR 2011) with the majority reporting groundwater at depths around 18-24 ft (ODNR 1980). An anthropogenic source of SO_4 could be gypsum as farm amendment. Although Morrow County is not heavy in agriculture, 41st ranked out of 88 counties in the state, farmland lies adjacent to IR-71 throughout the majority of these IR-71 projects. Deicing materials are also a potential source as sulfate in the greatest impurity in sodium chloride road salt (Granato 1996). Halite was not identified via XRD testing, but this could be to the higher solubility at 359 g/L in cold water compared to gypsum at 2.23 g/L (Perry & Green 2008).

CHAPTER VIII

ODOT SOIL BORINGS FROM 2011-2012

8.1 Results for 2011-2012 Soil Borings Analysis

ODOT provided over 150 soil borings from nearly 40 counties for soluble sulfate testing. A total of 127 samples were tested for sulfate and only 6% of these tested above 3,000 mg/kg SO_4. Four of the eight borings tested above 3,000 mg/kg were from Licking County while the remaining samples were from Gallia, Lawrence, Lorain and Muskingum (Table 33). Soil boring with average measured SO_4 > 3,000 mg/kg were analyzed with acid digestion followed by ICP analysis to measure total Fe, Al and Cr concentration in samples. Additionally XRD analysis was conducted to determine soil mineralogy. Results for Licking County and the other four counties are presented separately.

Table 33 2011-2012 soil borings that tested above 3,000 g/kg average soluble SO4 (n=3).

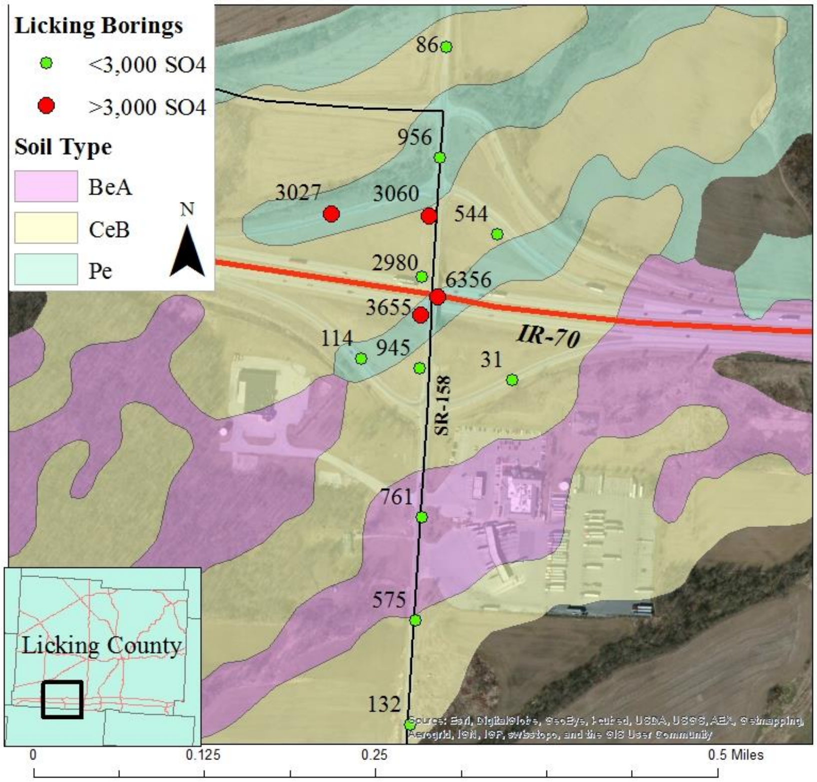
County	Boring ID	Soluble SO_4 (mg/kg)	Sample Type	Top Depth (ft)	Bottom Depth (ft)
GAL	27192	4,227±432	Pavement Subgrade	3	4.5
LAW	30443	3,764±116	Pavement Subgrade	1.5	3
LIC	27153	3,027±120	Pavement Subgrade	3.5	5
LIC	27149	3,060±191	Pavement Subgrade	6	7.5
LIC	27211	3,655±260	Pavement Subgrade	6	7.5
LIC	27290	6,356±173	Pavement Subgrade	6	7.5
LOR	29184	3,137±669	Pavement Subgrade	3.5	5
MUS	26811	11,062±646	Shoulder	3.5	5

8.2 Licking County Soil Borings

Licking County had the highest number of samples within the 2011-2012 soil boring that tested >3,000 mg/kg SO4. With these result additional tests to determine total metal concentration and soil mineralogy were also conducted to determine the mineral form of sulfate in these Licking County soils and possible SO4 origins.

8.2.1 Results for Licking County Soil Borings Soluble SO_4 Analysis

The four samples from Licking county, test above 3,000 mg/kg SO_4, were from 14 total boring collected for a preconstruction soil investigation for SR-158 raised bridge overpassing Interstate Route (IR) 70. Lime stabilization of clayey soil was not within the scope of these construction activities. Therefore, elevated sulfate levels within this project area were not a critical concern. The spatial distribution of measured SO_4 was mapped using latitude and longitude information for each sample provided by ODOT (Figure 38). Additionally, United State Department of Agriculture (USDA) web soil survey data for this area was added to the map. The spatial distribution of sulfates within this project area reveals higher levels of sulfate in borings collected closer to IR-70. Although high levels of SO_4 were not critical for the existing project, measured SO_4 results from these Licking boring samples indicate potential area of concern for future stabilization projects along IR-70. USDA web soil survey indicates soils in this region are composed of loam, silt and clay (Table 34, USGS Web Soil Survey). The bedrock of Licking County is predominantly Mississippian with slight streaks of Devonian running through the western edge of the county (ODGS 2006). Anthropogenic sources of SO_4 in Licking County could be gypsum applied as a farm amendment as Licking ranked 20th in the state in farm acres in 2010 (Figure 9 in section 2.4) (ODA 2010).



Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 38 Spatial distribution of measured SO4 in Licking County boring samples with soil type from USGS web soil survey.

Table 34 Characteristics of Licking Soils. Source: USGS Web Soil Survey

Soil Symbol	Soil Type	Slope (%)	Drainage	Depth to Groundwater (in)
BeA	Bennington silt loam	0-2	Somewhat Poorly Drained	12-30
CeB	Centerburg silt loam	2-6	Moderately well drained	18-36
Pe	Pewamo silty clay loam	0-2	Very poorly drained	0-12

8.2.2 Results of Total Metal Analysis for Licking County Soil Borings

Six borings from Licking County were analyzed for metal concentrations, four borings with average SO_4 >3,000 mg/kg and samples 27156 and 27223. Average total Fe and Al ranged from a 16,783±966 mg/kg to 27,375±6,562 mg/kg and 7,875±507 mg/kg to 12,108±1,834 mg/kg, respectively (Figure 39). Highest average SO_4 and Fe concentrations were measured in boring 27290. Total Cr (Figure 40) ranged from 7.8±1.0 mg/kg to 13.5±0.3 mg/kg. The results for Cr are consistent with levels reported in Licking County (Shane 2003).

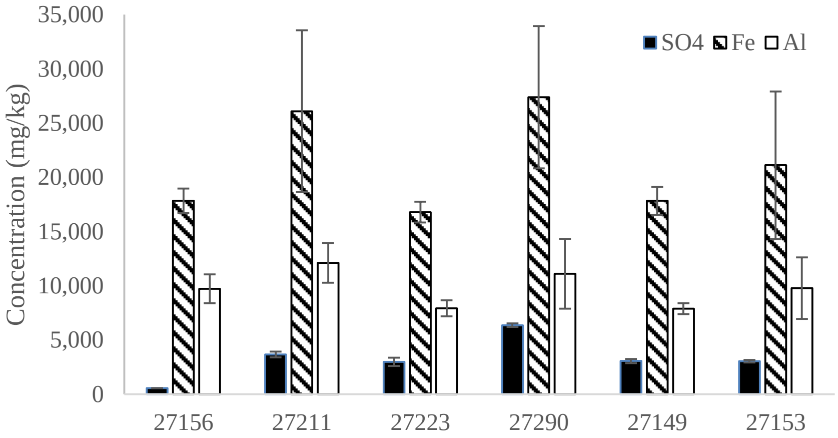


Figure 39 Average measured SO4, Fe and Al concentrations in Licking County Borings (n=3).

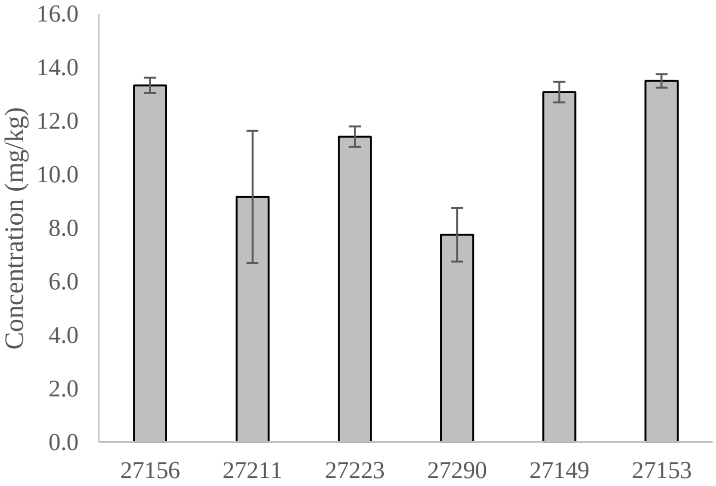


Figure 40 Average measured Cr concentrations in Licking County Borings (n=3).

8.2.3 Results of XRD Analysis for Licking County

XRD analysis was conducted on triplicate samples from four boring location: 27153, 27156, 27211 and 27290. Samples were retained after XRD testing and post XRD SO_4 testing was also conducted (Table 35). All samples contain typical minerals in Ohio soils: quartz, dolomite, calcite and clay minerals. The sulfate source for these Licking County soils were $CaSO_4 \cdot 2H_2O$ and a ferrous sulfate mineral, szomolnokite ($FeSO_4 \cdot H_2O$). XRD analysis of borings 27290, measuring highest in average post XRD SO_4, indicated the presence of gypsum (Figure 43(a)). No SO_4 source was identified in 27156 as this sample measured only 614±74 mg/kg SO_4 (Figure 41(b)).

Table 35 Dominant sulfate minerals identified in Licking County 2011-2012 soil borings tested.

Boring	Post XRD SO_4 (mg/kg)	Mineral Name	Mineral Symbol
27156	614±74	Anhydrite	$CaSO_4$
27153	3,477±142	Szomolnokite	$FeSO_4 \cdot H_2O$
27211	4,225±120	Gypsum	$CaSO_4 \cdot 2H_2O$
27290	6,470±644	Gypsum	$CaSO_4 \cdot 2H_2O$

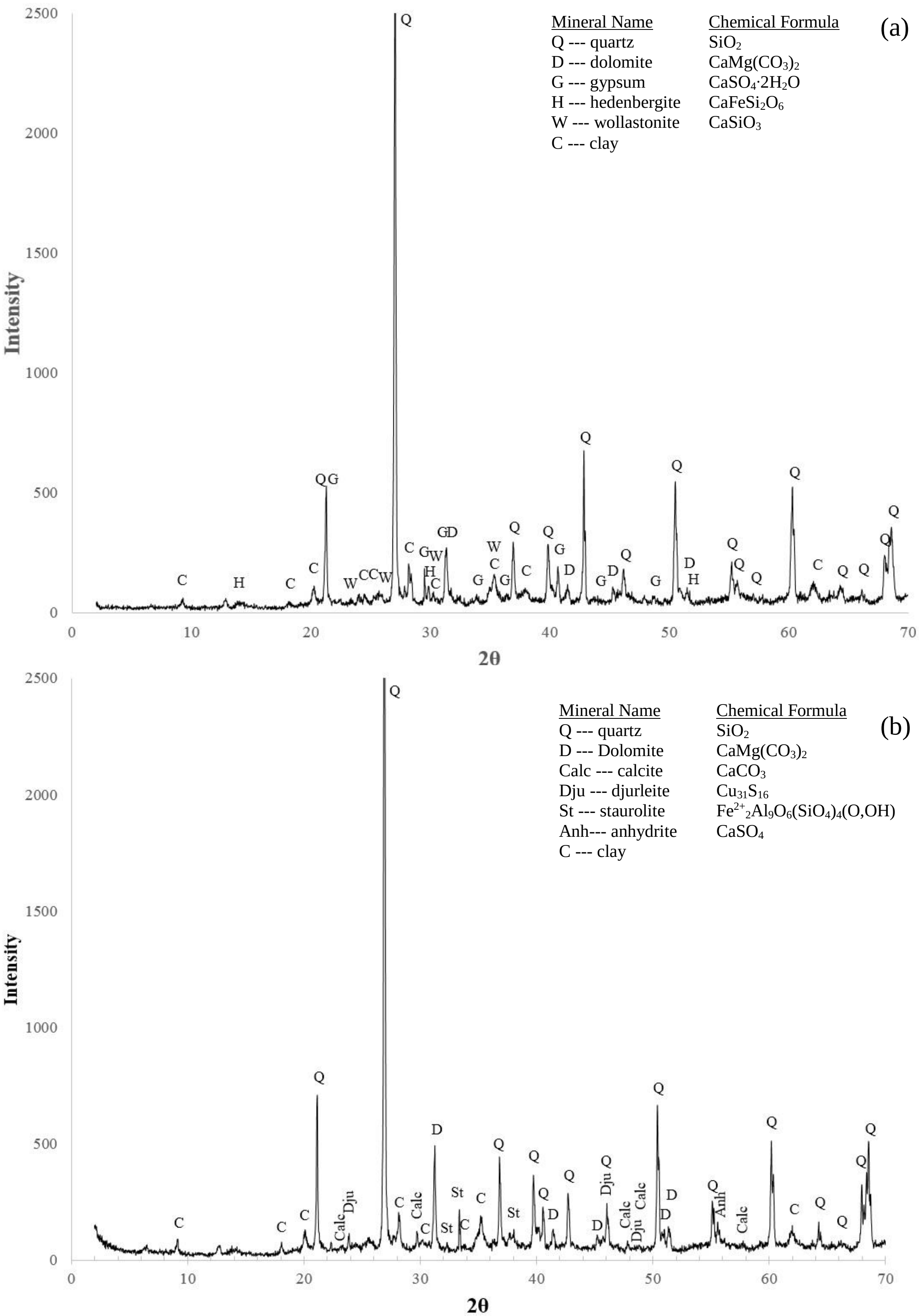


Figure 41 XRD diffractogram for (a) boring 27290 where gypsum was identified as SO4 source and (b) boring 27156 where anhydrite is possible sulfate source is anhydrite.

8.3 Gallia, Lawrence, Lorain and Muskingum County Soil Borings

Gallia, Lawrence, Lorain and Muskingum Counties each had one sample from the 2011-2012 soil boring that tested >3,000 mg/kg SO_4. The infrequent number of samples testing >3,000 mg/kg did not cause heightened concern for soils in these areas. However, to determine SO_4 mineral form and potential origins within these counties and to further understand these throughout the state, soils from these counties were subjected to additional testing.

8.3.1 Results of Sulfate Analysis for Gallia, Lawrence, Lorain and Muskingum County

Each of these counties had only one boring samples with an average SO_4 concentration above 3,000 mg/kg. Muskingum boring 26811, with an average SO_4 concentration of 11,062±646 mg/kg was collected from the shoulder near the intersection of SR-93 and the eastbound on-ramp of IR-70 south of IR-the interstate. This high sulfate location is similar to location of high SO_4 samples from Licking County, the intersection of a SR and IR-70. Additionally, like the sulfate distribution of Licking County samples, the two additional boring collected at this project location (26228 and 26794), north of IR-70, contained minimal amounts of SO_4, 0±0 mg/kg and 36±5 mg/kg respectively. SO_4 concentration from these counties was highly variable as is displayed in Figure 42 and Table 36.

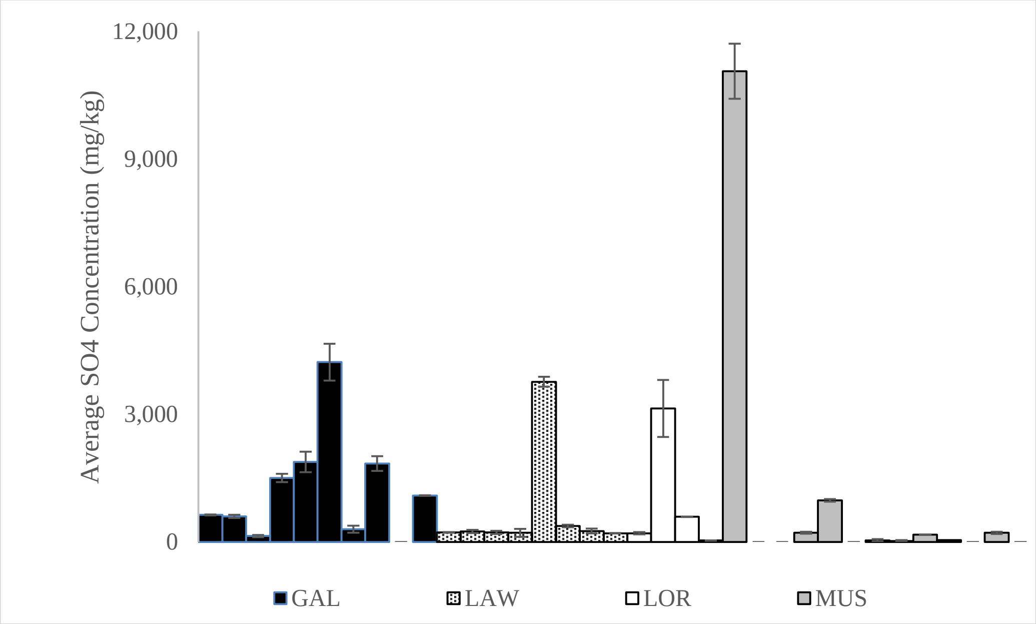


Figure 42 Variable Average SO4 concentrations with Gallia, Lawrence, Lorain, Muskingum Counties (n=3).

Table 36 Statistic of Sulfate Concentration in soils tested from Gallia, Lawrence, Lorain and Muskingum Counties.

County	GAL	LAW	LOR	MUS
No. of borings	10	8	3	14
Min (mg/kg)	0	205	206	0
Max (mg/kg)	4,227	3,764	3,137	11,062
Avg (mg/kg)	1,223	690	1,312	913
SD (mg/kg)	1,256	1,243	1,593	2,932

8.3.2 Results of Total Metal Analysis for Gallia, Lawrence, Lorain and Muskingum County Soil Borings

Boring sample 26811 of Muskingum County measured highest in average total Fe concentration at 40,088±6134 mg/kg (Figure 43). This concentration was more than double the Fe concentration measured for the other boring analyzed from Muskingum, 26828, at 14,238±194. Average Fe concentrations of samples from Gallia and Lawrence counties were all above 20,000 mg/kg. High Fe concentrations from these three counties is not surprising because past and current mining activities and verified AMD within watersheds in these counties (Figure 10 in section 2.4) (Crowell 2008 and Calhoun 2012). Chromium levels for were consistent with level reported throughout the state (Figure 44) (Shane 2003; OEPA 2013).

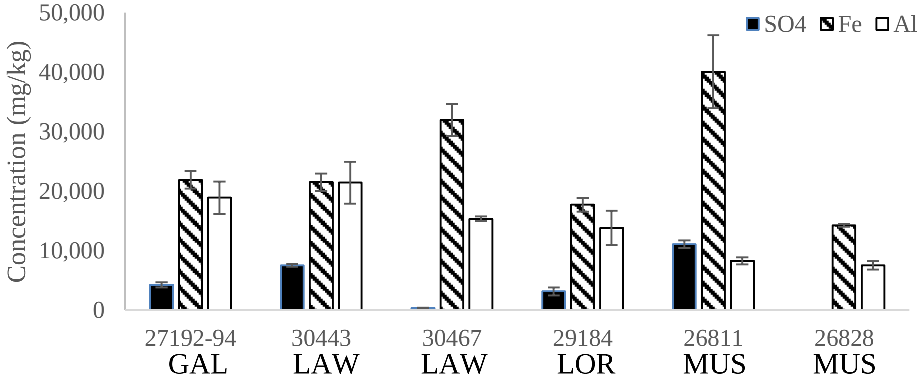


Figure 43 Average measured SO4, Fe and Al concentrations in Gallia, Lawrence, Lorain and Muskingum counties borings (n=3).

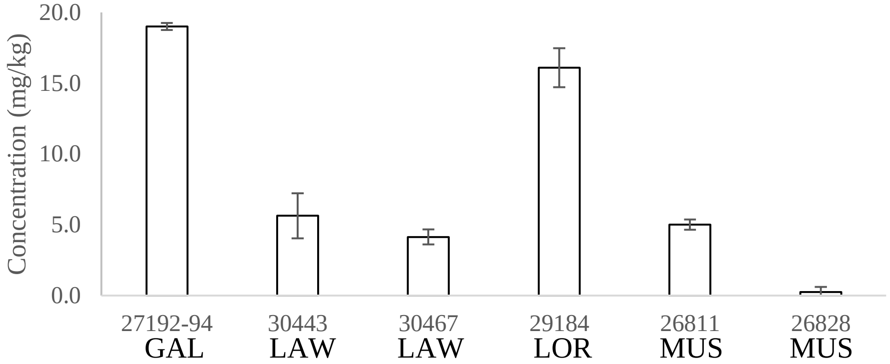


Figure 44 Average measured total Cr concentrations in Gallia, Lawrence, Lorain and Muskingum counties borings (n=3)

8.3.3 Results of XRD Analysis for Gallia, Lawrence, Lorain and Muskingum County Soil Borings

Results of TEX-145E soluble SO_4 testing identified four borings form these counties with average SO_4 >3,000 mg/kg. XRD analysis was conducted on these four borings as well as two borings testing <3,000 mg/kg as a comparison. The primary SO_4 minerals were gypsum and anhydrite (Table 37). There were also indications of pyrite and szomolnokite which could be due to mining activities in Gallia and Lawrence Counties as each county has watershed which were highly impacted by mining activities (ODNR 2002).

Table 37 Dominant sulfate minerals identified in 2011-2012 soil borings tested from Gallia, Lawrence, Lorain and Muskingum Counties.

County	Boring	Post XRD SO_4 (mg/kg)	S-Bearing Mineral	
Gallia	27192	6,470±644	Szomolnokite	-
Lawrence	30467	571±93	-	-
Lawrence	30443	4,693±32	Gypsum	Pyrite
Lorain	29184	2,901±80	Anhydrite	Lanarkite
Muskingum	26811	9,744±71	Gypsum	Anhydrite
Muskingum	26828	30±28	-	-

8.4 Discussion of results for 2011-2012 soil borings

The results of soils tests for the 2001-2012 soil borings further reveal the heterogeneity of sulfate concentrations in Ohio soils. The primary region identified was within Licking County and soils within this area are subject to flooding (Ostheimer 2012) which could cause the accumulation of surface sulfates in the form of applied farmland amendment or deposited SO_2 emissions. The impact of AMD and mining activities in southeastern Ohio are possible sources of sulfate in the soils from Gallia, Lawrence and Muskingum Counties.

CHAPTER IX

HERRICK RD SOILS IN TWINSBURG, OHIO

Twinsburg Township officials contacted ODOT regarding unevenness which developed throughout portions of Herrick Road in Summit County, Ohio which was rehabilitated via full depth reclamation. The proximity of this site (Twinsburg, Ohio) and sulfate-induced heave as a potential mechanism to the road failure led ODOT official to inquire if the research team at the University of Akron would perform soil analysis to determine if failure could be attributed to sulfate induced heave. The research team met with Twinsburg Township officials in October of 2013 at the Herrick Road location. Township officials were interview to determine construction activities and any additional relevant information. Information from this interview revealed the construction activities consisted of milling and removal of the top 4 inches of existing asphalt. The remaining asphalt and subgrade was stabilized to a depth of 12 inches. Within a month after rehabilitation horizontal unevenness (Figure 45) and cracking appeared. Soil sample of both bulk natural subgrade core sample of the stabilized subgrade were collected at six locations (Loc 1-Loc 6) along the road. These soil samples were tested at the University of Akron for SO_4, total Fe, Al and Cr and possible ettringite identification using SEM and EDAX. SEM and EDAX analysis was conducted on selected portions of material collected from cracks and pore spaces within the stabilized cores as they were processed.

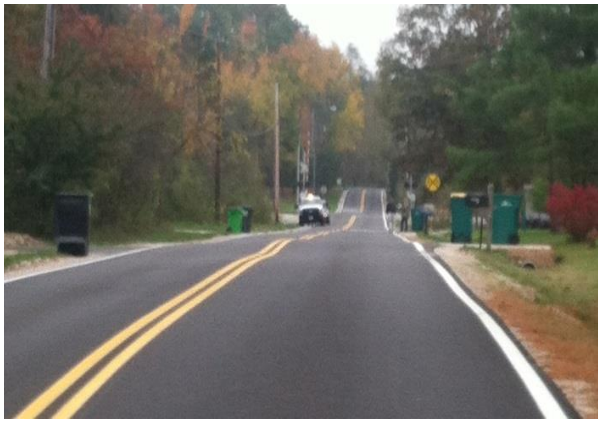


Figure 45 Visible unevenness along surface of Herrick Road (Photo taken October 15, 2013).

The average SO_4 concentration was under the 3,000 mg/kg threshold for low risk in five of the six natural subgrade samples and all of the stabilized subgrade samples (Table 38). The levels of Al were relatively high in comparison to ODOT soils tested, but similar to Al concentration for soil tested from Lake and Paulding/Defiance which both experience sulfate induced heave. This gave an indication that there is enough Al present within the

Table 38 Average Soluble Sulfate, Total Fe, Total Al and Total Cr for Herrick Road Natural Subgrade and Stabilized Soils (n=3).

Soil Identification	Soluble Sulfate (mg/kg)	Average Fe (mg/kg)	Average Al (mg/kg)	Average Cr (mg/kg)
Loc 1	871±26	30,333±3,229	14,208±1,509	6.25±1.39
Loc 1 Stabilized Core	653±32	28,942±4,537	16,900±2,419	12.75±0.43
Loc 2	2,863±212	28,592±4,106	16,667±3,066	6.67±0.14
Loc 2 Stabilized Core	1,022±72	21,825±6,845	10,408±2,777	6.83±0.52
Loc 3	2,494±121	35,500±728	22,108±95	10.5±0.9
Loc 3 Stabilized Core	456±165	29,750±5,201	18,283±3,496	10.5±0.9
Loc 4	5,403±493	31,558±1,687	21,833±1,437	11.67±0.63
Loc 4 Stabilized Core	1,209±168	28,167±1,248	18,575±2,626	14.33±0.29
Loc 5	1,661±109	31,575±8,839	18,000±2,902	8.75±0.25
Loc 5 Stabilized Core	613±39	19,475±4,376	10,008±1,463	13.42±1.18
Loc 6	682±28	39,742±2,236	19,808±2,311	11.17±0.29
Loc 6 Stabilized Core	568±3	22,617±2,761	12,217±747	18.92±1.26

Herrick Rd soil for formation of ettringite. Additionally, the Fe concentration were high which is not surprising because the natural subgrade samples could contain pyrite (FeS_2). When these samples were processed for testing, i.e., dried, ground and sieved, shale-like stones were found and shale in Ohio soils are known to contain pyrite (Hoover 1960). There was no testing to verify the presence of pyrite, but its presence could also explain the high levels of sulfate as oxidation of FeS_2 causes formation of SO_4.

Soil samples which were selectively collected from the top of Loc 4 and Loc 5 stabilized cores and additionally within cracks and pore space of Loc 3, Loc 4 and Loc 5 stabilized cores. These samples were analyzed using SEM and EDAX for the presence of ettringite. Presence of ettringite was verified in the Loc 3 samples as can be identified by the needlelike crystals in the SEM scan (Figure 46) and the EDAX verified presence of high concentration of Ca, Al, S and O (Figure 47).

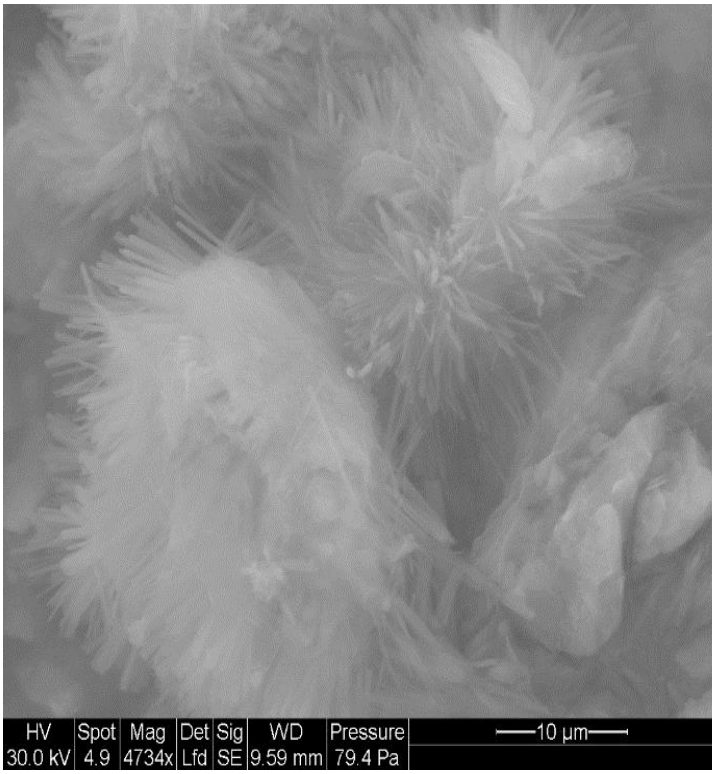


Figure 46 SEM scan of Loc 3 stabilized soil at 10 µm indicating the presence of ettringite by the needlelike crystals

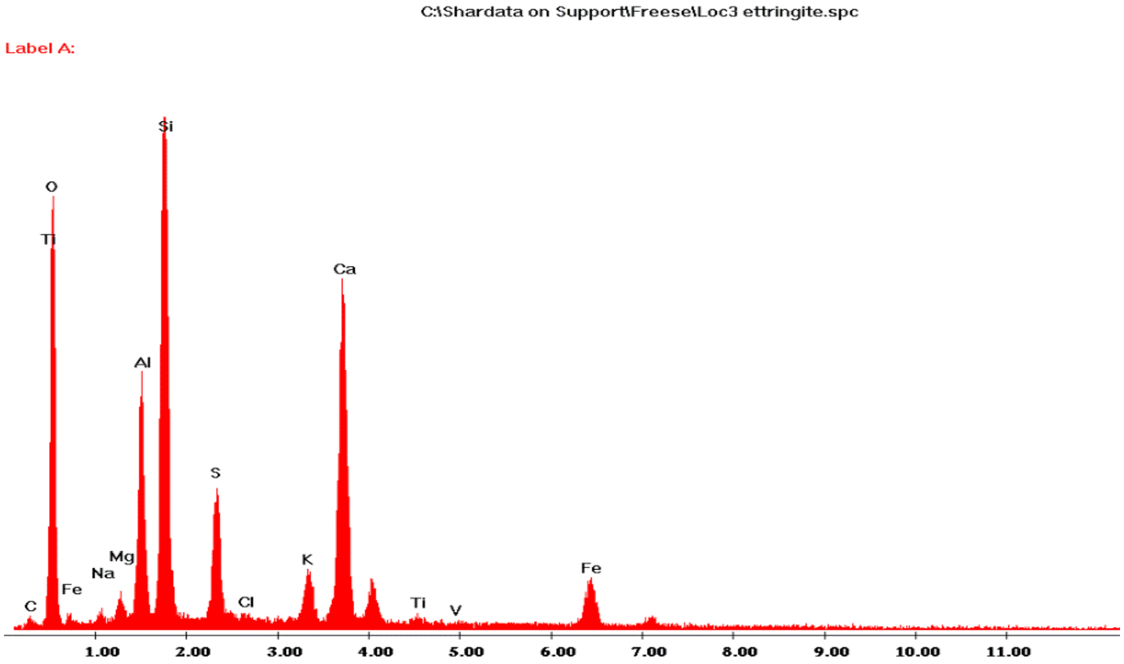


Figure 47 EDX analysis of Loc 3 stabilized sample indicating presence of Ca, O, Al and S. (Si (silicon) is a dominant mineral in soils.)

Of note was the high level of aggregate in the core samples. This is more than likely due to the construction/stabilization processes. Twinsburg officials verified the preexisting pavement was milled and mixed with the natural subgrade during cement stabilization. Additionally, comparison of SO_4 and total Al concentrations in the natural and stabilized subgrades show on average higher concentrations of both SO_4 and Al in the natural subgrade. This could be due to several factors. First could be due to dilution as both reclaimed asphalt and lime were introduced in the stabilization process. The presence of a large percentage of asphalt in the stabilized cores is visible in Figure 15 in section 3.5. However, this is unlikely the sole cause as the soil was sieved in a manner that removed large pieces of aggregate. Another cause of the difference could be formation of ettringite. Colorimetric soluble SO_4 analysis is effected by solubility of minerals. Ettringite is significantly less soluble at $10^{-44.9\pm0.32}$ mol/L (Perkins & Palmer 1999), compared to $CaSO_4 \cdot H_2O$ at 2.58 g/L (Talluri 2012) which can be converted to $10^{-1.824}$ mol/L by dividing by the molar mass of gypsum, 172.17 g/mol. The areas of pavement distress and potential sulfate induced swell were Loc 2, Loc 3, Loc 4 and Loc 5. A comparison of percentage of measured SO_4 of stabilized soil over measured SO_4 in natural subgrade shows recovery of 35.6 %, 18.3 %, 22.4 % and 36.9%, respectively. These results would coincide with the potential presence of ettringite at these locations. Also, the reduction in soluble sulfate and total Al concentrations between stabilized and natural subgrades could be due to other sulfate binding reactions possible with the asphalt material.

The results of SO_4, total metal and SEM/EDX testing indicate ettringite is present in Herrick Rd samples and could likely be the reason for the swell at several locations. The levels of soluble sulfate, and Al measured indicate sufficient amounts of each for ettringite formation. The addition of cementitious material in the stabilization process provides enough Ca. The final mineral needed for ettringite formation is water which could be provided at initial stabilization or in subsequent rain events.

CHAPTER X

QUARRY WATER SOLUBLE SULFATE ANALYSIS

ODOT provide water samples from Auglaize and Scott quarries near SR-24 in Paulding and Defiance counties. These water samples were tested for soluble sulfate to determine if water used in the stabilization process could have introduced SO_4. The SO_4 concentrations in these water samples was measured directly using colorimetry at 579±16 and 235±19 for Auglaize and Scott quarries respectively. Evaporated precipitate was also analyzed via XRD and sulfate sources were identified as pentahydrate ($Mg(SO)_4{\cdot}(H_2O)_5$) for Auglaize and calcium sulfate hydrate ($Ca(SO)_4{\cdot}(H_2O)_{0.5}$) and pentahydrate ($Mg(SO)_4{\cdot}(H_2O)_5$) for Scott Quarry. These minerals are similar to those found in groundwaters within northwest Ohio altered by soil geochemistry (McIntosh & Walter 2006). Although the level of sulfate induced heave risk is unknown with regards to SO_4 concentrations in potable water used during lime stabilization, these contamination should be considered in planning and design when considering soluble sulfate concentration of soils.

CHAPTER XI

COMPARISON OF LAKE, PAULDING/DEFIANCE AND MORROW SOILS

Based on the literature review, consultant data, soil samples analyzed and actual heave events, there were three areas of concern: SR-2 in Lake County, US-24 in Paulding and Defiance County, and IR-71 in Morrow County. Lake County exhibited heave after stabilization. Sections of 24 in Paulding-Defiance have had stressed pavement and Morrow had high soluble sulfate results, but has not heaved to date.

11.1 Sulfate Sources for Counties of Concern

Comparison of natural and anthropogenic SO4 sources and soil testing results for these three counties is provided in Table 39. All three of these project regions are underlain with Devonian Shale and bedrock, SR-2 and US-24 fully and the southern half of the IR-71 projects. As discussed earlier, this geologic system can leach the SO_4 from gypsum into migrating ground water. Natural soils from both SR-2 and US-24 project regions are both high in clay content and originated from glacial lacustrine deposits. It is of note that SR-2 subgrade soils could be fill material from another area. Morrow soils are ground and end moraines which originated from Wisconsinan glacial deposition (ODGS 2005). Ambient well groundwater testing data is not available for Lake County. Groundwater resources maps for Paulding, Defiance and Morrow counties all indicate the presence of H_2S in groundwater (Raab 1986; Schmidt 1982; Kostelnick 1981). Amongst these project areas, Lake was the only to have reported TRI releases of S-bearing minerals and has an active coal fire power plant which is currently in non-attainment of EPA standards for SO_2 emissions.

Table 39 Comparison of potential sulfate sources and soil testing results for Lake, Paulding/Defiance and Morrow counties.

Project			
County	Lake	Pau/Def	Morrow
Route Name	SR-2	US-24	IR-71
Occurrence of Heave	Yes	Yes	Not yet
Natural Sources of Sulfate			
Bedrock Type	Devonian	Devonian	Devonian/Mississippian
Glaciated	Yes	Yes	Yes
Soil origin	Lacustrine Deposit	Lacustrine Deposit	Ground and Ridge Moraine
WSS Soil Type	Udorthents udb	Paulding Clay	Centerburg Silt Loam
Ground Water	No Cited Source	H_2S	H_2S
Anthropogenic Sources of Sulfate			
SO_2 Emissions	Yes	No	No
AMD	No	No	No
Agriculture Activity	Low	High	Medium
S-bearing TRI release	Yes	No	No
Deicing	High	Low	Medium
Soil Test Results			
Average SO_4	2,405±2,183	7,235±5,699	1,481±2,390
Average Fe	31,087±1,040	22,723±3,214	28,588±7,227
Average Al	14,601±4,664	17,752±4,172	10,225±2,717
Average Cr	7.494±3.242	11.407±4.111	7.08±4.18
S-bearing mineral	Gypsum Anhydrite	Gypsum Anhydrite Ettringite	Gypsum Pyrite Lanarkite

11.2 Soil Testing Results for Counties of Concern

Figure 48 contains the average soluble sulfate results for each project analyzed for the aforementioned counties. Overall, Defiance County had the most samples that were

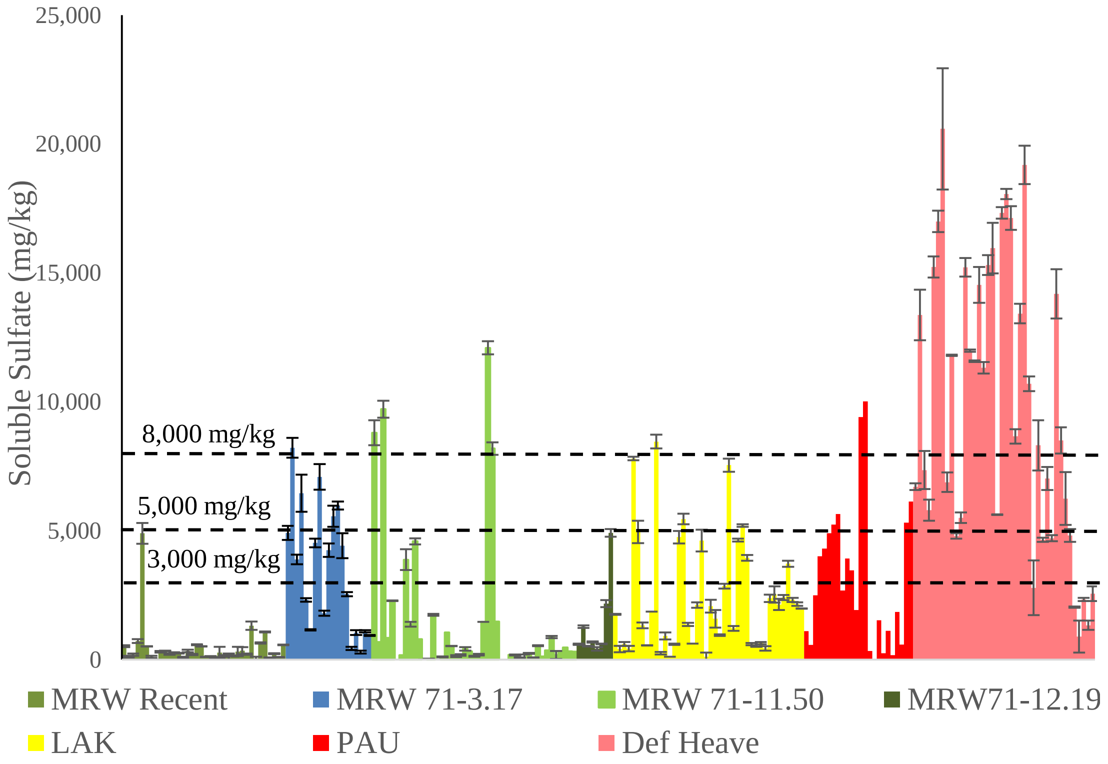


Figure 48 Overview of Soluble Sulfate Results for Counties of Concern.

above moderate (5000 mg/kg) and unacceptable (8000 mg/kg) risk. Morrow County had the next highest number of unacceptable sulfate levels. This could in part be due to the number of samples analyzed (i.e., the higher the number of test, the higher the probability of high SO_4) as well as the reanalysis of known problem areas. MRW 71-3.17 values correspond to the shoulder and pavements samples collected in March 2013. The specific samples selected for further analysis were those known to have high sulfate. Of the 42 Lake County soils analyzed by UA, 11 were above 3000 mg/kg SO_4.

Figure 49 contains the Al mg/kg for soils from the counties of interest. The results are grouped by soluble sulfate level: <3000 mg/kg, 5000-8000 and >8000 mg/kg for ease in comparison. The number above the error bar indicates how many samples were comprised in calculating the specific average. It is interesting that the MRW samples with unacceptable sulfate levels did not contain significant amounts of Al. As outlined in the introduction, the formation of ettringite requires 3 moles Ca, 2 moles SO_4 and 2 moles Al in the presence of 26 moles H_2O. The lack of heave in Morrow County where there was elevated sulfate levels could be due to the lack of available Al needed for ettringite formation. This hypothesis is corroborated by the fact that soils along SR 24 in Paulding-Defiance which did heave and had SO_4 levels > 8000mg/kg also had the highest Al content.

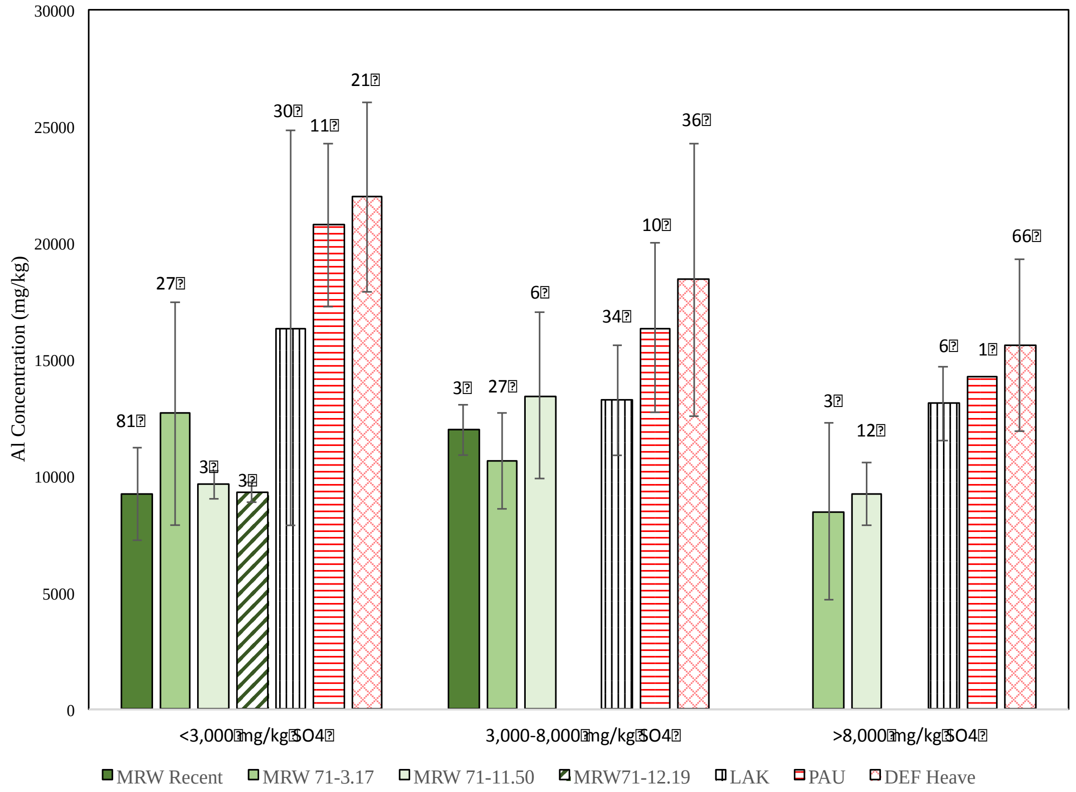


Figure 49 Overview of Total Al for Counties of Concern

Figure 50 and Figure 51 are similar to Figure 49 except they provide an overview of Fe mg/kg and Cr mg/kg, respectively. Total Fe concentrations were highest in Morrow County soils and total Cr concentrations were highest in Paulding and Defiance County soils. Determination of statistical difference in these observation was analyzed and presented below.

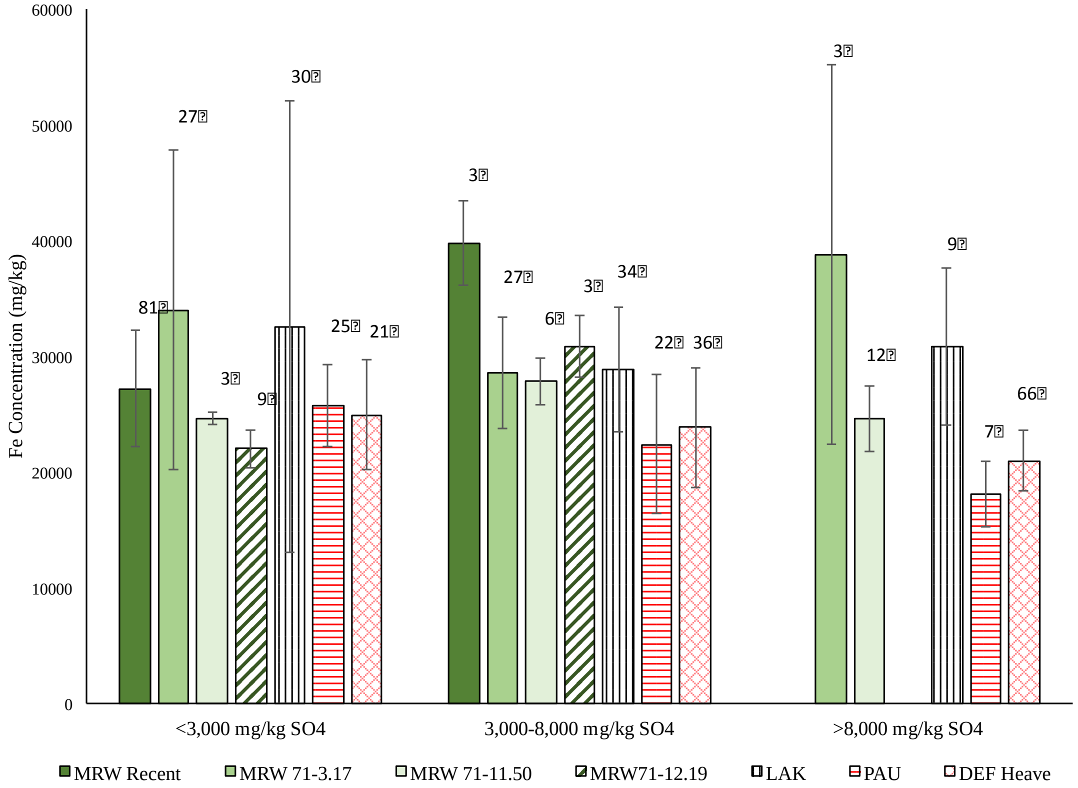


Figure 50 Overview of Total Fe for Counties of Concern

Table 40 is a brief comparison of the XRD results for the counties of concern. The numerator is the number of x-ray diffractograms that contained the specific mineral, the denominator the total number of samples analyzed. There were four different projects over two years that were analyzed for Morrow County. For 71-11.50 71-12.19, and the shoulder samples of 71-3.17, gypsum was found more than half the soils analyzed. For Lake County the dominant sulfur-bearing mineral was gypsum as it was found in 34 diffractograms. Pyrite was only detected in the half of pavement cores of 71-3.17. Anhydrite was the next dominant mineral (19 out of 55) for Lake County. Similarly, gypsum was the most frequently detected mineral for Defiance and Paulding counties.

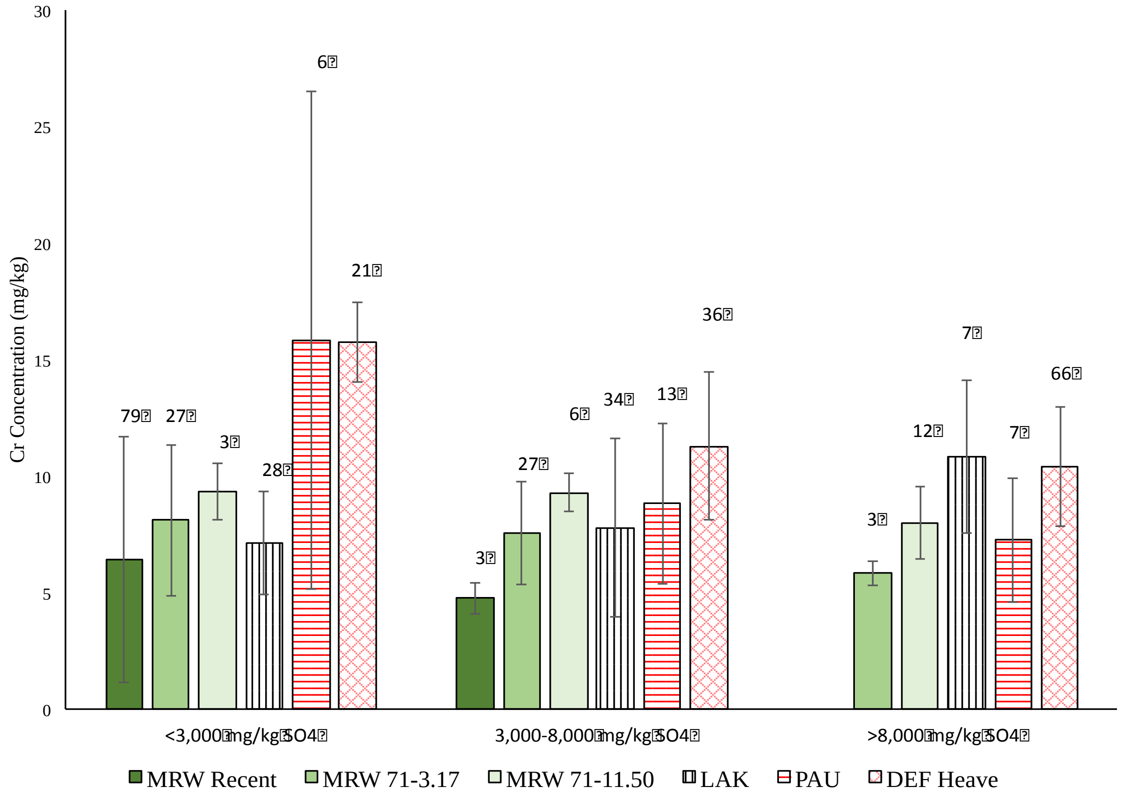


Figure 51 Overview of Total Cr for Counties of Concern.

Table 40 Sulfate and Sulfur Minerals Detected in Morrow, Lake, Paulding, and Defiance County Soils.

County	Project	Gypsum	Anhydrite	Arcanite	Lanarkite	Pyrite	Ettringite
Morrow	71-3.22	0/9	0/9	0/9	0/9	0/9	0/9
Morrow	71-11.50	4/9	0/9	0/9	1/9	0/9	0/9
Morrow	71.3-17Shldr	26/42	0/42	4/42	6/42	0/42	0/42
Morrow	71-3.17Pave	0/15	3/15	2/15	0/15	7/15	0/15
Morrow	71-12.19	17/21	0/21	1/21	4/21	2/21	0/21
Lake	SR2	34/56	19/56	6/56	6/56	0/56	0/56
PAU/DEF	24-cores	6/14	0/14	0/14	0/14	0/14	0/14
PAU/DEF	24-ground	6/33	1/33	1/33	1/33	0/33	0/33
PAU/DEF	24-4.51 cores	24/26	5/26	0/26	0/26	0/26	0/26
PAU/DEF	heave	64/90	0/90	0/90	0/90	0/90	3/90
PAU/DEF	Heave-acid wash	0/4	1/4	0/4	0/4	0/4	0/4

11.3.1 Soluble Sulfate Statistical Analysis for Counties of Concern

There were a total of a combined 215 soil samples tested for soluble sulfate from these project areas: 65 from PAU/DEF; 108 from MRW and 42 from LAK. A One-way ANOVA model with all 215 sulfate concentrations as the response and county as the treatment factor indicated mean sulfate concentrations were significantly higher (p-value < 0.001) in PAU/DEF soils at 7,235±5,699 mg/kg compared to LAK at 2,405±2,183 mg/kg and MRW at 1,481±2,390 mg/kg (Figure 52).

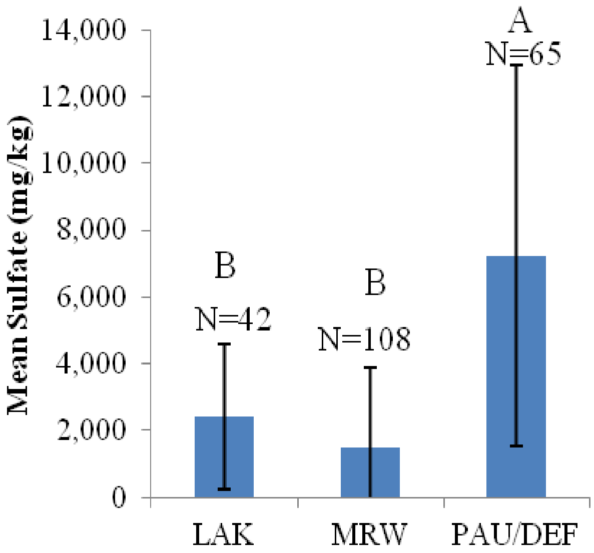


Figure 52 Significantly Higher Soluble Sulfate in Paulding and Defiance Counties

11.3.2 Total Fe. Al and Cr Statistical Analysis for Counties of Concern

There were a total of 138 soils tested from these three project areas for total metal concentration. The mean concentration of Fe, Al and Cr for these areas was compared using one-way ANOVA models with metal concentration as the response and project area as the treatment factor. The results of the model for Fe concentration by project area show the mean Fe concentration of soils from PAU/DEF at 22,723±3,214 mg/kg is significantly lower (p-value <0.001) compared to LAK at 31,087±1,040 mg/kg and MRW at 28,588±7,227 mg/kg (Figure 53). The higher concentration of Fe in MRW soils substantiates the XRD identification of pyrite in a number of MRW samples. Mean Al concentrations were significantly different (p-value <0.001) between all project areas with highest concentrations found in PAU/DEF at 17,752±4,172 mg/kg then LAK at 14,601±4,664 mg/kg and the lowest concentration in MRW at 10,225±2,717 mg/kg. These results are important because Al in one of the minerals required for ettringite formation. Swell tests of soils from LAK SR-2 examined by others showed percent swell did not follow sulfate concentration of soil. Although this has yet to be verified, one possible reason for lack of swell in the sample with the highest sulfate concentration is lower levels of aluminum in this soil. (Cutright & Wigdahl 2013). Finally mean chromium concentrations were significantly higher (p-value <0.001) in PAU/DEF at 11.407±4.111 mg/kg compared to LAK at 7.494±3.242 mg/kg and MRW at 7.494±3.242 mg/kg.

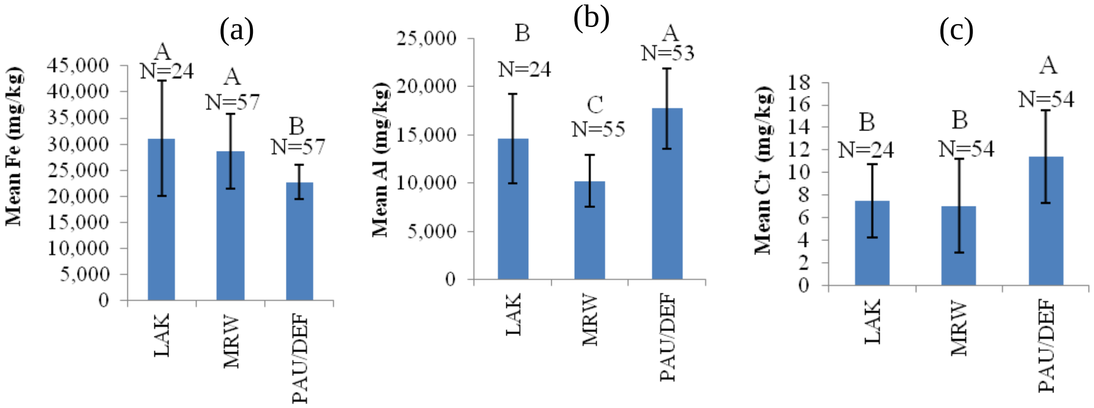


Figure 53 Results of statistical analysis of total (a) Fe, (b) Al and (c) Cr

11.4 Summary of Comparison of Counties of Concern

Comparison of these three counties indicate results which verify the ettringite formation in LAK SR-2 and PAU/DEF SR-24. Samples from the PAU/DEF project areas had significantly higher levels of SO_4. Another reason for the ettringite formation in both LAK and PAU/DEF is the elevated levels of Al. These two project areas are also similar in road construction activities and probable cause of sulfate, upward migration of sulfate in the form of gypsum through till fractures in glacial lacustrine deposit. The increased level of sulfate concentrations in PAU/DEF could be due to higher levels of farm activity in this area where gypsum is applied as a soil amendment. Soils from the MRW 71 project area are different. Fill used in road construction is much thicker than fill depths in LAK or PAU/DEF. This thickness nullifies probable impact of till fracture water migration. Additionally the soil original although glacial in nature, is form moraines less known for evaporate, gypsum, anhydrite or halite deposits. Rather, sulfate sources within the MRW 71 project area appear to be from the weathering and oxidation of pyrite. This can be explained by examining sulfate and XRD test results for the MRW 71-3.17 project. Samples obtained from under the pavement tested low in sulfate concentration and XRD analysis indicated the presence of pyrite and absence of gypsum. While sample obtained from the shoulder tested high in sulfate concentration and XRD analysis indicated the absences of pyrite and presences of gypsum.

CHAPTER XII

CONCLUSIONS

Sulfate induced heave, caused by the formation of ettringite in three road projects in Lake County, Ohio has caused ODOT to investigate the soluble sulfate concentratin in Ohio transportation subgrades. The objective of this research was to provide ODOT with information regarding the source and soluble concentration of sulfate in Ohio soils. These objectives were met through a thorough literature review and testing of primary and secondary minerals associated with ettringite formation. Nearly 350 separate soils from 39 different counties were assessed for soluble sulfate concentration and additional assessment of total Fe, Al and Cr via acid digestion and ICP-OES and soil mineralogy using XRD was conducted on many soils which tested above the 3,000 mg/kg range of low risk for sulfate induced heave damage. The results of these tests in conjunction with the literature review of sulfate sources revealed risk of heave due to elevated sulfate concentration is not a random issue for Ohio. Although test results from the limited number of soils fail to provide complete model for Ohio, three areas have been identified as Lake County, Paulding and Defiance Counties and Morrow County. Sulfate bearing minerals within these regions was not random either. Lake and Paulding/Defiance sulfate minerals were gypsum and anhydrite, while within Morrow soils, gypsum and pyrite were the sulfate/sulfur bearing minerals. Gypsum and anhydrite were deposited in glacial lacustrine environments in both Lake and Paulding/Defiance areas. However anthropogenic source of sulfate in these regions are different. Lake soils have been subjected to a high degree of industrial activity while the high degree of agricultural activity, especially application of gypsum as a soil amendment is suspected as a sulfate source in Paulding and Defiance soils. The sulfate sources in Morrow soils is the Devonian bedrock, found at shallower depths in this region compared to Paulding/Defiance counties. This bedrock contains pyrite which was confirmed in soils of Morrow County via XRD testing and oxidation of pyrite led to the formation of gypsum in these soils. Gypsum was identified as the primary source of sulfate in Ohio soils, however the origin of gypsum could come from the reaction of sulfate and Ca within calcite, abundant in Ohio. Soils are very heterogeneous and the limited number of soils fails to provide enough certainty to make clear determination of all regions in Ohio where ODOT will encounter high sulfate soils. Both natural sources such as glacial deposition and bedrock type likely contribute to sulfate content in soils. Additionally, anthropogenic sources like sulfur dioxide emissions, sulfate bearing soil amendments and acid mine drainage can impact sulfate in soils.

CHAPTER XIII

RECOMMENDATIONS

Further tests on soils from 24-Heave should be conducted including scanning electron microscope (SEM) to more accurately verify the presence of ettringite. Development of a consistent method for assessing soluble sulfate is recommended as well as independent verification of sulfate results from testing laboratories. Continued evaluation of sulfate content in soils is recommend as well as recording these results in a geospatial database. This will allow ODOT to gain even greater understanding of sulfate distribution throughout the state. Finally future work to consider consists of swell testing of different soil types within Ohio and at various sulfate concentrations. Additionally a study of seasonal variability in sulfate concentration especially after winter would provide insight into the effect deicing salts have on sulfate content in soils. Studying the effects of sulfate in potable water used during stabilization is also recommended.

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