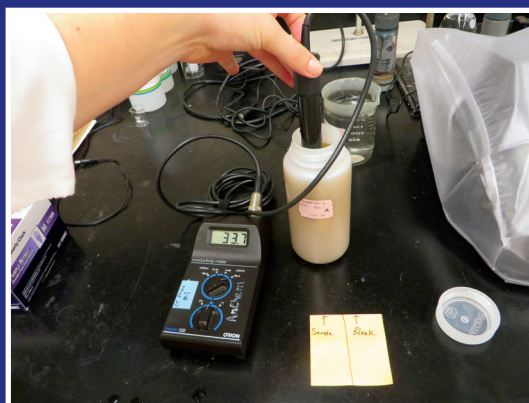
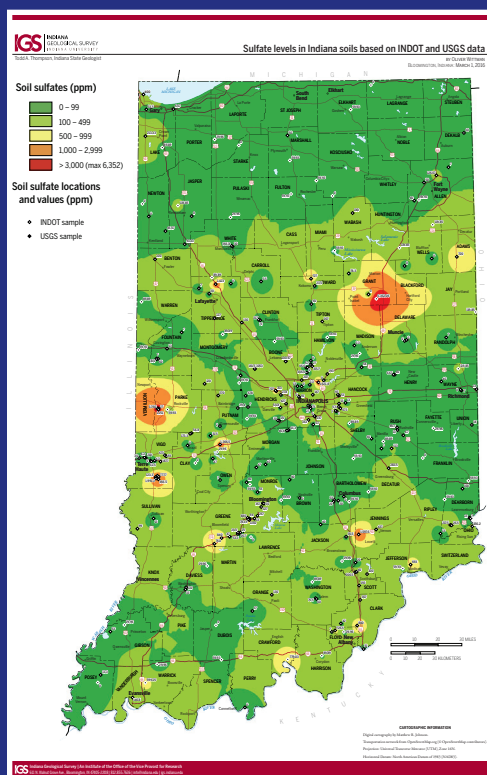


# JOINT TRANSPORTATION RESEARCH PROGRAM

INDIANA DEPARTMENT OF TRANSPORTATION  
AND PURDUE UNIVERSITY



## Sulfates in Indiana Substrates



Tracy Branam, Robin Green, Oliver Wittman, Anne Ayre

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## AUTHORS

### **Tracy Branam**

Researcher  
Indiana Geological Survey  
Indiana University  
(812) 855-8390  
tbranam@indiana.edu  
*Corresponding Author*

### **Robin Green**

### **Oliver Wittman**

### **Anne Ayre**

Indiana Geological Survey  
Indiana University

## JOINT TRANSPORTATION RESEARCH PROGRAM

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| <b>16. Abstract</b><br><p>This study was undertaken to develop modifications for improving cost and time efficiencies without sacrificing accuracy and precision to the current method employed by the Indiana Department of Transportation (INDOT) for determining sulfate content in soils. In addition, GIS maps of Indiana were prepared for displaying the distribution of sulfate concentration in soils and shallow groundwater to provide guidance where high sulfate areas might exist and to show where gaps occur in available data.</p> <p>The IGS study confirmed that the current INDOT test method using 1:20 soil/water ratio and turbidimetric method for analyzing sulfate are optimal. A conductivity screening test on soil leachate eliminated the need to run a turbidity sulfate test for most samples, reducing the time necessary for filtering, and the cost of materials for running the test. Of the 11 samples in this study, 73% had conductivity readings corresponding to &lt;3,000 ppm soil sulfate action threshold. A lower threshold of 1,000 ppm eliminated close to 60% of samples from sulfate determination. A much larger soil sulfate data set obtained from INDOT indicate sulfate analyses could be reduced by 50% to over 75%, depending on the threshold value.</p> <p>Contour maps of the distribution of sulfate in soils and groundwater were prepared with data from multiple agencies. Gaps in the data sets limit the usefulness of the current maps. In places of good data density, areas of minimal sulfate are distinguished from areas with elevated sulfate content, indicating how a more completed data set would be valuable as a guide to problem areas throughout the state. Some areas of elevated groundwater sulfate coincided with elevated soil sulfate, suggesting a correlation. However, the areal distribution gaps in both data sets prevent a more definitive interpretation.</p> |                                    | <b>13. Type of Report and Period Covered</b><br>Final Report  |                  |
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## EXECUTIVE SUMMARY

### SULFATES IN INDIANA SUBSTRATES

#### Introduction

The Indiana Department of Transportation (INDOT) conducts tests for sulfate in soils as a requirement for road construction projects. This is primarily due to the potential formation of sulfate-containing minerals that can cause swelling and cracking of road materials. Because of the large number of soil samples requiring sulfate testing, INDOT is incurring time and cost issues that it would like to see reduced. The Indiana Geological Survey (IGS) conducted an investigation where optimization of sulfate testing and screening methods were evaluated in an effort to provide INDOT with a more time- and cost-efficient procedure for sulfate testing in soils.

In addition, existing databases for soil sulfate and shallow groundwater sulfate were compiled, from which GIS maps were constructed. These maps provide information regarding the location of potential “hot spots” of high sulfate concentrations and a visual guide for where more data needs to be acquired for a more complete areal distribution of sulfate in soils and groundwater.

#### Findings

- The current INDOT test method for sulfate in soils, ITM 510, uses a 1:20 soil/water ratio for leaching, a minimum 12 hour leaching time, and a turbidimetric sulfate analysis method. The IGS investigation determined that no significant improvements are obtained from altering the soil/water ratio or the extraction procedure by heating. A consistent length of time for leaching is important as this produces some variability. The turbidimetric method for sulfate analysis is cheaper and correlates very well with ion chromatography. The IGS study confirms that this portion of ITM 510 should be retained.
- A conductivity screening test for soluble sulfate in soil extracts proved to be very beneficial. Many soil samples in Indiana have very few soluble anions due to the amount of annual rainfall across the state. As a result, sulfate concentration correlates closely with conductivity in soil leachates. By preparing a conductivity–sulfate concentration

curve, conductivity measurement of soil leachates can quickly be determined and correlated to sulfate concentrations. This screening step eliminates the need to analyze every soil sample for sulfate concentration by the turbidimetric method. Depending on the soil sulfate threshold value (1000 ppm or 3000 ppm), it is estimated that over 50% to as much as 75% of samples will not require sulfate determination by turbidimetric measurements.

- A GIS map of Indiana with concentration contours of sulfate in shallow groundwater (<100 ft, or 30.5 m) shows large areas of minimal data in the southern and western part of the state. The largest area of high-sulfate groundwater occurs south and east of Ft. Wayne. The large area of high sulfate along the Ohio River is due to sparse data.
- A GIS map of Indiana with concentration contours of sulfate in soils contains fewer data points than the groundwater map. As a result there are more areas with insufficient data points for an accurate representation of sulfate distribution in Indiana soils. However, there are a few locations of high sulfate concentrations coinciding with high groundwater sulfate. One is in the vicinity of Parke County; the other southwest of Ft. Wayne. This map in particular requires more data points in order to provide useful patterns of sulfate distribution in soils.
- A literature search revealed that variations in soil/water ratios exist among state and federal agencies conducting soil sulfate analyses. Most states establish 3,000 ppm as the action threshold for requiring special treatment. Most agencies used the turbidimetric method for sulfate analysis. None use a conductivity screening procedure, although it was investigated in Texas.

#### Implementation

Recommendations from this study include a modified soil sulfate test procedure. An example procedure written in ITM format incorporates the preparation of a conductivity–sulfate concentration calibration curve and a conductivity screening step along with the steps found in ITM 510. The screening step reduces the number of samples requiring sulfate testing by turbidimetry, reducing the amount of time and materials cost for soluble soil sulfate determinations.

Data used for generating GIS maps is provided to INDOT personnel so that map updates can be made as more data is added to the data set.



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## 1. INTRODUCTION

Soluble sulfate in soils can be deleterious to concrete highways. The amount of sulfate in soils and rocks (in mineral form) and in waters (as ions) varies greatly throughout Indiana. Glacial deposits, bedrock exposures, and anthropogenic activities contribute to the variability of sulfate found in Indiana soils. Some natural materials such as gypsum or anhydrite that occur in formations like the St. Louis Limestone (Mississippian) contain large amounts of sulfates. Geochemical research has identified a number of areas having high-sulfate groundwater, some interpreted to be coming from these deeply buried gypsum deposits. Coal-bearing strata of Pennsylvanian-age bedrock in the southwestern part of the state contain abundant sulfide minerals. Coal mining, occurring in the southwest part of the state, can expose the sulfide minerals to weathering that produces acidic, sulfate-rich soil, sediment, and acid mine drainage. In addition to sulfates from natural earth materials (soil and rock), man-made materials such as coal combustion products, slag, agricultural chemicals, and miscellaneous wastes can release sulfate. Coal ash from both pulverized coal combustion and fluidized bed combustion techniques contain high levels of sulfate when Illinois Basin coal is the primary fuel source. Many areas of naturally occurring sulfate-bearing rocks and waters, and mined sites producing acid mine drainage waters are known in Indiana, but a comprehensive, state-wide survey of either mineral sulfates in rocks and sediments, or dissolved sulfates in groundwater has not been conducted.

High sulfate concentrations are known to cause construction problems such as soil heave or other physical changes, primarily due to the formation of the sulfate-bearing mineral ettringite,  $\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot (\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ , which can exert high pressures caused by volumetric expansion sufficient to disrupt roads (Appendix A, Figure A.1). Chemical activity can initiate mineral formation that causes deterioration of concrete materials even inside buildings (Appendix A, Figure A.2). A number of analytical techniques are accepted for sulfate extraction and analysis. However, little attention has been paid to sulfate amounts in road substrates, exact techniques, and methods to address the typical range of sulfate concentrations occurring in substrates specific to Indiana since many tests were developed in regions, having soils, bedrock, and climates unlike Indiana's.

## 2. PROBLEM STATEMENT

The current method employed by the Indiana Department of Transportation (INDOT) for analysis of sulfate in soils, substrates and road construction materials (ITM 510-13T) is derived from Texas state highway department method 145-E. Soil samples are dried, disaggregated, split, sieved, weighed, leached, filtered, and the leachate analyzed for sulfate content. Sulfate can be determined using a spectrophotometer to measure insoluble barium sulfate turbidity in soil

leachate developed by the addition of barium chloride, or gravimetrically by collecting the barium sulfate precipitate and weighing, or the leachate can be analyzed directly for sulfate using an ion chromatograph for the most accurate values at low ranges (American Public Health Association et al., 2005). The net effect of employing the Texas method is a protracted and cost inefficient method for determining sulfates in Indiana soils. The most commonly employed analytical technique for measuring sulfate in water is by ion chromatography, which is also one of the most expensive methods. Due to the large number of samples routinely collected, prepared and analyzed for sulfate, INDOT has determined it to be worthwhile to fund a research project whereby preparatory techniques and analytical methods are evaluated for the purpose of improving time and cost efficiency.

One of the ways to improve efficiency is by anticipating areas of the state where sulfate can be expected to be a problem for road construction. Currently there are no statewide maps available for delineating sulfate concentration distribution in soils, rocks, or groundwater. An assessment of what is available would be beneficial for INDOT as it would provide information on where sufficient coverage exists and where gaps need to be addressed for future work. An additional method to improve efficiency is screening samples with conductivity before sulfate analysis and thereby reducing total number of sulfate analyses needed.

## 3. OBJECTIVES

The objectives of this research project are twofold. One is to compare existing methods of sulfate analysis on a set of Indiana soil samples and suggest the most suitable along with modifications to improve the efficiency of sulfate analysis without sacrificing accuracy. In considering the limited number of sulfate analytical methods, a combination of screening methods for expediting the analysis of soils will be the primary focus of the research. Comparisons of sulfate analytical techniques will also be evaluated to determine if less expensive, more rapid methods provide acceptable accuracy.

The second objective is to compile as much existing sulfate data as can be acquired into a GIS database in order to ascertain how useful the existing data is and where additional data is needed in order to construct statewide distributions of sulfate in soils and groundwater. There is limited data available, with gaps existing in the IGS groundwater database and no soil data readily available to the IGS. Part of this objective is to locate as much data outside of IGS data sets as can be acquired.

## 4. WORK PLAN

### 4.1 Evaluate Current Analytical Methods of Sulfate Determinations (Task 1)

The first objective consisted of evaluating the variation in current methods being used by various

agencies around the U.S. to extract and measure sulfate from soils. A literature review was performed and summary tables of sulfate extraction methods from Texas, California, University of Delaware, Oklahoma, American Society for Testing and Materials, US Bureau of Reclamation, and Colorado were compiled. Recommendations from the literature review were used to determine sulfate extraction and analysis methods to examine and modify for Tasks 2–4 of our study.

#### 4.2 Identify Optimal Analytical Methods for Indiana Substrates (Task 2)

Leachate experiments were designed to test the correlation between conductivity and sulfate in our sample set. A calibration curve was developed using  $\text{CaSO}_4$  for the purpose of optimizing the conductivity screening test to reduce the number of samples that require sulfate analysis. Comparing ion chromatography results to spectrophotometer results was essential for evaluating the accuracy of the spectrophotometric method, especially in the threshold sulfate range where the conductivity test will indicate sulfate analysis to be necessary. Ion chromatography was completed for triplicate analyses of 9 sieved and 9 unsieved samples field tests; 9 sieved and 9 unsieved continuous monitoring samples.

To verify that gypsum was the primary mineral from which sulfate in soils was being leached, calibration curves of sulfate versus specific conductivity for  $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$  were prepared and soil sample data plotted against to determine which curve generated the strongest correlation. The  $\text{CaSO}_4$  calibration curve was prepared by saturating 500 ml of distilled water with  $\text{CaSO}_4$  (~3 g) then stirring for 5 days.  $\text{Na}_2\text{SO}_4$  was prepared by adding 5.9 g  $\text{Na}_2\text{SO}_4$  to 1000 ml of distilled water (~4000 mg/L  $\text{SO}_4^{-2}$ ). For both calibration curves,

conductivity and sulfate concentration were measured for a series of dilutions (1:1, 7:8, 3:4, 2:3, 1:2, 1:3, 1:4, 1:8, 1:12, and 1:20 were used). For each dilution, sulfate concentration was measured with a spectrophotometer and conductivity was measured with an Orion conductivity meter. Multiple trials are also suggested to create a more robust calibration curve.

Near the end of the project activity period, an opportunity arose to analyze the samples for sulfur content using XRF analysis. Available sieved and unsieved sample portions were measured for sulfur content using a portable XRF unit. Data collected via this method were compared to sulfate leachate results. Adding this method was deemed an opportunity to increase efficiency and cost savings even more should it provide significant results compared to the leachate method.

#### 4.3 Measure Extractability of Sulfates from Indiana Bedrock Materials (Task 3)

Eleven soils samples from Central and Southern Indiana were provided by INDOT and collected by IGS (Table 4.1). Sulfate extraction generally following the TEX-145-E protocol with variations of dilution factor, grain size, mixing method (heating vs shaking), and leaching time. Visible foreign debris including large rocks and vegetation were removed from soil samples by hand. In all cases, 400 g of each soil sample were dried at room temperature and run first through a crusher and then a grinder. The samples were then split into two equal aliquots and one aliquot was passed through the 425  $\mu\text{m}$  (#40) sieve before continuing the analysis (only 10 of 11 samples were sieved, as ash sample was finer than 420 microns). Both the unsieved and sieved aliquots were split into three 10 g, three 25 g and two 12.5 g representative samples. Using a

TABLE 4.1  
Samples examined by IGS. INDOT provided samples 1–9 and IGS collected samples 10–12. Not all samples collected were processed (sites 4 and 12 were not analyzed).

| Site | IGS Sample ID | Rough Location | Location (Descriptive)  | Sample Type     |
|------|---------------|----------------|---|-----------------|
| 1    | INDOT-SO4-1   | US-50          | Station 245+98 63'  | Shale           |
| 2    | INDOT-SO4-2   | US-50          | #1: Station 249+07 32' Rt. Line B                                 | Soil            |
| 3    | INDOT-SO4-3   | US-50          | #2: Station 243+63 100' Rt. Line B                                | Soil            |
| 5    | INDOT-SO4-5   | US-24          | #1 Bull Rapids Rd pit, east side of project, north of new US24    | Soil            |
| 6    | INDOT-SO4-6   | US-24          | #2 Woodburn Rd pit, middle of project, south of new US24          | Soil            |
| 7    | INDOT-SO4-7   | US-24          | #3 Bruick Rd pit, west side of project, north of new US24         | Soil            |
| 8    | INDOT-SO4-8   | Greene Co.     | Vincennes District: Plummer                                       | Soil            |
| 9    | INDOT-SO4-9   | Clark Co.      | Seymour District: Station 16+65                                   | Soil            |
| 10   | INDOT-SO4-10  | Monroe Co.     | SR 37 near Rockport Rd. intersection<br>N039 07' 02" W086 35' 11" | Terra Rosa clay |
| 11   | INDOT-SO4-11  | Monroe Co.     | Hilltop at Independent Limestone Co.<br>N039 05' 34" W086 34' 51" | Terra Rosa clay |
| 13   | INDOT-SO4-13  | Vigo Co.       | Wabash River Generating Station                                   | Fly Ash         |

volumetric scoop, each subsample was placed in a volumetric liquid container and 250 ml of distilled water (with conductivity reading less than 10  $\mu\text{S}/\text{cm}$ ) was added. This procedure resulted in soil: water dilution ratios of 1:25, 1:10, and 1:20 respectively. For the 1:10 and 1:25 soil/water solutions, the lid was placed on volumetric container and shaken vigorously by hand for 1 minute. Specific conductivity readings of the soil-water solutions were taken in triplicate immediately after shaking then at 2, 4, 8, and 12 hours after initial reading. Soluble sulfate concentration was measured on a Hach 2700 spectrometer at 420 nm wavelength using the turbidity method. To obtain results in ppm of dry weight, the sulfate concentration of leachate was multiplied by the dilution factor.

For the 1:20 soil/water solution, one aliquot was heated to  $40^\circ \pm 2^\circ \text{C}$  and the other was shaken vigorously by hand for 1 minute then both samples were left to leach for 7 days. Specific conductivity was continuously monitored at 1 hour intervals the entire duration. At the end of the leaching period, soluble sulfate concentration was measured using the turbidity method on the Hach spectrometer at 420 nm wavelength.

#### **4.4 Develop New Indiana Test Method (ITM) for Sulfate Determination Modified from Current TX 145 Method (Task 4)**

Based on the results from Tasks 1–3, important cost and time saving modifications of the current ITM510-13T method are proposed and a flowchart created showing suggested modifications to the existing method. The greatest benefit should be derived from implementing a screening test. A proposed procedure for an ITM is included in the appendix.

#### **4.5 Survey Existing Sulfate Data for Indiana Substrates (Task 5)**

An integrated database related to the geochemical and mineral characteristics of soils is not available for Indiana so data directly linked to sulfate content were obtained from an INDOT soil geotechnical properties database, a consultant (Alt and Witzig Engineering) database and the U.S. Geological Survey (USGS). USGS data were obtained from a report that summarized geochemical data for soils of the conterminous U.S. (Smith et al., 2013) and the National Geochemical Survey database (USGS, 2008) that includes both soils and stream sediment data. Data for soil C horizons were used from the Smith et al. (2013) report because it was assumed that construction activities often entail removing topsoil during excavation.

Dissolved sulfate data for Indiana groundwater was derived from an IGS groundwater chemistry database. The IGS maintains a database of groundwater samples that have been collected and analyzed across the state. The data in the database was compiled from various regional studies. The regional studies were focused in several river basins in Indiana. Samples in the database

were also taken from boreholes of various depths, some into deep bedrock, and some into shallow overburden. Some river basins have not been sampled, so there are large areas without data (Wabash River Basin, East Fork White River Basin). A supplemental groundwater chemistry database from Indiana Department of Environmental Management (IDEM) was added to attempt to fill in the gaps. The samples from this data set are taken from several locations throughout the state representing groundwater aquifers in river basins, sediment deposits and bedrock aquifers as part of an IDEM aquifer characterization program.

#### **4.6 Develop Maps and a Preliminary Spatial Database for Sulfate Contents in Indiana Substrates (Task 6)**

This objective was addressed using sulfate data from four primary sources. First, dissolved sulfate data and sampling locations were queried from the IGS groundwater geochemistry database and transferred to a geographic information systems (GIS) format. Because the focus of this report is to better understand the distribution of sulfate in near-surface substrates, queries were further refined to only include shallow groundwater data represented by samples from wells with total depths less than 100 ft.

Next, databases from Alt and Witzig Engineering (INDOT consultant database) and various projects throughout Indiana (INDOT combined database) were edited to standardize location information and resolve sample data collected along transects. Preliminary soil sulfate maps indicated that significant variability exists within most counties in Indiana. Therefore, the INDOT consultant database was not used for further mapping efforts because only county location information were provided after multiple requests for more detailed locations were unsuccessful. The INDOT combined database included soil samples collected along road transects but only one site location was provided in the data sets delivered to the IGS. Therefore, averages were calculated for those sites with multiple samples and the mean value was used for subsequent spatial analyses.

The INDOT combined database included soluble sulfate concentrations in parts per million (ppm) the units used for maps presented in this report. However, the USGS data were presented as a weight percentage for soil samples so the data were converted to ppm. Additional processing for the USGS data entailed setting non-detect values at the detection limit such that these data could be included in geostatistical algorithms used to develop predictive maps of sulfate distribution.

The INDOT combined and USGS sulfate data sets were converted from spreadsheets to geographic information systems (GIS) coverages using best available locations (latitude and longitude geographic coordinates were provided with the data sets) and then mapped using GIS software to determine the suitability of available data for identifying areas of potential concern in Indiana.



## 5. ANALYSIS OF DATA

### 5.1 Evaluate Current Analytical Methods (Task 1)

Sample preparation techniques are similar to the procedures summarized from other states in Table 5.1 and Appendix B; however, primary differences related to drying techniques and extraction ratios are prevalent (Table 5.2). In all cases, the samples are collected from areas of interest, dried, pulverized and sieved. Drying techniques include air-drying or oven drying, but microwave drying is not recommended as it may alter results. Extreme temperatures may also alter samples, so these are to be avoided. A study conducted through the University of Delaware suggests overnight drying using forced air at ambient temperatures as the preferred method for laboratory samples. Gelderman and Mallarino (2012) suggest that supplemental heat should not exceed 40°C. Often crushing and sieving are not described in great detail, but avoidance of contamination is emphasized. Crushing can be accomplished through motorized means, mortar and pestle, hammer-mills, or roll-crushers. All studies suggest that bulk samples should be thoroughly homogenized before splitting into smaller sample increments. This can be accomplished using spatulas, stirring rods or other means. While weighing samples a minimum precision of 0.5 g is suggested, but some studies recommend accuracy no greater than 1%. Scooping from the homogenized bulk sample should take place at the center. Each study accentuates the importance of clean tools and glassware, but does not necessarily specify cleaning methods. Extraction ratios vary by study, although 3 of the 7 studies examined suggest a 10:1 ratio. Some studies suggest that samples containing gypsum require higher ratios in order to ensure all gypsum is in solution.

Methods for measuring sulfate content vary to a greater degree than those for sample preparation. Brief explanations of various methods are found below. For soils containing high levels of sulfate, turbidity method gives satisfactory results. However, ion chromatography with conductivity detectors is a much more sensitive analytical tool for determining low sulfate concentrations in soil samples.

TABLE 5.1  
Field and laboratory sulfate methods summarized in Appendix A.

| Appendix Sections | U.S. State or Institution                  | Field Soil Sulfate Test | Laboratory Soil Sulfate Test |
|-------------------|--|-------------------------|------------------------------|
| 1.1, 1.2          | Texas                                      | Turbidity               | Turbidity                    |
| 2.1, 2.2          | California                                 | –                       | Ion chromatograph (IC)       |
| 3.1, 3.2          | University of Delaware                     | –                       | Turbidity                    |
| 4.1, 4.2          | Oklahoma                                   | –                       | Turbidity                    |
| 5.1, 5.2          | American Society for Testing and Materials | –                       | Turbidity                    |
| 6.1, 6.2          | US Bureau of Reclamation                   | –                       | Ion chromatograph (IC)       |
| 7.1, 7.2          | Colorado                                   | –                       | Turbidity                    |

### 5.2 Identify Optimal Analytical Methods for Indiana Substrates (Task 2)

The samples provided to IGS by INDOT had a range of sulfate concentrations from 10 to 40,000 ppm with a distribution heavily weighted toward low concentrations and without data from 14,000 and 34,000 ppm (Appendix C, Figure C.1). Given the small number of samples and limited range of sulfate concentrations analyzed, there are few procedural changes INDOT could employ to improve their sulfate analyses method. The key method change is to use conductivity as a screen for sulfate concentration prior to actual sulfate analysis. The data in this project determined a strong correlation between the faster and cheaper turbidity/spectrophotometry analytical method instead of the more commercially used ion chromatography method. However, the benefits of additional data from a larger sample set with a greater range of sulfate concentrations (especially those with elevated sulfate concentrations) would be to refine accuracy and uncover potential differences in sample preparation techniques.

The relationship between specific conductance and sulfate was tested to determine if a screening method using conductivity would be acceptable to eliminate more expensive sulfate tests on low concentration samples. Since conductivity measures all ions, sulfate levels can be overestimated as other ions may be present. But the primary anion contributing to conductivity of soil extracts is believed to be sulfate because in Indiana where annual rainfall is around 40 inches, chloride and nitrate are too soluble to remain in mineral form within soils, and carbonates are minimally soluble. This is further supported by testing results in which soil leachate conductance correlates strongly with sulfate ( $R^2 = 0.95$ ) indicating conductivity screening could provide a quicker way to estimate sulfate levels (Appendix C, Figure C.2). However, anthropogenic products (such as fly ash from sample 13) did not fall within the correlation because a different mineral assemblage than found in natural soils contributes to conductivity.

The conductance-sulfate correlation from Indiana soil extracts was compared to potential mineral sources ( $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$ ). The relationship between conductivity and

TABLE 5.2  
Summary of sample preparation techniques for sulfate methods described in Appendix A.

| U.S. State or Institution                  | Bulk Sample Size (g) | Sieve Size (µm) | Volume of Distilled H <sub>2</sub> O for Dilution (mL) | Individual Sample Size (g) | Initial Agitation Time (minutes)        | Drying time (hours) and Temperature (°C) | Equilibration Time (hours) |
|--|----------------------|-----------------|--|----------------------------|---|--|----------------------------|
| Texas                                      | 1500                 | 425             | 400  | 40                         | 1                                       | To a constant mass; 60                   | 12                         |
| California                                 | –                    | –               | 300  | 100                        | 15                                      | –  | –                          |
| U of Delaware                              | –                    | 2000            | 25   | 10                         | 30                                      | Overnight; <36                           | 0.016                      |
| Oklahoma                                   | 300–5000             | 2000            | 200  | 5                          | 15                                      | To a constant mass; 110                  | 16                         |
| American Society for Testing and Materials | 5000                 | 600             | 80:1; 8:1 Water/soil                                   | 30<br>80:1; 8:1 water/soil | 60                                      | 24; 110                                  | –                          |
| US Bureau of Reclamation                   | 453                  | 2000; 600       | 100  | 10                         | 60                                      | 24; 60                                   | Until settled              |
| Colorado                                   | –                    | 420             | 250  | 25                         | Until no material is left at the bottom | To a constant mass; 60                   | 16                         |

sulfate of soil extracts more closely aligns with CaSO<sub>4</sub> (Appendix C, Figure C.3). However, the difference between soil and both the CaSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> regressions are not significant due to limited numbers of soil samples with medium to high sulfate levels. It was assumed that the primary source of sulfate in Indiana soils is CaSO<sub>4</sub> and the equations associate with the CaSO<sub>4</sub> data are suggested for conductivity screening. Additionally, using the CaSO<sub>4</sub> regression equation removes variability in the soil data (especially the variability in samples below instrument detection limits). The power regression for CaSO<sub>4</sub> conductivity and sulfate (Appendix C, Figure C.4) has a better fit with R<sup>2</sup> = 0.9982. However the polynomial (Appendix C, Figure C.5) and linear (Appendix C, Figure C.6) regression also has strong correlations (R<sup>2</sup> = 0.9976 and R<sup>2</sup> = 0.9891 respectively). Bagnato, Longinotti, and Corti (2003) showed the polynomial rather than the power equation best matched the sulfate-conductivity relationship for their data. Estimated sulfate concentrations from the soil extracts can be calculated using the power relationship between sulfate and conductivity developed using our instrumentation and shown in equation 5.1.

$$SO_4 \left( \frac{mg}{L} \right) = 0.1865xSpC \left( \frac{\mu S}{cm} \right)^{1.1773} \quad (5.1)$$

The conductivity needed for 3000 ppm dry weight sulfate (150 mg/L at the 1:20 soil: water ratio used in the INDOT method) was calculated as 289.0 µS/cm using equation 2. A slightly lower cutoff value of 250 µS/cm was chosen to allow for measurement variability. Samples that are above the specific conductivity cutoff limit should then be tested for sulfate concentrations while those below will have soil sulfate values below 3000 ppm. If the samples from this study are at all representative of Indiana soils in general, this new method could cut out as much as 70-80% of sulfate testing. INDOT should replicate the CaSO<sub>4</sub> calibration curve using their instruments

to determine the conductivity cutoff value. If a soil sulfate threshold value of 1000 ppm is designated, then equation 5.2 would generate a specific conductivity value of 116 µS/cm for a soil/water ratio of 1:20. This lower threshold value would result in more samples requiring testing for sulfate concentration in soil filtrate but is estimated to still reduce the number of samples requiring sulfate testing by at least 60%.

$$SpC \left( \frac{\mu S}{cm} \right) = \sqrt[1.1773]{SO_4 \left( \frac{mg}{L} \right) / 0.1895} \quad (5.2)$$

Too few samples were analyzed to suitably evaluate the usefulness of XRF as a screening method. The actual method is extremely fast, requiring only sample drying, crushing and sieving prior to analysis with the instrument. The analysis takes less than 4 minutes and can provide several elemental determinations. Because it only provides elemental analyses sulfate is not determined but rather sulfur in ppm units. The action threshold for sulfate of 3000 ppm in soil is equivalent to a soil-sulfur concentration of 1000 ppm or 0.1% sulfur. The lowest measured concentration for the INDOT samples by XRF was 340 ppm, which would be equivalent to 1020 ppm sulfate in soil. For half of the samples analyzed that contained measureable leached sulfate (samples 1, 3, and 5), leached sulfate results generated lower sulfur concentrations than XRF analyses, ranging from 9% to 45% of the XRF value. Two samples, 10 and 11, contained barely detectable leached sulfate-sulfur that were below detection for XRF. The coal ash sample, 13, generated the closest results between the two methods with the leachable sulfur within 61% of the XRF value. For samples with higher sulfur concentrations measured by XRF, the cause could be attributed to calibration discrepancies, or non-sulfate, sulfur-containing minerals in the soils such as pyrite, or possibly non-soluble sulfate minerals such as barite or anglesite. Because too few samples were analyzed a factor

analysis of the XRF data was inconclusive with some samples indicating a strong correlation between sulfur and iron, suggesting sulfide mineralogy the prevalent sulfur source, while other samples had a stronger correlation between sulfur and calcium, suggesting the sulfate mineral gypsum should be the dominant sulfur-containing mineral. While the sample preparation and rapid analysis for this method are attractive, further evaluation on a larger sample set is required in order to ascertain the feasibility of XRF as a screening method for sulfate in soils.

The final component of this task was to compare the less expensive turbidity/spectrophotometric (T/S) method to the highly accurate but costly ion chromatography method. The results of this study indicates that the T/S method compares favorably to ion chromatography for the small sample set analyzed. Using a linear equation, the  $R^2 = 0.999$  (Appendix C, Figure C.7). This confirms that the T/S method can be used instead of the more expensive ion chromatography method.

### 5.3 Measure Extractability of Sulfates from Indiana Soils and Bedrock (Task 3)

Sulfate extraction methods (sieving, soil: water dilution factor and heating samples during sulfate extraction) did not appear to have a substantial effect on sulfate values as determined from the small sample set. There were only minor differences in soluble sulfate concentrations between sieved and unsieved samples (Appendix C, Figure C.1), with site 1 having slightly higher values for unsieved samples and site 5 having higher values for sieved samples. These differences do show that sieving can have an impact on sulfate extraction but a larger sample set is needed to determine if a statistically significant difference exists. The soil: water dilution ratio had very similar patterns between sieved and unsieved for sites 1 and 5. However, the samples with a 1:25 dilution ratio had slightly higher values for both sites 1 and 5 (Appendix C, Figure C.1). The differences in sulfate concentration between shaken and heated are negligible for both the sieved and unsieved samples (Appendix C, Figure C.2). The absence of noticeable differences in sulfate extraction methods is potentially the result of a low sample size in the current study.

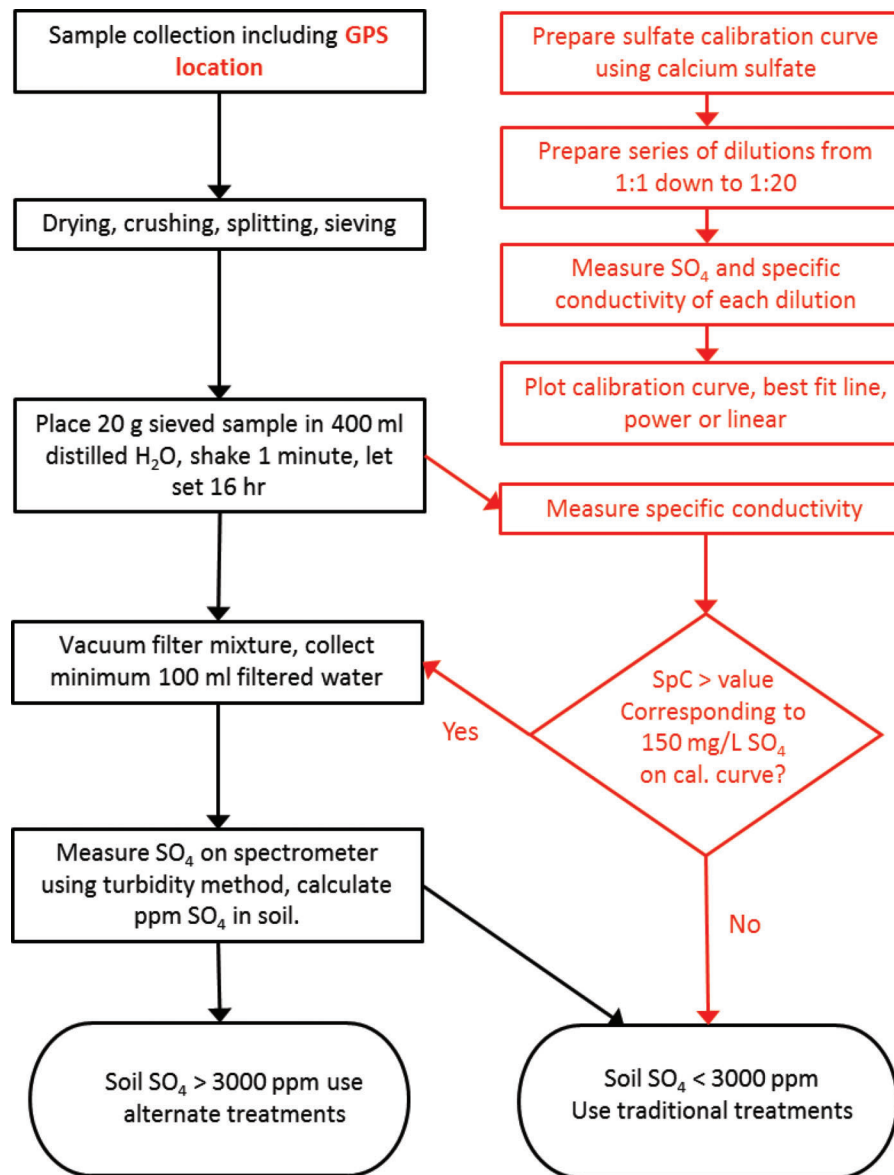
### 5.4 Develop New Indiana Test Method (ITM) for Sulfate Determination (Task 4)

Based on the study results, a flowchart was developed to streamline and standardize sulfate measurements for Indiana soils (Plate 1). The key points are to collect GPS location of all samples collected and screen for sulfates using conductivity to eliminate more expensive  $SO_4$  test on low conductance samples. An outline of the proposed method follows with a complete, proposed modification of the current ITM for soluble soil sulfate in Appendix E.

1. Sample collection
  - a. Collect sample from area of interest
  - b. Take special care to note exact locations with GPS
2. Prepare sample
  - a. Dry, pulverize, split, and sieve (40 mesh) the sample
  - b. Drying heat should not exceed  $40^\circ C$
3. Sulfate extraction
  - a. Place 20 g sieved sample in 400 ml distilled  $H_2O$ , shake for 1 minute then let set 16 hours
  - b. Use consistent methods
  - c. Based on our results, dilution ratio and heating or sieving during sulfate extraction is inconclusive given small population of samples.
4. Conductivity screening
  - a. Measure specific conductivity of leachate
  - b. Use previously prepared calibration curve
    - i. The calibration curve should be prepared using in-house lab instruments
    - ii. Prepare a calcium sulfate stock with concentration of approximately 1000 mg/l
    - iii. Prepare a series of dilutions (1:1, 7:8, 3:4, 2:3, 1:2, 1:3, 1:4, 1:8, 1:12, and 1:20 are suggested)
    - iv. Measure conductivity and sulfate concentration of each dilution
    - v. Plot data from each dilution and add most significant fit line (polynomial, power, or linear regression)
  - c. Estimate sulfate concentration with conductivity
    - i. If leachate has conductivity below a threshold value ( $250 \mu S/cm$  using our curve), soil sulfate should be under 3000 ppm and there is no need for sulfate testing.
    - ii. If leachate has conductivity greater than a threshold value ( $250 \mu S/cm$  using our curve), sample should be filtered and sulfate concentration should be measured using the turbidity method.

### 5.5 Survey Existing Sulfate Data and Develop a Preliminary Database and Maps for Indiana Substrates (Tasks 5 and 6)

Two statewide sulfate distribution maps were developed for Indiana: soluble sulfate in soils (Plate 2), and groundwater sulfate from shallow wells (Plate 3). The predictive maps were developed by interpolating data using an Inverse Distance Weighting algorithm. The database used to develop the soils map was gleaned from USGS soils data and INDOT data. The USGS data was obtained from a database of elemental and mineral characterization of soil samples from the continental U.S., broken down into soil horizons. For this study the data from the C horizon was included as it is most likely to contain the highest sulfate concentrations while sulfate in the A horizon was deemed



**Plate 1.** Proposed method flow chart for rapidly predicting sulfate content of sulfate Indiana substrates. Black boxes show current method and red boxed show the new improvements added by IGS.

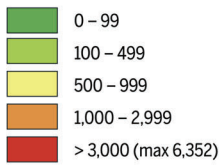
more likely to have been depleted due to dissolution. The remainder of the soils data was provided by INDOT from their soil-sulfate database. This data set did not have location information for each individual soil sample but rather a location for the project with multiple samples collected from the project area. Because the individual samples were not located, the data used for the map consist of a single point for each location provided, comprised of an average ppm sulfate value for the samples collected and associated with that project location. The combined data provided 343 total points. An important point to consider when viewing Plate 2, the soils map, is that sampling protocols for the data sets may very well differ, thereby contributing to a bias between the data sets. Protocols that call for collecting soil samples based on soil horizon identification

may differ significantly from a protocol that requires sampling to a specified depth. This may be one reason for a larger number of samples from the INDOT data set containing high sulfate as compared to the USGS data set.

Dissolved sulfate in shallow groundwater was also contoured for the state of Indiana using 594 data points that were recovered from the top 100 feet of material (Plate 3). Data for this map was gleaned from the Indiana Geological Survey groundwater chemistry database and supplemented by data from the Indiana Department of Environmental Management (IDEM) Groundwater Section's groundwater monitoring network. Few sampling protocol differences exist between these databases. The most important sampling protocol that water samples are filtered prior to analysis was

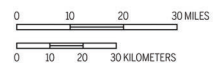
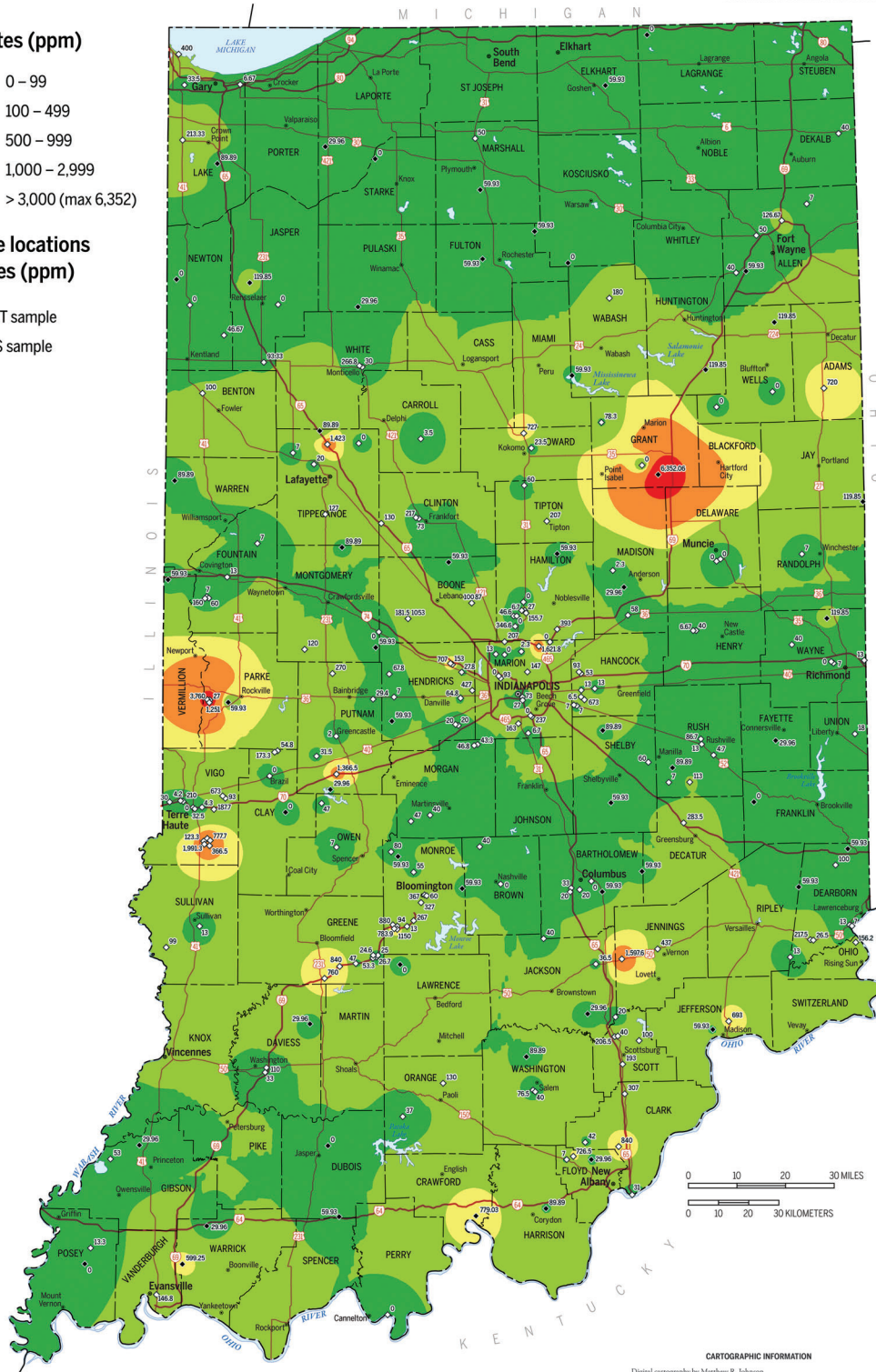


**Soil sulfates (ppm)**



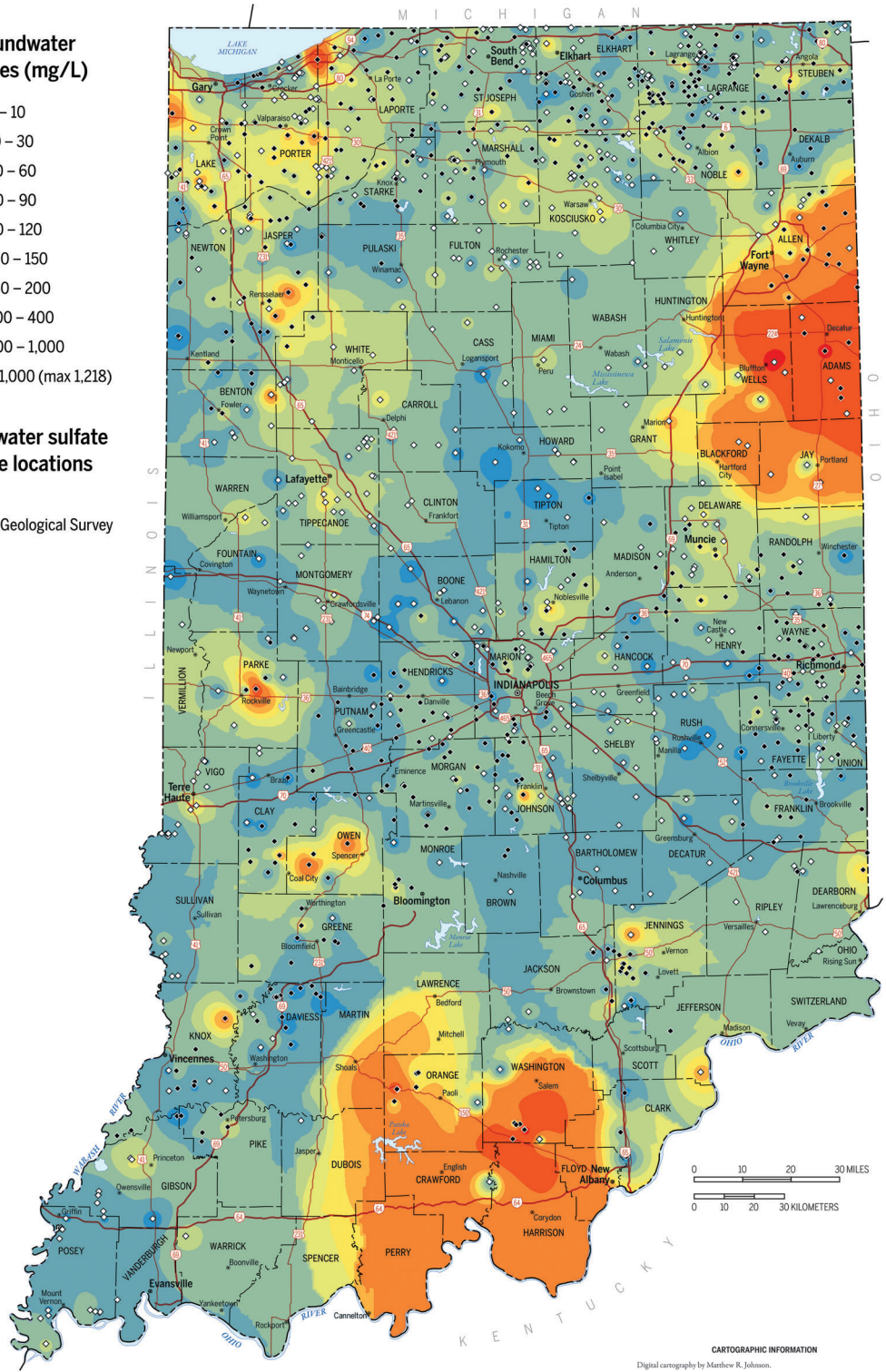
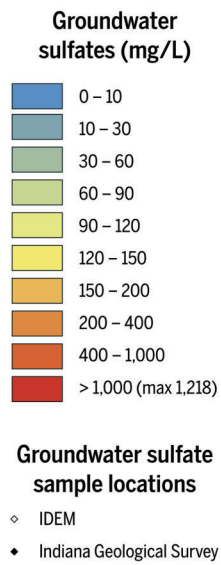
**Soil sulfate locations and values (ppm)**

- ◇ INDOT sample
- ◆ USGS sample



**CARTOGRAPHIC INFORMATION**  
 Digital cartography by Matthew R. Johnson.  
 Transportation network from OpenStreetMap.org (© OpenStreetMap contributors).  
 Projection: Universal Transverse Mercator (UTM), Zone 16N.  
 Horizontal Datum: North American Datum of 1983 (NAD83).

**Plate 2.** Sulfate levels in Indiana soils based on INDOT and USGS data.



**CARTOGRAPHIC INFORMATION**  
 Digital cartography by Matthew R. Johnson.  
 Transportation network from OpenStreetMap.org (© OpenStreetMap contributors).  
 Projection: Universal Transverse Mercator (UTM), Zone 16N.  
 Horizontal Datum: North American Datum of 1983 (NAD83).

**Plate 3.** Sulfate levels in shallow (less than 100 ft.) Indiana groundwater based on IGS and IDEM data.

consistent for both data sets. The net effect is high confidence in using both data sets on the same contour map.

While there are significant gaps and insufficient sampling densities in some areas for both maps to prevent a comprehensive measure of sulfate distributions, a comparison of Plates 2 & 3 show parallels in the data sets in some regions of the state. In west-central Indiana, an area of high sulfate is shown extending into Parke County in both maps. In north-west Indiana, in the Gary region, there is a mix of very high sulfate levels and low sulfate levels. An area of high sulfate levels is shown centered in Adams County, in north-east Indiana. Both maps show the St. Joseph and Kankakee River valleys having mostly lower recorded sulfate levels. Also, both maps show lower sulfate levels in the Whitewater River areas of Randolph, Wayne, Fayette, Union, and Franklin Counties in east-central Indiana. In contrast, a large area near the Ohio River in southern Indiana appears to contain high levels of sulfate in shallow groundwater, yet very little sulfate in soils. This is an area where sample density is extremely low for both data sets, resulting in widely discrepant results.

## 6. CONCLUSIONS

Current analytical methods employed by state and federal agencies and institutions employ a variety of drying, pulverizing, and grain size requirements; as well as differences in dilution ratio, extraction temperature, agitation time, and leaching time. Additionally, both ion chromatography and turbidity are used to analyze sulfate concentration. Our results show no significant difference in sulfate concentrations from variable dilution ratios (1:10, 1:20, and 1:25), grain size (unsieved and 40 mesh) and using either heating or agitation during sulfate extraction. Additionally our work illustrates that the cheaper and faster spectrophotometric analysis performs just as well as ion chromatograph method for samples with sulfate concentrations above 5 mg/l. However, a follow-up study on a greater number of soils samples with a larger range of sulfate concentrations would better compare accuracy and precision, as well as uncover potential significant differences in sample preparation techniques.

Screening for sulfates using conductivity can eliminate more expensive  $\text{SO}_4$  tests on low conductance samples that correspond to low soluble sulfate. In our Indiana soil leachates, conductance correlated strongly with sulfate concentration. The best fit conductivity-sulfate line for soil-leached sulfate aligned with a calcium sulfate curve which is assumed to be the primary source of sulfate in Indiana soils. The calibration curve for conductivity screening was based on the power equations for calcium sulfate, though a polynomial curve would have worked equally well. On our calibration curve, the conductivity threshold limit of 3000 ppm dry weight soluble soil sulfate was calculated as 289.0  $\mu\text{S}/\text{cm}$  and for 1000 ppm threshold the corresponding conductivity would be 116  $\mu\text{S}/\text{cm}$ . INDOT

should create a calibration curve adjusted for their in-house instruments to determine conductivity threshold limits. Samples that are above the threshold limit need to be tested for sulfate concentrations while those below have sulfate values below 3000 ppm and do not require further sulfate testing. Alternatively, sulfur analysis using XRF could potentially be a faster screening method than conductivity screening, however additional work is needed for testing to properly evaluate the effectiveness of this method and whether it could be used as an alternative or as a precursor to conductivity screening.

Based on available databases compiled from multiple sources, two concentration contour maps were developed for soluble sulfate in Indiana soils. When completely developed for the entire state these maps will allow INDOT to know where to expect areas of concern and where sulfate concentrations are likely to be low. In their current form the maps provide some indication of where additional data needs to be generated for a more complete coverage, but also provides a sense of what can be expected in parts of the state with good control such as in the northern tier counties and the central part of the state. Most of the high density sampled areas contain low sulfate concentrations in both soils and groundwater. Because of variability potential for sulfate concentrations in soils and groundwater within a single township, GPS points are vital to construct maps and make detailed assessments of spatial variability in sulfate concentrations.

## 7. RECOMMENDATIONS

Our main conclusion is that soil samples should be screened before doing sulfate analysis. At this time, conductivity screening of soil leachate is the recommended method, though XRF may prove to be faster and just as effective should this method be more thoroughly vetted for use. The implementation of a screening method will save time and eliminate more expensive and needless sulfate test on low conductance samples. It is recommended by this research that after soil samples are prepared and sulfate is extracted, the leachate should be immediately tested for conductivity. The measured specific conductance should be compared to a threshold value correlating to 3000 ppm (or slightly below for a margin of error) determined with a calibration curve prepared in-house. If conductivity is below this threshold value, the sulfate concentration is below 3000 ppm and no special treatment is necessary at the sample site for road construction. This research has determined that INDOT can continue using their current sulfate extraction method as the dilution ratio, grain size, and heating during sulfate extraction was inconclusive in our study. A larger scale study with a minimum of 20 samples is suggested in order to distinguish between these procedural differences and further improve the accuracy of sulfate measurements.

Knowing that INDOT continues to collect soil samples for sulfate analysis provides an excellent opportu-



nity to refine the soil-sulfate map included in this report. It is our recommendation that each sample collected include GPS location of the sampling site as part of the sample identification. For generating mapping data points, the location data and sulfate data should be used. If samples screened with conductivity indicate sulfate values less than a threshold soil-sulfate value (e.g., <1000 ppm), a new range of values should be generated where the lowest partition for the range of values on the soil-sulfate map would be all samples less than the threshold value determined by the conductivity screening test.

## 8. EXPECTED BENEFITS, DELIVERABLES, IMPLEMENTATION, AND COST SAVINGS

Conductivity screening can be performed to eliminate more expensive and time-consuming sulfate tests on low concentration samples. Based on 11 samples, 73% had conductivity values below our determined threshold limit of 250  $\mu\text{S}/\text{cm}$ , and corresponding leachable sulfate concentrations below the 3000 ppm action threshold. Even with this conservative threshold limit, it is estimated from the soil data sets used for the GIS map construction that sulfate testing could be cut by over 75%. However, if sulfate testing is desired for a 1000 ppm dry weight soil sulfate, then the 11 samples would have had 2 additional samples with conductivity corresponding to the regression curve threshold value, even though the determined soil sulfate content was much less than 1000 ppm. The lower the threshold, the more likely false positives for exceeding the soil sulfate content are to occur. The number of the 11 samples not requiring testing for the lower threshold value drops to 55%.

Sample preparation and sulfate extraction should be performed using the same methods for both conductivity screening and sulfate analyses. Necessary equipment include a conductivity meter, either benchtop or handheld, and a spectrophotometer. The one time cost of adding conductivity screening to the current INDOT method (510-13T) includes a conductivity meter (\$1,283.16 for a Thermo Scientific Orion Star A222) and the time needed to generate a calibration curve (est. one day). Recurring costs are conductivity check standards (chosen from

100, 500, 1000, and 1413  $\mu\text{S}/\text{cm}$ ) and time to measure conductivity (~2 min/ sample including time for conductivity reading to stabilize and time to rinse probe and beaker). Measurement of sulfate by turbidity on a spectrophotometry is slower, estimated at ~11 minutes/ sample including 5 min. for filtering sample, 5 min. for sample dilution and analysis, and 1 min. for cleaning vials. Additionally, regular purchases of sulfate reagents (\$30.79/100 pk SulfaVer 4) and filter paper (\$31.95/100 pk) are required. For 100 samples, the total time saving is 15 hours and for materials cost is \$62.74.

Comprehensive GIS sulfate levels maps can be used to guide INDOT on where high sulfate concentrations in both water and soil occur and therefore most likely to be encountered for future developments. One important addition recommended from this study is to include GPS locations on samples collected. An equally important aspect is to acquire more data from areas of little or no data points.

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APPENDICES

APPENDIX A: PHOTOGRAPHS OF SULFATE DAMAGE



Figure A.1 Photograph of sulfate induced heave on an Indiana road. (Courtesy of INDOT.)



Figure A.2 Photograph of sulfate from shale causing disruption inside the West Baden Springs Hotel. (Courtesy of CFC, Inc.)

APPENDIX B: LITERATURE REVIEW FOR SAMPLE PREPARATION  
AND MEASURING SULFATE CONTENT

**Sample Preparation and Measuring Sulfate Content (in situ)**

1.1 Texas

1.1.1 *Sample Preparation*

An appropriate sample is selected and a 300 g representative sample is collected with a hand auger. The sample is air-dried for an unknown amount of time and pulverized to pass through a 425  $\mu\text{m}$  sieve. Next the sample is homogenized and split into 10 g increments.

1.1.2 *Measuring Sulfate Content*

A 10g sample is then placed into an HDPE bottle and combined with 200 mL of distilled or deionized water. The bottle is vigorously shaken for 1 min. and then set aside for a minimum of 12 hrs. After the appropriate amount of time has passed filter paper is placed in the mouth of a funnel and the neck of the funnel is placed into an empty beaker. The bottle containing the sample is shaken again for 1 min. before the solution is poured through the filter. After the solution has drained into the beaker it is pipetted into a clean sample vial that has been carefully wiped free of dirt, residue, etc. The sulfate content is then measured with a colorimeter and reported in ppm. If the results exceed or surpass measuring range, sample dilution is adjusted.

2.1 California: Field testing is not specified; laboratory methods are detailed in 2.2.

3.1 University of Delaware: Field testing is not specified; laboratory methods are detailed in 3.2.

4.1 Oklahoma: Field testing is not specified; laboratory methods are detailed in 4.2.

5.1 American Society for Testing and Materials: Field testing is not specified; laboratory methods are detailed in 5.2.

6.1 US Bureau of Reclamation: Field testing is not specified; laboratory methods are detailed in 6.2.

7.1 Colorado: Field testing is not specified; laboratory methods are detailed in 6.2.



## Sample Preparation and Measuring Sulfate Content (laboratory)

### 1.2 Texas

#### 1.1.3 *Sample Preparation*

First the unseparated sample is dried in an oven and cooled in a desiccator to constant weight. Next the sample is crushed, ground, and split into a 1500 g representative sample to be run through a 4.75 mm sieve. Lastly, the sample is split into three 40 g representative samples.

#### 1.1.4 *Measuring Sulfate Content*

20 g of sample are placed in an HDPE bottle and combined with 400 mL of distilled or deionized water. Similar to field testing, the bottle is hand shaken for 1 min. and set aside for a minimum of 12 hrs. After the prescribed time period has elapsed the sample is again agitated, filtered and tested in concordance with the method detailed in section 1.1.2. Replications are recommended for greatest accuracy.

### 2.2 California

#### 2.2.1 *Sample Preparation*

100 g of soil is weighed and then combined with 300 mL of deionized water in an Erlenmeyer flask. Next the sample is agitated for 15 min., centrifuged, and either filtered or allowed to gravitational settle overnight. The sample is then pipetted into a sample vial and cap using syringe filters to reduce particulate contamination.

#### 2.2.2 *Measuring Sulfate Content*

A calibration curve is determined using standards at various concentrations. A blank is analyzed at the beginning of every run to determine possible contamination. Samples should be pipetted using syringe filters. Programs on the IC are set up for each sample by running a blank, calibration curve standards, and then samples.

### 3.2 University of Delaware

#### 3.2.1 *Sample Preparation*

10 g of sample are weighed or scooped, sieved, and combined in an Erlenmeyer flask with an extractant solution (several are suggested). The flask is then oscillated at a 30 per/min rate. Afterwards a 0.25 g of activated charcoal is added and the flask is hand shaken for three minutes. Then the sample is filtered through a sulfate-free filter paper.

#### 3.2.2 *Measuring Sulfate Content*

First an Acid seed and a standard solution are made; The acid seed solution is a 6 M solution of HCl containing  $K_2SO_4$ , the standard solution is reagent grade  $K_2SO_4$  in acidified  $NH_4OAc$  or monocalcium phosphate. Then different proportions of working S standard solutions are prepared using the extracting solution and multiple volumes of 100 mg S/L standard. 0.25 g of activated carbon is added to each of the prepared

standards, and each is shaken vigorously for three minutes. Filters are washed with extracting solution before each solution is filtered. Filtrate is combined with 1 mL of the acid seed solution in an Erlenmeyer flask. The solution is swirled before adding  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  crystals. The mixture is set aside for one minute before being swirled until the crystals dissolve. Within the 3-8 minute time interval the transmittance or optical density is read with a spectrophotometer or colorimeter.

#### 4.2 Oklahoma

##### 4.2.1 *Sample Preparation*

A sample is taken, air dried for an unspecified amount of time, and split. Minimum sample mass is determined by the diameter of the largest grain. The specimen is then crushed, sieved, and oven dried to a constant mass.

##### 4.2.2 *Measuring sulfate content*

5 g of soil are combined with deionized water in an HDPE bottle. The bottle is capped and then shaken by hand or with a mechanical shaker for 15 minutes. The slurry is left to soak for 16 hrs. Then wet a filter with deionized water and place it into a funnel. Allow the solution to gravitationally filter. Then using a clean pipette, fill a clean sample vial with the filtrate solution. Gently tap to free bubbles. Use colorimeter to test and record sulfate concentrations. Special notes advise on waste disposal and clean-up.

#### 5.2 American Society for Testing and Materials

##### 5.2.1 *Sample Preparation*

A field sample is taken from at least 1 ft. of depth. Visible roots, sticks and leaves are removed. A warning to avoid soil from excessively wet areas is issued. After the soil is received by the lab it is oven dried for 24 hours and then sieved. Next the sample is placed in a beaker and diluted with deionized water and filter twice under suction.

##### 5.2.2 *Measuring sulfate content*

Sulfate is measured using the turbidimetric method; It is diluted appropriately, combined with conditioning reagent and  $\text{BaCl}_2$ . The solution is stirred using a magnetic stir bar for exactly one minute at a constant speed. The beaker is removed from the stirrer and the turbidity is measured.

#### 6.2 US Bureau of Reclamation

##### 6.2.1 *Sample Preparation*

Samples are collected from appropriate locations using stainless steel implements before being double bagged. Samples are then crushed, split and separated using a 2.0mm sieve and air dried or oven dried. The samples are then ground using a mortar and pestle. Next 30 grams of sample is placed in an Erlenmeyer flask with at least 300mL of water and

agitated for 1 hour on a magnetic stir plate then allowed to settle. For IC the samples are diluted to a 10:1 ratio and filtered through a 0.45- $\mu\text{m}$  membrane filter or decanted to a centrifuge vial and centrifuged at 4,500 rpm for 10 minutes.

#### 6.2.2 *Measuring sulfate content*

After the one hour agitation and subsequent settling period the electrical conductivity of the sample is measured using a standard meter and probe ensuring that the probe is completely submerged. Sufficient equilibration time is allowed, and the probe is rinsed between samples. Next the solution is prepared for IC analysis by filtering or centrifuging discussed above. The IC system is equilibrated by pumping eluent through the analytical column for a minimum of 1 hour. The remaining procedure is conducted according to the manufacturer's instructions.

### 7.2 Colorado

#### 7.2.1 *Sample Preparation*

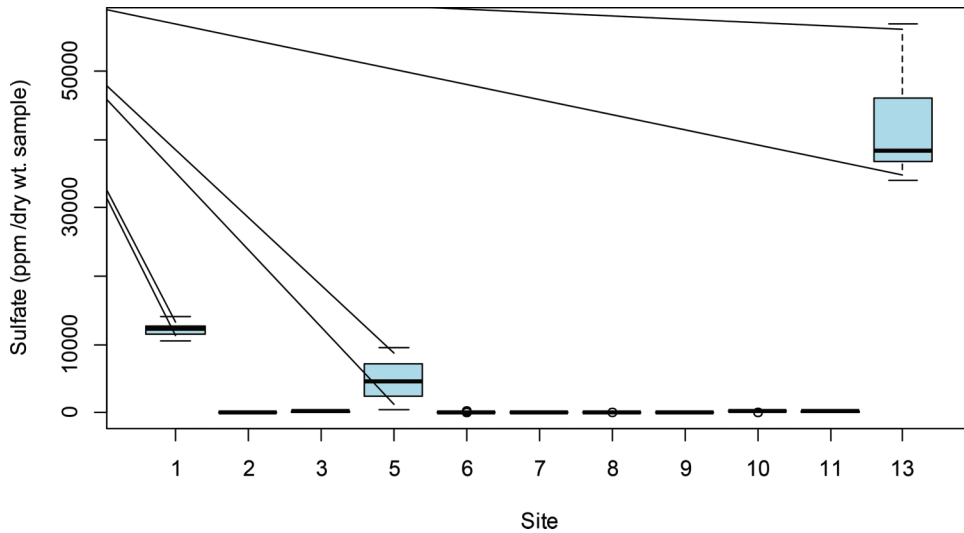
The sample is collected and dried to a constant weight. The material is then processed over a #4 sieve. In the lab, the material is sieved again and mixed for uniformity. Next an appropriate sized sample is weighed, placed in an Erlenmeyer flask and diluted. The flask is mixed thoroughly and allowed to equilibrate at a constant temperature. If the sample still exhibits turbidity it is filtered until clear. Using a pipette 25mL of solution is placed into a clean flask distilled further and mixed.

#### 7.2.2 *Measuring sulfate content*

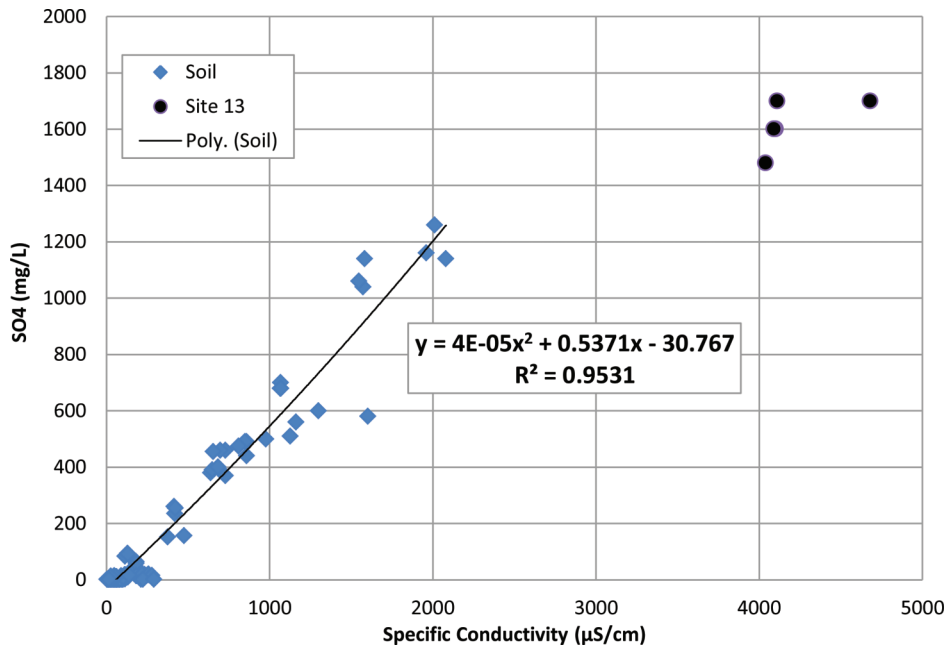
The solution is placed into sample cells with reagent, shaken and left undisturbed for a minimum of 5 minutes, but not more than 10 minutes. After that the sample is measured using the colorimeter.

APPENDIX C: TASK 2 GRAPHS

Identify Optimal Analytical Methods for Indiana Substrates

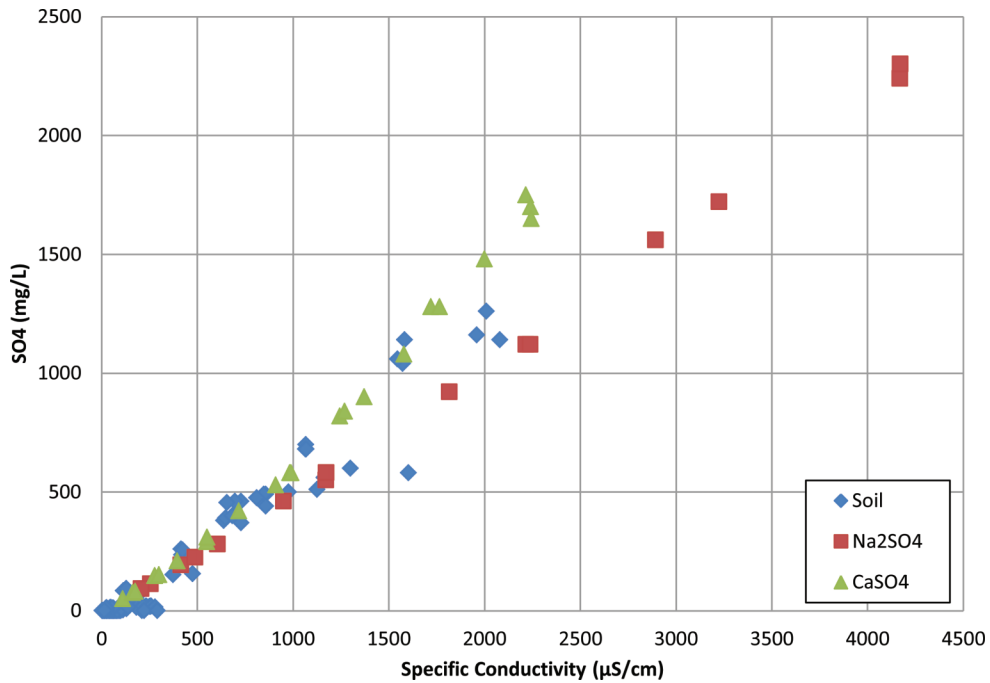


**Figure C.1** Box and whisker plots of all sulfate data in ppm from the dry weight of the samples separated by sampling site. The horizontal line within the box indicates the median, boundaries of the box indicate the 25th and 75th percentile, and the whiskers indicate the highest and lowest values of the results. The ranges around the medians result from variability in sulfate extraction a method (heated/shaken, sieved/unsieved, and soil: water ratio).

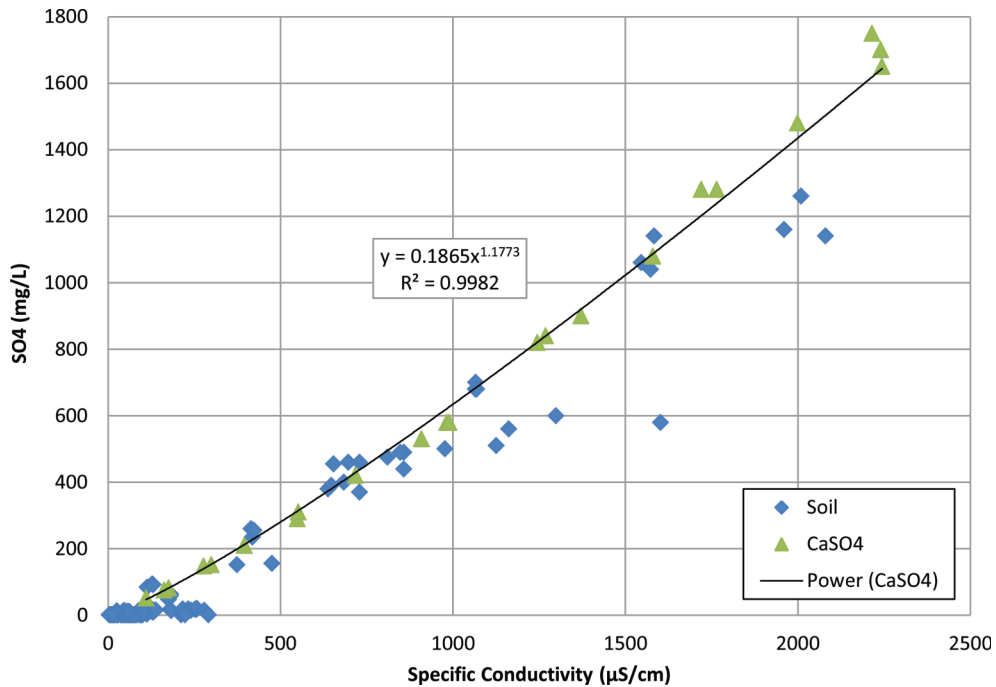


**Figure C.2** The relationship between specific conductance and sulfate in Indiana soils. There was a polynomial relationship with an  $R^2$  of 0.95 for the measured site (excluding site 13). The polynomial relationship was only very slightly more significant ( $R^2 = 0.953$ ) than the linear ( $R^2 = 0.952$ ).





**Figure C.3** Comparison of soil sulfate and conductivity relationship to potential mineral sources. The soil relationship aligns more closely with  $\text{Ca}_2\text{SO}_4$  although some data points are shifted toward the  $\text{Na}_2\text{SO}_4$  data.



**Figure C.4** The relationship between sulfate and conductivity best fits a power equation ( $R^2 = 0.9982$ ).

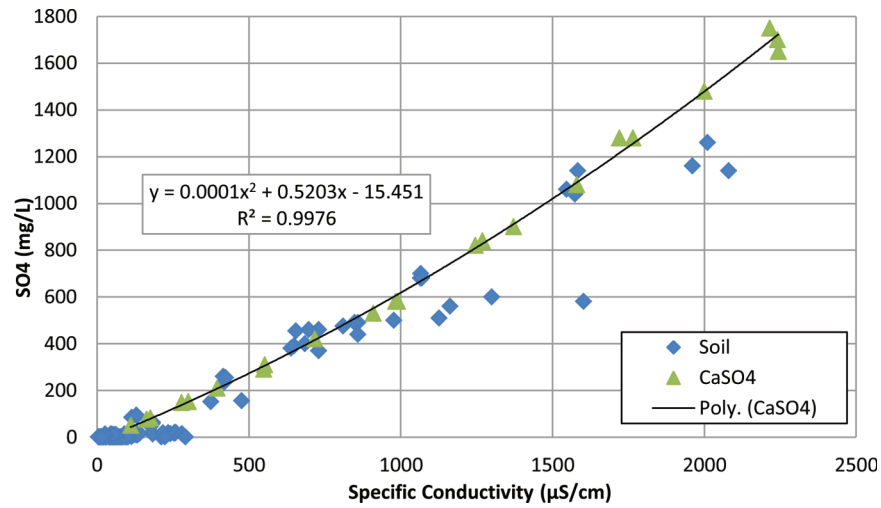


Figure C.5 The relationship between sulfate and conductivity described by a polynomial equation.

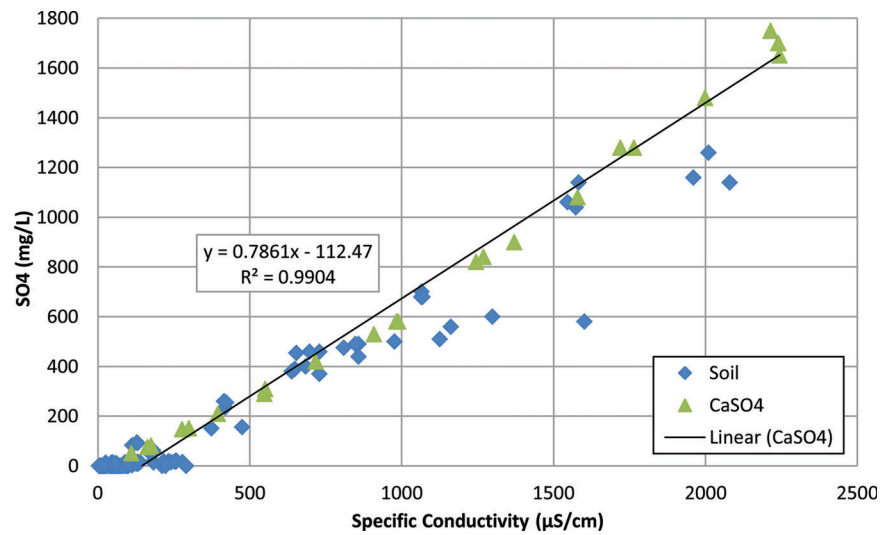
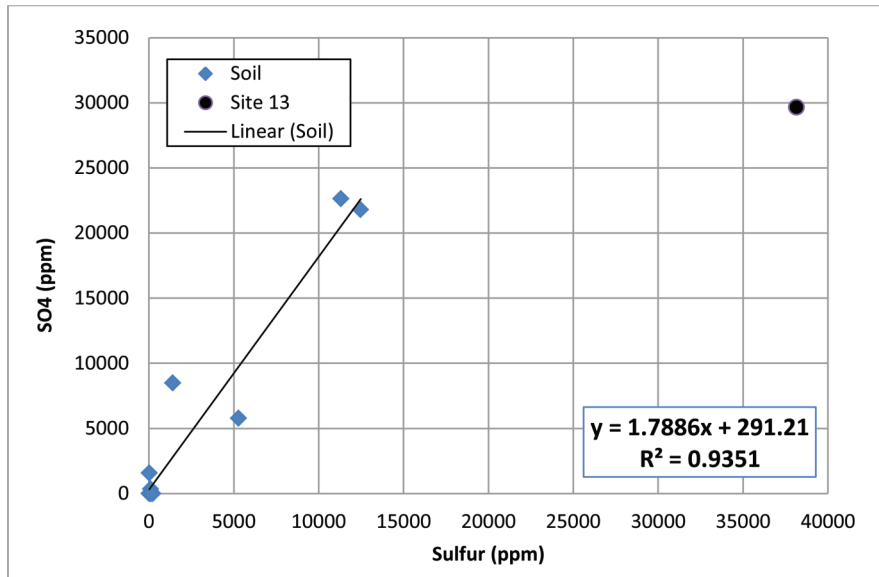
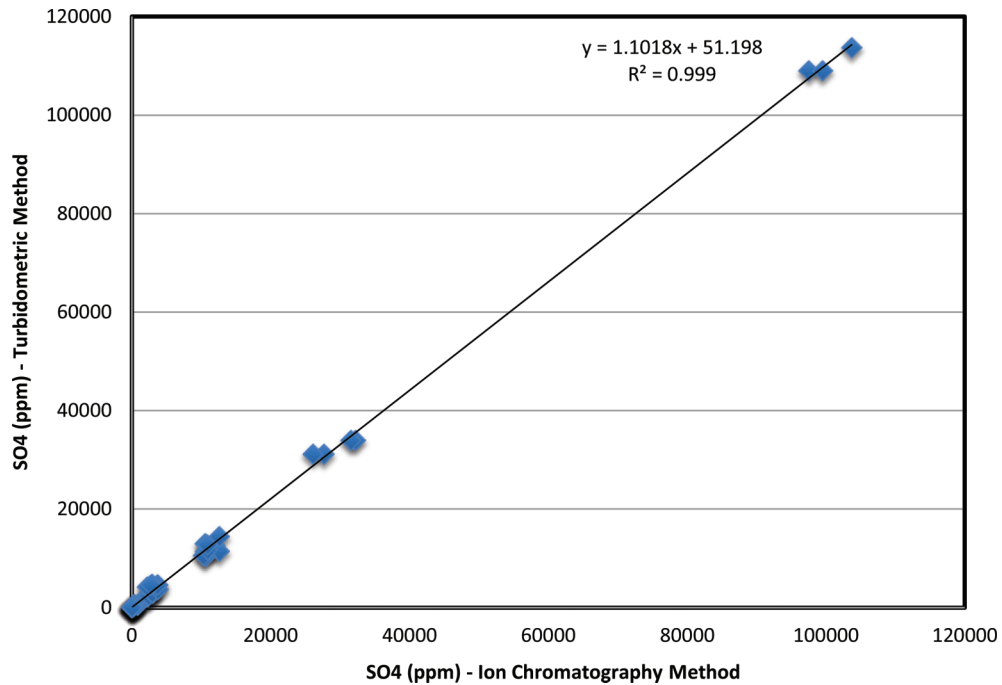


Figure C.6 The relationship between sulfate and conductivity described a linear equation.



**Figure C.7** The relationship between extractable sulfate and sulfur described a linear equation. More data points are needed to test the relationship.



**Figure C.8** Strong correlation of sulfate values measure from spectrophotometric and ion chromatography methods.

APPENDIX D: TASK 3 GRAPHS

Measure Extractability of Sulfates from Indiana Bedrock

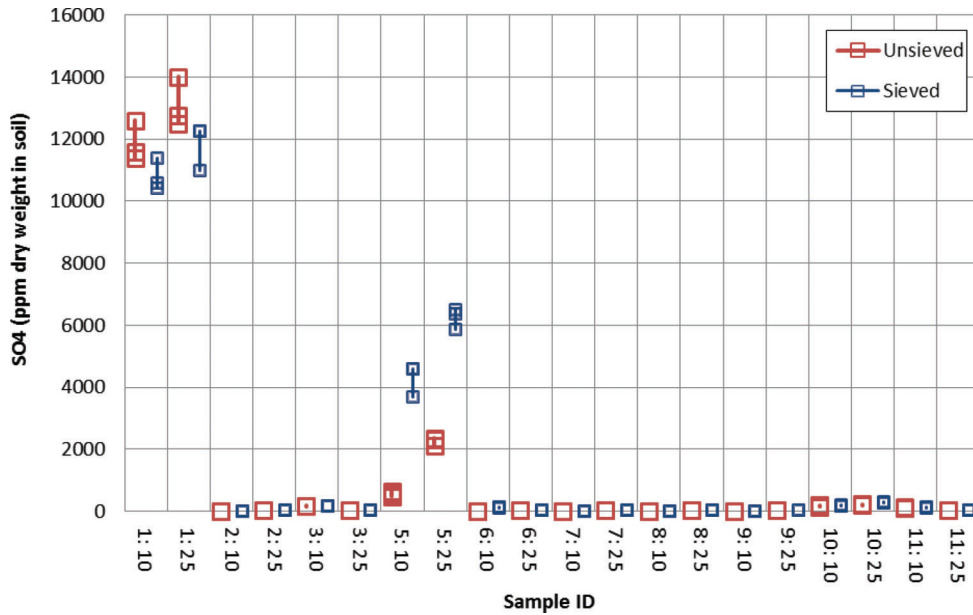


Figure D.1 Differences in sulfate concentrations for variations in grain size and dilution ratio. Triplicate measurements for each sample ID (site: dilution factor) were taken with to observe if there were differences. Site 13 did not have a sieved sample for comparison.

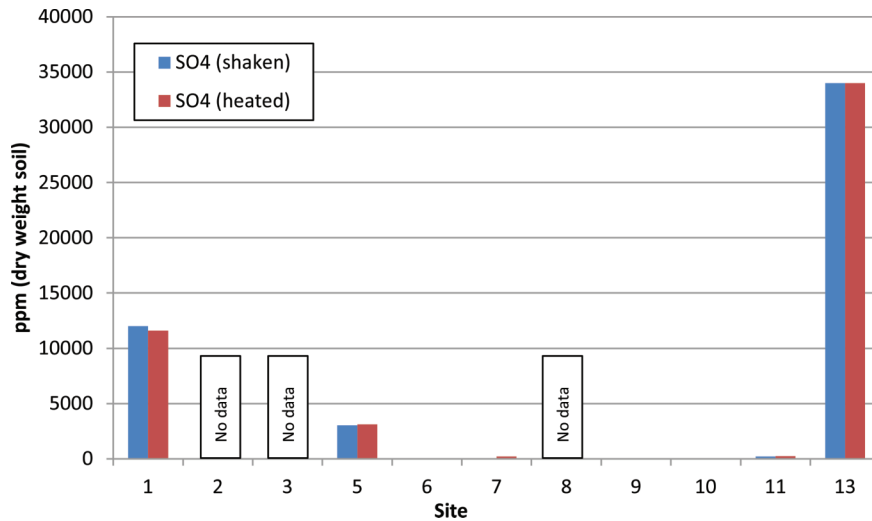
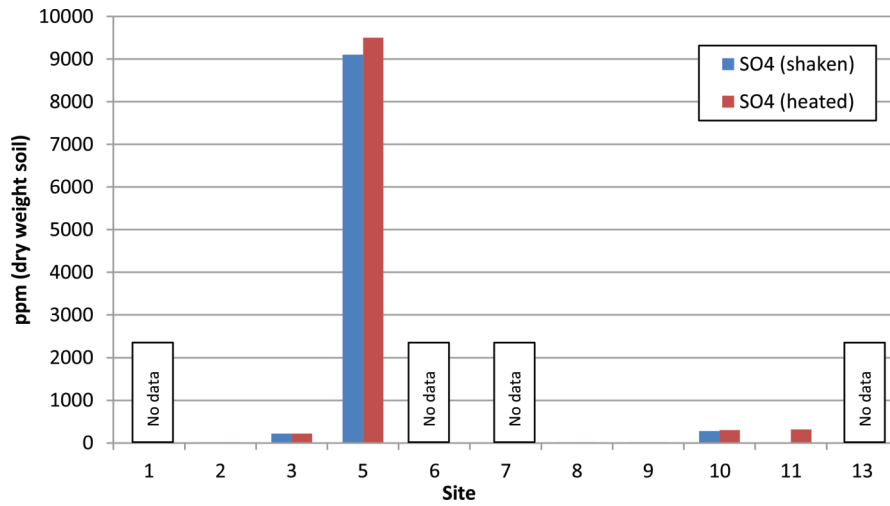


Figure D.2 Heated and shaken sulfate values for unsieved soil samples. Site 11 only had data for the heated sample recorded.



**Figure D.3** Heated and shaken sulfate values for sieved soil samples. Site 11 only had data for the heated sample recorded.

## APPENDIX E: PROPOSED ITM METHOD FOR DETERMINING SULFATE CONTENT IN SOIL BY CONDUCTIVITY SCREENING FOR LOW CONCENTRATIONS AND TURBIDIMETRIC METHOD FOR HIGH CONCENTRATIONS

### 1.0 Scope

- 1.1 This test method uses conductivity of soil leachate water to screen out low soluble sulfate concentration samples in subgrade soils.
- 1.2 Leachate samples with conductivity values above an established threshold conductivity value are measured for soluble sulfate concentration by using a turbidimetric method.
- 1.3 This ITM may involve chemical handling during operations, and may not address all of the safety problems associated with the use of the turbidimetric portion of the test method. The user of the ITM is responsible for establishing appropriate safety and health practices and determining the applicability of regulatory limitations prior to use.
- 1.4 Latex gloves are required to be used when handling the turbidity sulfate test reagent. The reagent is toxic and care is required to be taken to avoid ingestion or contact with the skin or eyes. Disposal procedures of hazardous materials should be followed for used reagent.

### 2.0 References

- 2.1 AASHTO Standards
  - 2.1.1 R 58 Dry Preparation of Disturbed Soil and Soil-Aggregate Samples for Test
  - 2.1.2 M231 Weighing Devices Used in the Testing of Materials
- 2.2 Standard Methods for the Examination of Water & Wastewater published by APHA, AWWA, WEF
  - 2.2.1 2510 Conductivity
  - 2.2.2 4500-SO<sub>4</sub><sup>2-</sup> E. Turbidity sulfate test

### 3.0 Terminology

- 3.1 Terms and Abbreviations. Definitions for terms and abbreviations will be in accordance with Department's Standard Specifications, Section 101 and the following:
- 3.2 Filtrate. Soil/water slurry that has passed through a filter
  - 3.2.1 Leachate. Aqueous portion of soil/water slurry
- 3.3 Specific Conductivity. The electrical conductance of a water sample normalized to 25°celcius. Most commercial conductivity meters have an automatic conversion feature allowing specific conductivity to be displayed.
- 3.4 Micro Siemen/cm. A unit of measure for electrical conductivity in water.
- 3.5 Turbidimetry. The measure of the loss in transmittance of a light beam as the beam passes through a solution. The terms "colorimetry" and "spectrophotometry" are also used, referring to wavelength-specific light transmittance or absorbance.
- 3.6 Ppm – parts per million, refers to concentration of sulfate in soil samples.

**4.0 Significance and Use** This ITM shall be used to screen for and determine the water-soluble sulfate ion content in soil. The results are used to determine if chemical stabilization of the soil is appropriate.

## 5.0 Apparatus

- 5.1 Balance, Class G2, in accordance with AASHTO M231
- 5.2 Conductivity meter and probe with temperature, conductivity, and specific conductivity reading options.
- 5.3 Beakers, 600 ml
- 5.4 Beakers, 150 ml (2)
- 5.5 Pipet, graduated 10 ml in 1.0 and 0.1 ml increments
- 5.6 Buchner funnel
- 5.7 Colorimeter and accessories
- 5.8 Dry, lint-free tissue
- 5.9 Filter paper, fine porosity, 2 micron
- 5.10 Graduated cylinder, 25 ml
- 5.11 1 L volumetric flask, class A
- 5.12 1 or more 50 ml volumetric flasks, class A
- 5.13 Latex gloves
- 5.14 Mortar and pestle
- 5.15 Oven, capable of maintaining a temperature of  $60 \pm 5^{\circ}\text{C}$  ( $140 \pm 9^{\circ}\text{F}$ )
- 5.16 Pans, brush and spatula
- 5.17 Pipettes, 2 ml disposable
- 5.18 Pulverizing apparatus
- 5.19 Sample cells (vials), glass, 10 ml
- 5.20 Side arm flask
- 5.21 Sieves, No. 4 and No. 40, conforming to the requirements of AASHTO M 92
- 5.22 Vacuum
- 5.23 Wash bottle, 500 ml, for distilled or de-ionized water
- 5.24 Wide-mouth rectangular or round high density polyethylene (HDPE) bottles, 500 ml
- 5.25 Wide-mouth rectangular or round high HDPE bottles, 125 ml

## 6.0 Materials and Reagents

- 6.1 Distilled or de-ionized water
- 6.2 Conductivity check standards, 100 micro Siemen/cm and 500 micro Siemen/cm
- 6.3 Sulfate reagent (Powder pillow) for 10 ml sample volume
- 6.4 Calcium sulfate dehydrate analytical reagent grade powder,  $\geq 99.8\%$  purity

## 7.0 Sample Preparation

- 7.1 The sample may be air dried or oven dried at a temperature not exceeding  $60^{\circ}\text{C}$  ( $140^{\circ}\text{F}$ )
- 7.2 After the sample is dried, the sample is crushed, ground, and split to obtain an approximately 500g sample that is then passed through a No. 4 sieve.
- 7.3 The sieved sample is pulverized and then passed through a No. 40 sieve.
- 7.4 The finely-sieved sample is split to obtain three approximately 20g samples and each sample is weighed to the nearest 0.1g.



## 8.0 Procedure

### 8.1 Conductivity instrument performance check

- 8.1.1 Turn conductivity meter on and place in SpC mode (specific conductance).
- 8.1.2 Place enough 100  $\mu\text{S}/\text{cm}$  standard in 150 ml beaker to cover electrodes in conductivity probe.
- 8.1.3 Place probe in solution, allow to equilibrate, record reading.
- 8.1.4 Rinse probe with distilled or de-ionized water, place in beaker containing 500  $\mu\text{S}/\text{cm}$  standard solution, rinse and discard. Put more standard in beaker, place probe in solution and allow to equilibrate, record reading.
- 8.1.5 If check standard readings deviate from actual value by more than 10  $\mu\text{S}/\text{cm}$ , probe should be cleaned. Follow cleaning instructions established by probe manufacturer.

### 8.2 Sulfate Concentration/Specific Conductivity Curve preparation

- 8.2.1 Curve should be prepared before initial conductivity tests of leachates performed.
- 8.2.2 New curve should be prepared when probe cleaning or replacement required.
- 8.2.3 Prepare saturated solution of calcium sulfate by weighing approximately 2.5 g of powdered calcium sulfate dihydrate and placing in 1 L volumetric flask. Fill flask to mark with distilled or de-ionized water. Cap and invert several times. Allow to sit. Powder will require up to 48 hours to dissolve. Powder not dissolved after 48 hours is indicative of saturation.
- 8.2.4 Prepare multiple dilutions of stock calcium sulfate solution using graduated pipet.
  - 8.2.4.1 Recommended dilutions include: 1:1, 4:5, 1:2, 1:5, 1:10, 1:25, 1:50, where each dilution represents the portion of stock solution in the total volume (example: a 1:10 dilution means 1 part stock solution in 10 total parts. For a 50 ml volume this would be 5 ml stock solution in a total volume of 50 ml). Above dilutions require the following amount of stock solution in a total volume of 50 ml, respectively: 50, 40, 25, 10, 5, 2, 1.
  - 8.2.4.2 If fewer 50 ml volumetric flasks are available than the number of dilutions, always prepare the most dilute solution first to minimize carryover contamination in subsequently prepared dilutions.
  - 8.2.4.3 Rinse volumetric flask between dilutions with distilled or deionized water when using same flask for multiple dilutions.
  - 8.2.4.4 Place dilutions in 125 ml wide-mouth HDPE bottles, cap and label with dilution ratio.
- 8.2.5 Turn on conductivity meter and set for specific conductivity reading. Place probe in each standard dilution, starting with most dilute. Ensure

probe electrodes completely immersed in solution. Record conductivity reading of solution. Rinse with distilled water, dry off outside surface of probe with kimwipe or equivalent lab wipe. Repeat procedure until specific conductivity of all solutions measured.

8.2.6 Measure the sulfate content of each solution using following procedure:

8.2.6.1 Turn on colorimeter by pressing power key.

8.2.6.2 Prepare dilution of concentrated solutions as follows:

8.2.6.2.1 For 1:1 solution prepare a 1:50 dilution

8.2.6.2.2 For 4:5 solution prepare a 1:40 dilution

8.2.6.2.3 For 1:2 solution prepare a 1:20 dilution

8.2.6.2.4 For 1:5 solution prepare a 1:10 dilution

8.2.6.2.5 For 1:10 solution prepare a 1:5 dilution

8.2.6.2.6 For 1:25 solution prepare a 1:2 dilution

8.2.6.2.7 For 1:50 solution run without dilution

8.2.6.3 Using a clean, uncontaminated disposable pipette, measure 10 ml of a diluted solution and transfer to a colorimeter glass vial and designate vial to be sample blank.

8.2.6.4 Cap vial, wipe outside to remove light beam obstructions.

8.2.6.5 Repeat procedure for a second glass vial to be labeled sample.

8.2.6.6 Place vial designated sample blank into colorimeter chamber/holder aligned with housing mark.

8.2.6.7 Cover sample blank with instrument cover.

8.2.6.8 Press ZERO/SCROLL key. The display will show “—” then “0”, confirming zero calibration.

8.2.6.9 Add sulfate reagent powder (SulfaVer 4 Powder Pillow) to second vial designated sample.

8.2.6.10 Cap vial and invert several times to mix the sample.

8.2.6.11 Wait 5 minutes for reaction to complete.

8.2.6.12 Wipe outside of vial, place in vial chamber/holder aligned with housing mark.

8.2.6.13 Cover sample cell with instrument cover

8.2.6.14 Press READ/ENTER key. The display will show “—” followed by the results in mg/L sulfate.

8.2.6.15 Take minimum of three readings for each solution and average the results.

8.2.6.16 Multiply each solution by the dilution made for analyzing sulfate content.

8.2.7 Prepare calibration curve.

8.2.7.1 Place conductivity and sulfate concentration values in Excel spreadsheet. Highlight data.

8.2.7.2 Click on Insert from main menu.

- 8.2.7.3 In the Insert menu click on scatter chart icon. Choose basic scatter chart format, without connecting line.
- 8.2.7.4 Once chart created, click on add chart element from chart tools menu.
- 8.2.7.5 From drop down menu choose trendline
- 8.2.7.6 From trendline drop down menu choose more trendline options.
- 8.2.7.7 A Format Trendline menu on the right of the spreadsheet will appear with trendline options. Click on Display Equation on chart and Display R-squared value on chart at bottom of menu.
- 8.2.7.8 Click on trendline option for linear, polynomial and power functions to find the best fit curve from R-squared value.
- 8.2.7.9 Use best fit equation for determining sulfate value of soil leachate conductivities.

### 8.3 Soil Slurry

- 8.3.1 Place one sample of soil into a tared HDPE bottle and record the weight of the soil slurry to the nearest 0.1 g.
- 8.3.2 Add approximately 400 ml distilled or de-ionized water to the sample. The ratio of the water to soil should be approximately 20:1.
- 8.3.3 Cap the bottle and shake the soil slurry for 1 minute.
- 8.3.4 Let bottle stand for 16 – 24 hours.
- 8.3.5 Turn on conductivity meter to read specific conductivity.
- 8.3.6 Place conductivity probe in settled slurry solution so that probe electrodes are immersed.
- 8.3.7 Record specific conductivity and determine corresponding sulfate concentration from calibration curve.
- 8.3.8 If measured conductivity indicates sulfate concentration is less than 50 mg/L, sample can be classified as low sulfate (<1000 ppm soil sulfate, for 1:20 soil: water ratio).
- 8.3.9 If measured conductivity indicates sulfate concentration is greater than 50 mg/L but less than 150 mg/L, sample can be classified as moderate sulfate (>1000 ppm, <3000 ppm soil sulfate).
- 8.3.10 If measured conductivity indicates sulfate concentration is greater than 150 mg/L sample is classified as high sulfate (>3000 ppm soil sulfate).
- 8.3.11 For all samples with conductivity reading corresponding to sulfate concentration less than 50 mg/L, analysis completed, no further action required.

### 8.4 Sulfate Measurement of Soil Leachates

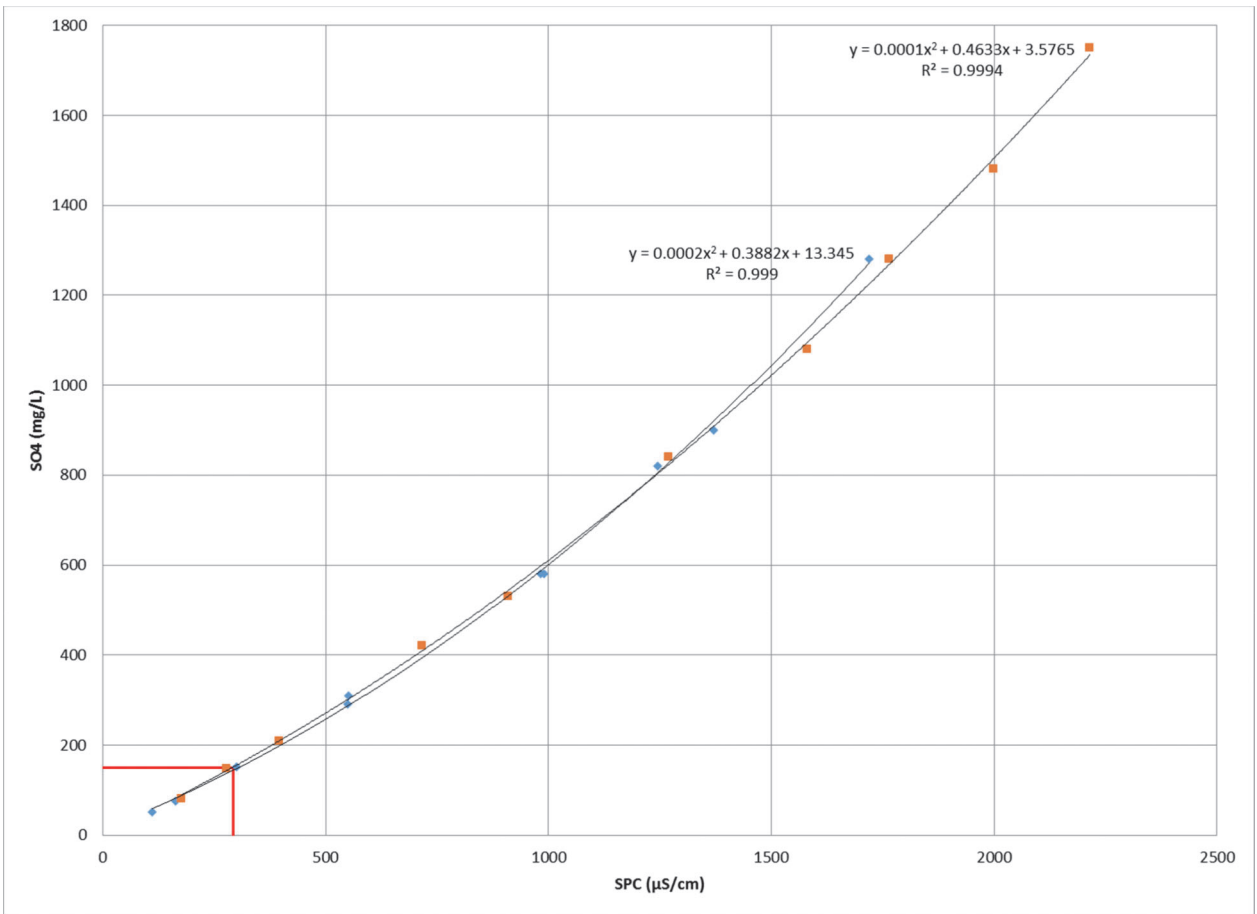
- 8.4.1 For sulfate concentration values desired on leachate samples with conductivity measurements indicating  $\geq 150$  mg/L.



- 8.4.1.1 Not required as these leachate samples are indicative of high sulfate content in soil and therefore require additional treatments for construction.
- 8.4.2 For sulfate concentration values on leachate samples with conductivity measurements indicating >50 mg/L and <150 mg/L.
- 8.4.3 Filter leachate samples from conductivity measurements to be tested for sulfate concentration using following procedure:
  - 8.4.3.1 Place a filter paper into the Buchner funnel and slightly moisten the filter paper with distilled or de-ionized water.
  - 8.4.3.2 Place the stem of the funnel through the rubber stopper and affix the stopper/funnel assembly onto the top opening of the side arm flask.
  - 8.4.3.3 Start the vacuum, decant the soil slurry sample into the funnel, and collect the filtrate in the side arm flask. Do not rinse material into the Buchner funnel or add any water. A filtration of 100-150 ml of the leachate is adequate.
  - 8.4.3.4 Repeat filtration procedure for all samples and replicates, collecting filtrate in separate flasks.
- 8.4.4 Sulfate measurement
  - 8.4.4.1 Use all steps defined in section 8.2.6 above, except step 8.2.6.3 to measure sulfate concentration for each leachate sample.
  - 8.4.4.2 Convert leachate sulfate concentration value in mg/L to soil sulfate content in ppm (parts per million) by multiplying mg/L value by soil/water ratio value (method requires 1:20 ratio).  
Example: 50 mg/L results from colorimeter X dilution factor of 20 = 1000 ppm soluble soil sulfate concentration.
  - 8.4.4.3 If sample leachate soil sulfate concentration is beyond the measurable range of the colorimeter, indicated by either a blinking number or an out-of-range message (occurs above approx. 70 mg/L) a dilution of the sample is required.
  - 8.4.4.4 Use the conductivity/sulfate concentration curve to find the approximate concentration of sulfate in the soil filtrate. Make a dilution of the sample that will bring the sulfate value within the range of instrument measurement (approx. 2 – 70 mg/L).
  - 8.4.4.5 When correct dilution determined, multiply mg/L by dilution factor, and then by soil/water ratio factor (20 for this method unless modified) to get final soil sulfate value in ppm.

## 8.5 Report

- 8.5.1 For low conductivity samples, report <1000 ppm.
- 8.5.2 For moderate conductivity report sulfate value in ppm.
- 8.5.3 For high conductivity, report either sulfate value, or if conductivity sufficiently high to warrant no further analysis, report >3000 ppm.



**Figure 1.** Example of calibration curve for sulfate concentration versus specific conductivity. Inside box area is where sulfate concentration and specific conductivity correspond to soil sulfate concentrations below 3000 ppm. Polynomial equations and  $R^2$  values are shown for two calibration curves.

## About the Joint Transportation Research Program (JTRP)

On March 11, 1937, the Indiana Legislature passed an act which authorized the Indiana State Highway Commission to cooperate with and assist Purdue University in developing the best methods of improving and maintaining the highways of the state and the respective counties thereof. That collaborative effort was called the Joint Highway Research Project (JHRP). In 1997 the collaborative venture was renamed as the Joint Transportation Research Program (JTRP) to reflect the state and national efforts to integrate the management and operation of various transportation modes.

The first studies of JHRP were concerned with Test Road No. 1—evaluation of the weathering characteristics of stabilized materials. After World War II, the JHRP program grew substantially and was regularly producing technical reports. Over 1,500 technical reports are now available, published as part of the JHRP and subsequently JTRP collaborative venture between Purdue University and what is now the Indiana Department of Transportation.

Free online access to all reports is provided through a unique collaboration between JTRP and Purdue Libraries. These are available at: <http://docs.lib.purdue.edu/jtrp>

Further information about JTRP and its current research program is available at: <http://www.purdue.edu/jtrp>

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