ATTACHMENT 11

EVALUATION OF ENVIRONMENTAL IMPACTS FROM DUST SUPPRESSANTS USED ON GRAVEL ROADS

PRESENTED TO	PRESENTED BY
Pennsylvania Department of Environmental Protection, Office of Oil and Gas Management Harrisburg, PA	**William D. Burgos** Penn State University University Park, PA

Release date:

May 26, 2022

Prepared by:

William Burgos, Ph.D.

Nathaniel Warner, Ph.D.

Xiaofeng Liu, Ph.D.

Eric Chase

Andrew Kearney

James Farnan

Andrew Eck

Hassan Ismail, Ph.D.

Table of Contents

List of Figures

List of Tables

EXECUTIVE SUMMARY

This report was prepared by a group of faculty, staff, and graduate students at The Pennsylvania State University (Penn State) for the Pennsylvania Department of Environmental Protection's (PADEP) Office of Oil and Gas Management to assess environmental impacts associated with dust suppressants used on dirt and gravel roads. Test systems were developed to conduct rainfall-runoff experiments to evaluate water quality impacts from gravel roads treated with dust suppressants, and dust generation experiments to evaluate efficacy of dust suppressants. Funding for the rainfall-runoff experiments was provided by PADEP. Penn State personnel independently conducted the dust generation experiments. Six dust suppressants were tested in rainfall-runoff and dust generation experiments: synthetic rainwater, calcium chloride ($CaCl_2$) brine, soybean oil, and three oil and gas produced waters (OGPWs). Two additional commercially available calcium chloride dust suppressants were tested in dust generation experiments.

When applied as a dust suppressant, oil and gas produced waters were essentially no more effective than rainwater. Oil and gas produced waters are likely ineffective dust suppressants because of their relatively high concentrations of sodium. Sodium is a monovalent cation that does not effectively bridge clay particles (the size-fraction most likely to be mobilized as road dust) to promote dust suppression. Instead, sodium can destabilize gravel roads and increase long-term road maintenance costs. Based on dust generation experiments, only the $CaCl_2$-based brines and the organic-based soybean oil were effective dust suppressants. Based on rainfall-runoff experiments, the $CaCl_2$-based brines led to the lowest concentrations of total suspended solids (TSS) washed off the roadbeds. There was no difference in the amounts of TSS washed off the roadbeds treated with OGPWs as compared to synthetic rainwater.

Maximum constituent concentrations in the runoff were related and essentially proportional to constituent concentrations in the dust suppressants. Contaminants of interest related to salinization of freshwater resources include electrical conductivity, total dissolved solids (TDS), chloride, and bromide. Contaminants of interest related to human health include combined radium (^{226}Ra + ^{228}Ra), barium, strontium, lithium, iron, and manganese. Contaminants of interest related to irrigation water include sodium, magnesium, and calcium. Contaminants of interest related to organic-based dust suppressants include chemical oxygen demand and dissolved organic carbon. Contaminants of lesser concern include aluminum, arsenic, lead, nitrate, and sulfate. Through mass balance analysis of material applied to, washed from, and retained by the roadbed, most contaminants of interest were washed from the

roadbed. An important exception occurred with roadbeds treated with oil and gas produced waters. For oil and gas produced waters, the roadbeds retained radium, sodium, iron, and manganese.

Runoff from $CaCl_2$ brine-treated roadbeds contained the highest concentrations of most contaminants of interest – including total dissolved solids, electrical conductivity, chloride, bromide, barium, strontium, lithium, iron, manganese, sodium, magnesium, and chloride. Roadbeds treated with calcium chloride brine produced runoff with high TDS (up to 57,000 mg/L) and chloride concentrations (up to 34,000 mg/L Cl) and elevated activities of combined radium (up to 48 pCi/L). Aside from calcium and chloride, most of the contaminants of interest were likely sourced from impurities in the brine.

OGPWs-treated roadbeds led to the highest concentrations of combined radium in the runoff. Combined radium activities in the three OGPWs when applied to the roadbeds ranged from 84 to 2,500 pCi/L, within the anticipated range for OGPWs from western Pennsylvania. Combined radium activities in runoff from the OGPW-treated roadbeds exceeded 60 pCi/L, the effluent standard for industrial wastewater discharges, during both the ‘first flush’ and the ‘maximum flush’ parts of the rain event. Roadbeds treated with OGPWs also produced runoff with high TDS (up to 19,000 mg/L), chloride (up to 12,000 mg/L Cl), and bromide (up to 300 mg/L Br) concentrations.

1. INTRODUCTION

This project was conducted for the Pennsylvania Department of Environmental Protection's (PADEP) Office of Oil and Gas Management by faculty and staff of The Pennsylvania State University (Penn State) to address potential environmental issues associated with the practice of spreading oil and gas produced water (OGPW) on unpaved dirt and gravel roads for dust suppression. The objectives of this project were to investigate water quality issues associated with runoff from OGPW-treated gravel roads and evaluate the efficacy of OGPWs as dust suppressants. These objectives were addressed by completing the following tasks: (1) design and fabricate a lab-scale test bed to conduct rainfall-runoff experiments from gravel roadbeds, (2) conduct a series of controlled rainfall-runoff experiments using a gravel roadbed treated with different dust suppressants to measure surface water quality parameters, (3) conduct a series of lab-scale experiments to measure dust generation, and (4) integrate and analyze all test results into a final report with recommendations on the suitability of OGPW and other products for dust suppression and their potential environmental impacts. Funding for the rainfall-runoff experiments was provided by PADEP. Penn State personnel independently conducted the dust generation experiments. The project began on June 1, 2020 and all testing was completed by May 31, 2021. A draft of this report was provided to PADEP on December 30, 2021.

2. SCOPE OF WORK

The number of experimental variables was minimized to constrain the overall amount of time and effort of this project. The only variable in the rainfall-runoff experiments was the dust suppressant. Six dust suppressants were tested: synthetic rainwater, calcium chloride brine, soybean oil, and three OGPWs. Synthetic rainwater served as the experimental control. Calcium chloride ($CaCl_2$) represented a common commercially available inorganic product used for dust suppression. Soybean oil represented a brine-free, common commercially available organic product used for dust suppression. The three OGPW represented fluids that could have been historically spread on dirt and gravel roads in northwestern Pennsylvania. These six dust suppressants and two commercially available $CaCl_2$ dust suppressants were tested in lab-scale dust generation experiments.

The constants in the rainfall-runoff experiments included: the road aggregate (PennDOT 2RC, a well-graded pit run gravel obtained from a sand and gravel plant in northwestern Pennsylvania), the size of the lab-scale gravel roadbed (9-foot long by 3 foot-wide), the side slope of the roadbed (5%), the depth of the roadbed (loose depth of 9-inch compacted to 6-inch), the initial moisture content of the treated roadbed before road compaction (6.5% mass/mass), the extent of compaction (≥95%), the application rate of the dust suppressants after compaction (0.5-gallons per square yard of road surface, except for 0.25-gallons per square yard of road surface with soybean oil), the storm event (2-year, 24-hour rainfall, 2.44-inch total rain), the rain distribution system (grid of controlled nozzles), the synthetic rainwater chemistry (distilled water + H_2SO_4/HNO_3, pH = 4.2, EC = 31 µS/cm), the water runoff sampling frequency (sampled after every 1/24th of the storm volume using an automated sampler, and sampled every 10-seconds using a multimeter probe), and the water chemistry analytes (cations, anions, radium, and organics).

All rainfall-runoff experiments were conducted in at least triplicate starting with newly constructed roadbeds for each test. One of the OGPWs was tested four times, the calcium chloride brine was tested four times, the synthetic rainwater was tested five times, and all other dust suppressants were tested three times for a total of 22 tests. At the conclusion of select tests, shallow (1 to 2 inch-depth) roadbed samples were collected to measure radium and petroleum hydrocarbons retained in the road.

The constants in the dust generation experiments included: the road aggregate (PennDOT 2RC, a well-graded pit run gravel obtained from a sand and gravel plant in northwestern Pennsylvania), the size and rotational speed of the mechanical tumbler, the mass and dimensions of the road aggregate discs, the moisture content of the treated discs before application of dust suppressant, the extent of compaction (modified Proctor test), the application rate of the dust suppressants after compaction, the air sampling rate of the DustTrak dust measurement device, the sampling frequency of dust concentration (sampled every second for 3 minutes), and the elapsed time of the test (between 2:00-3:00 minutes) to calculate the average dust concentration. A previous study confirmed that the lab measurements were in direct agreement with DustTrak measurements collected in the field from the back of a moving vehicle (Stallworth et al., 2020).

3. BACKGROUND

Produced waters from oil and gas wells are allowed to be spread on roads for dust suppression and/or deicing in at least 12 states in the United States (Tasker et al., 2018). On May 17, 2018, the use of OGPWs for dust suppression was put on hold by PADEP in response to a decision by the Pennsylvania Environmental Hearing Board.

OGPWs are commonly referred to as brines whose chemical compositions are somewhat like commercial inorganic products commonly used for dust suppression (e.g., saturated solutions of calcium chloride or magnesium chloride). However, OGPW is not a pure solution of calcium chloride, magnesium chloride ($MgCl_2$) or sodium chloride (NaCl). Instead, OGPW from formations in the Appalachian Basin, including western Pennsylvania, are typically classified as Na-Ca-Cl waters containing a blend of alkali metals (Na, K, Li) and alkaline earth metals (Mg, Ca, Sr, Ba) charge-balanced primarily by chloride. OGPWs also contain a variety of contaminants of interest raising questions about the practice of spreading them on roads. Based on analysis of 14 OGPW samples used for road spreading in northwestern Pennsylvania, Tasker et al. (2018) reported median concentrations of chloride, barium, strontium, arsenic, lead, and combined radium (^{226}Ra + ^{228}Ra) above corresponding drinking water maximum contaminant limit (MCL) standards. The median concentration of combined radium (^{226}Ra + ^{228}Ra) was 1,230 pCi/L as compared to the US Nuclear Regulatory Commission's (NRC) industrial wastewater discharge standard of 60 pCi/L and the US Environmental Protection Agency's (EPA) drinking water maximum contaminant limit (MCL) standard of 5 pCi/L. Graber et al. (2017) also reported that application of OGPW may lead to higher concentrations of contaminants of interest in both the dust and the runoff water. The ratio between alkali metals to alkaline earth metals in brines and OGPW is expected to be one of the key factors with respect to dust suppressant efficacy (Graber et al., 2019). One measure of the ratio of alkali to alkaline earth metals based on dissolved metal concentrations, expressed as the sodium adsorption ratio (SAR), is defined as (Equation (1)):

$$SAR = \frac{Na^{+}\left(\frac{meq}{L}\right)}{\sqrt{0.5*\left(Ca^{2+}\left(\frac{meq}{L}\right)+Mg^{2+}\left(\frac{meq}{L}\right)\right)}} \tag{1}$$

Increasing SAR tends to decrease dust suppressant efficacy (Stallworth et al., 2020a; Graber et al., 2019). Magnesium chloride and calcium chloride commercial products have very low SAR values and demonstrated effectiveness at reducing dust generation. While there are few previous studies on OGPW use as dust suppressants, one field study indicated that OGPW applied to dirt and gravel roads in North Dakota was not effective at reducing dust compared to an untreated road (Graber et al., 2017). This contrasts with field studies that tested dust suppression products such as magnesium chloride, cellulose, or synthetic fluids that all reduced dust relative to untreated roads (Kunz et al., 2015). A literature review conducted by Payne (2018a) concluded that evidence for the use of OGPW for dust suppression was questionable because of previous study designs and the use of OGPW on dirt and gravel roads may destabilize the road surface leading to more dust and road maintenance. However, a laboratory study that measured clay dispersion in salt solutions indicated that, if electrical conductivity was high enough, then the OGPW was effective at reducing dispersion regardless of elevated SAR (Graber, et al., 2019).

This project sought to simulate conditions most relevant to northwestern Pennsylvania. Specifically, 2RC gravel was sourced from a local quarry (Glenn O Hawbaker's Brokenstraw Sand and Gravel Plant in Pittsfield PA, Warren County), the design storm hyetograph was programmed to match a 2-year 24-hour rain event for Warren County, PA (Section 7.7 in PennDOT Drainage Manual 2015; United States Department of Agriculture 1986), a synthetic rainwater was designed to match chemistry of northwestern Pennsylvania (EPA publication SW-846), and OGPWs were sourced from northwestern Pennsylvania (under confidentiality agreements). The 2RC used in this study was a well-graded aggregate that consisted of a mix of coarse crushed stone (48.3% m/m) and fine materials including sand (42.2%), silt (6.6%), and clay (2.9%) with a maximum wet density of 144.3 pound/cubic foot.

4. RESEARCH METHODS

4.1 Dust suppressants

Six fluids were applied to laboratory-scale gravel roadbeds to measure water quality characteristics in rainfall-runoff experiments over a 24-hour test. Three of the six fluids tested were conventional OGPWs from western Pennsylvania provided by oilfield service companies under nondisclosure agreements to maintain confidentiality of all project participants. These OGPWs were selected by PADEP, Penn State, and project participants. These three OGPWs and all their associated runoff and roadbed samples are identified as O&G PW1, O&G PW2, and O&G PW3 in this report. Two of the six fluids tested, a calcium chloride brine and a soybean oil, were included as materials representative of commercially available dust suppressants. Calcium chloride anhydrous was purchased from Fisher Science Education (>95% mass/vol assay range). Calcium chloride brine was created by adding solid calcium chloride to distilled water more than its calculated solubility limit. Because of kinetic limitations, fully 'saturated' conditions (commonly 35% m/m) were not achieved. Saturation extents ranged from 17.2 – 25.4% m/m for the four replicate tests with calcium chloride brine. The calcium chloride brine and all their associated runoff and roadbed samples are identified as $CaCl_2$ Brine in this report. Soybean oil was provided by a soybean crushing company and is a mechanically extracted, degummed, all-natural soybean oil (>95% fatty acid). This soybean oil is currently used for dust suppression by a township in northwestern Pennsylvania. The soybean oil and all its associated runoff and roadbed samples are identified as Soybean Oil in this report. Synthetic rainwater was included as a control to represent natural wetting of the road. The synthetic rainwater recipe was designed to match rainfall chemistry of northwestern Pennsylvania. The synthetic rainwater and all its associated runoff and roadbed samples are identified as Synthetic Rainwater in this report. These six dust suppressants and two commercially available calcium chloride dust suppressants were tested in lab-scale dust generation experiments.

Commercial Brine 1 was a liquid solution that ranged from 28-42% $CaCl_2$ (m/m). This brine is marketed primarily for dust suppression and road deicing and is approved by the West Virginia Department of Environmental Protection for use on unpaved roads. Commercial Brine 1 used in this study was 28% $CaCl_2$ (m/m). Commercial Brine 2 was a blended brine comprised of Ca, Mg, K, and Na chlorides, with $CaCl_2$ being the most concentrated at 21-24% (all other salts reported <5%). This product is commonly used as a deicer in the Mid-Atlantic and Northeast United States but is also sold as a dust suppressant for underground and open cut mining operations. Commercial Brine 2 used in this study was 25% $CaCl_2$ (m/m).

4.2 Test bed for rainfall-runoff experiments

A laboratory-scale roadbed system was constructed for rainfall-runoff experiments (Figure 4.1). A rectangular steel frame (9-foot long, 3-foot wide, 1-foot tall) was fabricated with a reinforced floor strong enough to hold the weight of the gravel roadbed and withstand loads delivered from roadbed compaction equipment (Figure 4.2). Stainless-steel panels were fixed to the bottom and three sides of the frame. The roadbeds were constructed by placing a 9-inch-deep loose lift of 2RC gravel into the frame and then using a motorized vibrating plate compactor to tamp the gravel to 6-inch deep, equivalent to 95% or greater compaction. At the start of the project, road compaction was verified for two roadbeds in accordance with ASTM D6938 – Density and Moisture Content of In-Place Soil and Soil Aggregates Using Nuclear Methods (Shallow Depth) by CMT Labs (State College, PA). The number of vibratory plate tamper passes to achieve a minimum of 95% compaction was recorded for the right, middle, and left portions of each of the two constructed roadbeds. For the rest of the tests, the operationally defined number of tamper passes (one pass up and back per section of roadbed) was used to compact each roadbed. During compaction, a solid plastic insert was placed at the 'downstream' end of the frame to retain the gravel. After compaction, the plastic insert was removed, and the gravel was retained by a heavy gage stainless-steel screen with ¼-inch openings. A stainless-steel discharge chute was bolted onto the downstream end of frame to funnel runoff to a flow-through sampling bucket.

A moisture-density curve for the roadbed material was developed by Aggregates & Soils Testing Co (Enola, PA). From these data it was determined that a moisture content of 6.5 wt% (m/m) was optimal for compaction. Before each roadbed was compacted, the moisture content of the gravel was measured by drying in a microwave oven until constant weight. A 22.2-ton load of crushed gravel was delivered to the CITEL Building in State College on June 19, 2020. The gravel was stored outside on pavement until the pile began to freeze in January 2021. At that point, a portion of the remaining gravel pile was stored inside the building. Distilled water was added and manually mixed into the roadbed such that roadbeds reached 6.5 wt% at the start of each test before compaction. The exact volume of added distilled water was calculated based on the measured moisture content before the test and the target value of 6.5 wt%. After the roadbed material was compacted within the test frame, the whole frame was lifted onto a steel I-beam. A steel bar was first positioned on top of the upstream end of the I-beam such that the slope of the bed was 5% towards the sampling bucket. The slope was used to simulate the sideslope of a gravel road from the crown to the edge of the road.

A rainfall simulator was designed to meet PADEP's request to use a 2-year, 24-hour Type II storm event, the specified rainfall distribution type for Warren County, Pennsylvania based on Figure B-2 in US Department of Agriculture (USDA) TR-55 (Figure 4.3; 2.44-inch total rain) to generate runoff from the roadbed. The pumping and plumbing systems were designed to spray water uniformly over the roadbed and minimize evaporation (Figure 4.4). The rainfall simulator included a supply tank, submersible pump, constant head feed tank with supply tank, diaphragm pump, flow meter, pressure manifold and gauges, solenoid valves, and spray nozzles. The supply tank was a 55-gallon plastic drum positioned on the floor of the lab. A submersible pump was placed inside at the bottom of the drum. The drum was fitted with a plastic lid and tubing from the submersible pump to the constant head feed tank was routed through the bung hole of the lid. A scaffold was positioned next to the roadbed frame to hold all other components of the rainfall simulator. The scaffold deck was positioned at approximately the height of the roadbed and an elevated frame system was constructed such that the whole roadbed could be contained by plastic shower curtains to capture any overspray from the nozzles and minimize evaporation loss from the road during the test. The constant head feed tank was a 2-gallon plastic storage container equipped with an outlet pipe to the diaphragm pump. A bypass valve after the diaphragm pump and before the flow meter was used to recirculate water back to the supply tank to regulate the discharge to the spray nozzles. An overflow orifice and tube were connected to the constant head tank to ensure the water elevation in the head tank remained constant. This ensured the pump's performance was consistent during testing. The diaphragm pump conveyed water through the flow meter and into the pressure manifold system. Solenoid valves were used to control flow to the spray nozzles over the 24-hour test. The rainfall intensity was discretized into 5-minute bursts and rainfall volumes were computed for each 5-mintue burst. The solenoids were open for a fraction of time in each 5-minute burst, then closed for the remainder. The pre-specified open/close times were computed beforehand to ensure the volume sprayed by the nozzles equaled that shown in Figure 4.3. The solenoid valves were actuated with a microcontroller. The microcontroller was programmed to open the solenoid valves for the pre-determined open/close times. Near the beginning and end of the 24-hour rain event, the microcontroller would open the valves for only a few seconds in each 5-minute burst. At peak rainfall, the microcontroller would open the valves for approximately 95% of the 5-minute burst. Three square-pattern spray nozzles each covered a 9-ft^2 area and were positioned 12-inches above the roadbed to minimize overspray.

Runoff samples and continuous meter readings were collected from a 2-gallon plastic bucket that was hung off the end of the discharge chute (Figure 4.4). Overflowing water was collected in a large tub below the chute and disposed of after the experiment. A Hanna HI98195 Multiparameter pH/ORP/EC/Pressure/Temperature Waterproof Meter was placed within the bucket and programmed to continuously read pH, oxidation-reduction potential (ORP), electrical conductivity (EC), pressure, and temperature every 10 seconds over the 24-hour test for a total of approximately 8,640 sample points per test. A Model 6712 Portable ISCO sampler was used to automatically collect 500-mL grab samples of the runoff each time that 1/24th of the total storm volume (ca. 6.3-liter) had been applied to the roadbed. A sample collection tube was secured to the sampling bucket and connected to a suction pump in the ISCO unit. The time stamps for this sampling scheme were programmed into the sampler and are presented in Table 4.1. At each time stamp, the ISCO sampler initiated a sampling sequence where the suction pump purged the suction line, filled the sample bottle, and re-purged the suction line. This process took about 45-seconds to complete, including 15-seconds for the pump to fill the bottle. Sample bottles were arranged in a circular carousel that was stored in the bottom portion of the ISCO unit. The Hanna multimeter, the ISCO sampler, and the program controlling the solenoid valves were all started at approximately the same time to keep the rain event and sampling procedure on the same experimental timeline (rainfall simulator started ~5-seconds before sampling equipment).

4.3 Rainfall-runoff experiments on gravel roadbeds treated with dust suppressants

A single rainfall-runoff experiment with an individual roadbed treated with one dust suppressant required three days to complete followed by an extended period to complete all chemical analyses on the runoff samples. The roadbed was constructed and treated with the dust suppressant on Day 1. The treated road was allowed to rest under ambient conditions until Day 2 when the rainfall simulator started to deliver the 24-hour storm to the roadbed. The test was completed on Day 3 with removal of the sample bottles from the ISCO sampler, retrieval of the data from the Hannah multimeter, collection of post-storm roadbed samples, deconstruction of the roadbed, and cleanup of the test frame. Detailed descriptions of each step are provided below.

Synthetic rainwater

Synthetic rainwater used for all experiments was prepared to simulate the chemistry of rainfall in northwestern Pennsylvania. Synthetic rainwater was made by adding a 3:2 m/m solution of 15 N sulfuric and 15 N nitric acid to distilled water until a pH of ~4.2 was reached. The electrical conductivity

(EC) of the synthetic rainwater averaged 31 µS/cm. Synthetic rainwater was prepared in ca. 50-gallon batches stored in 55-gallon drums. Prior to use, drums were either cleaned with hot, soapy water and thoroughly rinsed or lined with plastic drum liners. All drums remained covered during storage.

Roadbed construction

Before the roadbed was constructed, samples were collected from the gravel pile to measure the initial moisture content. An initial mass of ca. 2,000-grams of gravel was placed in a Pyrex container and dried in a microwave oven until constant mass was achieved. The moisture content (m/m %) was calculated as the difference between the initial and final masses divided by the final mass.

Before the gravel was loaded into the test frame, the gravel was mixed with distilled water to reach a moisture content of 6.5%. The total mass of gravel added to the roadbed was calculated to be approximately 1,850-pounds based on the laboratory-measured maximum wet density and the compacted bed volume. The volume of distilled water added to the gravel was calculated based on the total gravel mass and its initial moisture content. This volume was slowly added to the gravel while it was in a skidloader scoop and thoroughly mixed with shovels and pickaxes. The gravel was then poured into the test frame while the frame rested on the ground. A ca. 9-inch-deep bed of loose gravel was spread evenly inside the test frame before compaction.

The gravel bed was compacted with a hand tamper and a vibratory plate compactor to a final depth of 6-inches. These same pieces of equipment were used to compact the bed when its extent of compaction was measured by ASTM D6938 – Density and Moisture Content of In-Place Soil and Soil Aggregates Using Nuclear Methods (Shallow Depth) by CMT Labs (State College, PA). A hand tamper was first used to create a solid gravel surface. A 16-inch x 22-inch vibratory plate compactor was used for three passes up and down the roadbed (up and back on the left, center, and right of the bed with some overlap due to the size of the compactor). The hand tamper was used again to compact gravel on the edges of the frame and to flatten any ridges created by the plate compactor. The roadbed was compacted with the plastic insert placed at the downstream end of the frame. The plastic insert was removed before the rainfall simulator was started. A heavy gage stainless-steel screen with ¼” openings secured the bed after the plastic insert was removed.

The compacted gravel bed was treated with six different dust suppressants: synthetic rainwater, calcium chloride brine, soybean oil, and three OGPWs. The same procedures were used for the application of synthetic rainwater, calcium chloride brine, and the OGPWs. A different procedure was used to apply the soybean oil. For the synthetic rainwater, calcium chloride brine, and OGPWs, 1.5-gallons of liquid was poured into a plastic watering can and then sprinkled evenly onto the roadbed (equal to application rate of 0.5-gallons per square yard). For the soybean oil, the oil was first heated to 120 °F (common in-field practice) and, because of the low viscosity of the oil, a paintbrush was used to evenly apply 0.75-gallons onto the roadbed. After application of any dust suppressant, a large fan was used to dry the road for 20-30 minutes to allow for infiltration and minimize runoff before the test frame was lifted onto the I-beam.

A boom crane was used to lift the test frame onto the I-beam using crisscrossed metal cables attached to the eyebolts on the frame. The test frame was positioned onto the I-beam such that the downstream end aligned with two bolts drilled into a hinge secured to the I-beam. A metal block was positioned at the upstream end of the I-beam under the test frame to create a 5-degree slope. The stainless-steel chute was attached to the end of the frame and plumber's putty was used to seal the gap between the chute and the frame to prevent any runoff loss. The sampling bucket was hung off the end of the chute. With the test frame in place, shower curtains were positioned such that the entire roadbed was surrounded with no gaps in between curtains. The bottoms of the curtains rested inside the test frame, not touching the gravel (Figure 4.5). In some areas, zip ties were used to secure the shower curtains onto the frame and ensure the curtains did not block the nozzles of the rainfall simulator.

24-hour storm event

Synthetic rainwater was pumped through the nozzles of the rainfall simulator to deliver rain to match the time-dependent quantities of the 2-year, 24-hour storm for Warren County, Pennsylvania (Figure 4.3; 2.44-inch total rain). The pH and EC of the rainwater were measured at the start of each test. The Hannah multimeter and the ISCO suction line were secured into the sampling bucket hung off the end of the chute. The Hanna multimeter, the ISCO sampler, and the program controlling the solenoid valves were all started at approximately the same time to synchronize the sampling time stamps with the 24-hour rain event.

The rainfall-runoff experiment was concluded after the final, 24th runoff sample was collected by the ISCO sampler 24-hours after the experiment was started. All ISCO sample bottles were removed from the sampler's carousel and capped. All data from the Hannah multimeter was downloaded to a desktop computer. Three gravel samples were collected from the top 1-2 inches of the roadbed. The roadbed was then manually disassembled using shovels and pickaxes. Used gravel was disposed of into a dedicated road aggregate dumpster. All tools and sampling equipment were carefully cleaned before the next experiment.

4.4 Analysis of dust suppressants, runoff samples, and roadbed samples

A comprehensive set of chemical analyses were used to characterize the dust suppressants, runoff samples, and synthetic rainwater (Table 4.2). Solid samples from the gravel pile or the roadbeds (at the conclusion of the rainfall-runoff experiments) were also analyzed for many of these same analytes (Table 4.3). Samples were divided, handled (e.g., filtration, digestion), and preserved (e.g., acidification, refrigeration) before being measured using a variety of analytical instruments.

Measurement of inorganic constituents

Samples collected for dissolved analysis were filtered through a 0.45-µm filter and acid preserved to pH < 2 with high purity nitric acid. If necessary, samples were gravimetrically diluted with 2% high purity nitric acid. Samples collected for total metals were unfiltered and only acid preserved until they were digested following a modified EPA method 3010A. 1.5 mL of concentrated ultra-pure nitric acid was added to 50-mL of sample, which was then covered with a plastic-ribbed watch glass, and gently evaporated to < 5-mL. Additional 1.5-mL aliquots of nitric acid were added as necessary until the sample turned a pale yellow, after which the sample was evaporated to 3-mL. 5-mL of trace metal grade hydrochloric acid was added to the sample and refluxed for 15-minutes. Once the digestion was complete, the evaporated sample was reconstituted to 50-mL with deionized water.

Major cation (Ca, K, Mg, Na and Sr) concentrations were measured with a ThermoFisher iCAP 7400 inductively coupled plasma optical emission spectrometer (ICP-OES) housed in the Penn State Laboratory for Metals in the Environment (LIME). Calibration standards were prepared from a 100 mg/L multi-element standard, SCP28AES, with calibration levels ranging from 0.01 to 100 mg/L. Analyte emission frequencies were optimized to avoid interferences using Qtegra ISDS software. Some analytes were measured in both radial and axial modes to improve quantification across wider concentration ranges. A 5 mg/L Lu solution was used as an internal standard to monitor instrument drift. Continuing calibration verification standards (CCVs) and a USGS M-220 CRM was analyzed with each sample batch. The acceptance criteria were 10% agreement with expected values for CCVs and 20% agreement with established values for the certified reference material (CRM).

Trace metal (Al, As, B, Ba, Co, Cr, Fe, I, Li, Mn, Ni, Pb, V, and Zn) concentrations were measured with a ThermoFisher iCAP RQ inductively coupled plasma mass spectrometer (ICP-MS) in the Penn State

LIME. Calibration standards were prepared from high purity stock solutions at calibration levels ranging from 0.01-1,000 ng/mL. A 100 ng/mL Sc solution was used as an internal standard to correct for differences in detector responses. A NIST 1640A CRM for trace elements in water was used to validate calibration curves. Quantification was taken as valid if measured concentrations agreed to within 20% of established values.

Anion (Cl^-, Br^-, SO_4^{2-}, NO_3^-) concentrations were measured by ion chromatography (IC) following a modified EPA Method 300.1. Filtered (0.45-µm) samples were injected into a Dionex 1100 IC system with a 25-µL sample loop and a 1 mL/min flowrate. 35 mM potassium hydroxide was used as the eluent solution. An AG18 guard column and a 4-mm AS18 analytical column held at 30°C were used to carry out the separation. A 4-mm AERS 500 suppressor poised at 87 mA and a Carbonate Removal Device 200 were used to reduce background conductivity and remove carbonate interferences, respectively. A 1000 mg/L calibration stock solution was made from pure salts that had been oven dried at 105°C for four hours. Calibration standards were made gravimetrically from this stock, and calibration levels ranged from 0.1 to 500 mg/L. CCVs, a laboratory fortified matrix sample (LFM), a duplicate sample, and a USGS M-220 CRM were run with every sample batch. The analysis quality control criteria were as follows: agreement within 10% for CCVs, agreement within 25% for the LFM, agreement within 20% for the duplicate sample, and agreement within 20% for the CRM.

Total dissolved solids (TDS) were calculated from the sum of the concentrations of Cl, SO_4, Br, Ca, Mg, Na, K, Sr, Ba and reported as mg/L TDS. Standard Method 2540 C (evaporation at 180^{o}C) was not used to measure TDS because the required amount of sample volume was not available from the ISCO sample bottles.

Total suspended solids (TSS) were measured with a HACH DR2800 spectrophotometer following the suspended solids 8006 photometric method.

Measurement of organic constituents

COD was measured using the USEPA Reactor Digestion Method 8000 and HACH COD digestion vials. Samples with chloride concentrations >1,000 mg/L Cl could not be measured because of reagent interferences. HACH COD2 digestion vials were used for all runoff samples associated with O&G PW1, O&G PW2, O&GPW 3, and calcium chloride brine. Dissolved organic carbon (DOC) was measured using a TOC-V CSN analyzer. Dissolved inorganic carbon (DIC) was calculated by difference between total carbon (measured on TOC-V CSN analyzer) and DOC.

Sample extraction

Selected runoff samples, dust suppressants, and roadbed samples were analyzed for diesel range organics (DRO) (aliphatic carbon chain lengths of C10-C28) and targeted organic compounds. 125 mL of each runoff sample was first acidified to pH < 2 with 1:1 (v/v) sulfuric acid and spiked with acid, base, and neutral surrogate compounds (final extract concentration: 1000 pg/µL) to evaluate extraction recoveries. The sample was extracted three times in a 1-L separatory funnel with 20-mL aliquots of dichloromethane (DCM). The pH of the sample was then increased to >11 with 10 N sodium hydroxide and extracted three times with 25-mL aliquots of DCM. Kuderna-Danish evaporative concentration was used to reduce the combined extract volume to <10-mL. The extracts were further concentrated to a final volume of 1000 µL under a steady stream of nitrogen. Duplicate 200 mL volumes of each dust suppressant (except for soybean oil) was extracted in the same manner except 25-mL aliquots of DCM were used for the serial extractions and surrogate compounds were spiked in at 2000-5000 pg/µL depending on anticipated dilution.

Soybean oil is miscible with DCM and, therefore, was extracted according to Wu and Yu (2012). Briefly, 1-g of oil was weighed into a glass centrifuge tube and dissolved into 4-mL of *n*-hexane. 8-mL of *N,N*-dimethyl formamide (DMF) was added, and the mixture was vortexed for 15-seconds, sonicated for 5-minutes, then centrifuged for 5-minutes at 2000 rpm. The DMF phase was transferred to a 125-mL separatory funnel and the extraction was repeated. The combined DMF was back-extracted three times with 8-mL aliquots of *n*-hexane. The n-hexane extract was then washed with a 4% sodium chloride solution, concentrated to 1-mL under a gentle stream of nitrogen, and cleaned up with 6-mL, 1000 mg florisil SPE cartridges. Final extract volume was reduced to 1000 µL under a steady stream of nitrogen.

Roadbed material was extracted following EPA method 3540C for Soxhlet extractions. 20-g of roadbed material was weighed into a cellulose extraction thimble and spiked with acid, base, and neutral surrogate compounds for a final extract concentration of 5000 pg/µL. 250-mL of 1:1 DCM:Acetone was added to a flat bottom flask, which was then heated in a water bath such that the Soxhlet extractor cycled six times every hour. After 24-hours, a Kuderna-Danish concentration was used to reduce the solvent volume to <10-mL. A gentle stream of nitrogen was used to further concentrate the sample volumes to 200 µL, which were then reconstituted to 1000 µL with DCM.

Gasoline range organics (GRO) were analyzed only for the dust suppressants by headspace solid phase microextraction (HS-SPME). 5-mL of each dust suppressant stock was transferred into a 10-mL headspace vial. Samples were initially incubated in the thermal agitator of a Gerstel Multipurpose Autosampler held at 50°C and shaken at 250 rpm for 10 minutes. A 50/30 µm DVB/CAR/PDMS SPME fiber assembly was then exposed to the headspace at 50°C and shaken for 250 rpm for 30 minutes.

Sample analysis

All sample extracts were analyzed on a Pegasus 4D GCxGC-TOFMS system equipped with an Agilent 7890A GC and a Gerstel Multipurpose Autosampler. DRO analyses were carried out in one dimension using a 30-m x 0.25-mm ID x 0.25-µm df Rxi-5MS column. 1 µL of extract was injected into a 300°C split/splitless inlet operating in splitless mode with a straight 4mm liner packed with deactivated wool. The carrier gas was helium at a constant flow rate of 4.00 mL/min. The oven was initially held at 40°C for 1 min, increased to 300°C at 20°C/min, then increased to 340°C at 5°C/min and held for 3 min. The TOFMS ionization energy was 70 eV, with a scanning rate of 10 Hz from 35 to 550 amu.

Targeted organic analysis was performed with a two-dimensional separation to maximize peak capacity. The chosen column ensemble for all samples was a 60-m x 0.25-mm ID x 0.25-µm df Rxi-5SilMS in the first dimension and a 0.85-m x 0.25-mm ID x 0.25-µm df Rxi-17SilMS in the second dimension with a 0.6-m x 0.18-mm ID transfer line leading to the detector. For all extracts, 1 µL was injected into a 250°C split/splitless inlet operating in splitless mode with a Topaz 4-mm single taper inlet liner packed with deactivated wool. The carrier gas was helium at a constant flow rate of 1.4 mL/min. For dust suppressant stocks, the oven was initially held at 35°C for 1.5-min, then increased to 315°C at 3°C/min and held for 8-min. The secondary oven was offset +5°C from the primary oven. The modulator was offset +15°C from the secondary oven and programmed with a 3-second modulation period (0.90 s-hot pulse and 0.6 s-cooling period). The TOFMS ionization energy was 70 eV, with a scanning rate of 200 Hz from 50 to 550 amu. For runoff and roadbed samples, the instrument conditions were kept the same expect the oven temperature ramp was increased to 5°C/min and the detector scan rate was decreased to 150 Hz.

GRO characterization of the dust suppressants was carried out by desorbing the exposed SPME fiber assembly in a 260°C split/splitless inlet outfitted with a 0.75-mm ID SPME inlet liner for 10-minutes. The splitless purge valve opened after 120-sec, and the purge flow was set to 100 mL/min. A 30-m x 0.25-mm ID x 1.4-µm Rxi-624SilMS column. The He carrier gas flow rate was set to 1.5 mL/min. The oven was initially held at 35°C for 3-minutes followed by an 8°C/min ramp to 60°C then a 30°C/min ramp to 225°C and a 6-minute final hold.

Measurement of radioactivity

Samples of roadbed aggregate were collected prior to treatment with OGPW, following application of the dust suppressant, and following the 24-hour rain event. Roadbed solid samples were sieved to remove material larger than coarse sand (1.18-mm) then placed in a 24-mL incubation tube for bulk radium analysis. Roadbed material was also sieved into sand smaller size fractions for analysis of sand (45 to 90-µm) as well as silt and clay (<45-µm). Liquid samples of the dust suppressants were all collected immediately prior to application on the roadbed. Liquid samples were acidified and placed in 24-mL incubation tubes for a minimum of 21-days. Runoff samples were collected at the same time as the inorganic samples listed above, acidified, and placed in 50-mL centrifuge tubes. Samples were then transferred to 24-mL incubation tubes prior to analysis.

Radioactivity was measured in all samples on a small anode germanium detector (Canberra Instruments) at geometries consistent with both liquid and solid internal standards. After a minimum of 21-day equilibration, ^{226}Ra was measured using Bi-214 (609 keV) and Pb-214 (295 and 351 keV) decay products. ^{226}Ra was calculated using the average of the activities in the three daughter decay products. Direct measurement of ^{228}Ra was performed using the average of its ^{228}Ac daughter at 911 keV and ^{212}Pb at 239 keV. Measurements were collected until counting errors were typically below 5% for all energies. For solid samples this was typically less than 24-hours but for many liquid samples this led to count times between 2-4 days. Method detection limits vary based on counting times of samples, but generally the detection limit for liquid samples counted for 4-days was 20 pCi/L. Values reported below this detection limit should be qualified as estimated values.

Calculation of element mass retained in roadbed

A mass balance approach was used to calculate the mass of select elements retained in the roadbed at the conclusion of the rainfall-runoff test according to Equation (2):

$$M_{j,retained} = C_{j,DS} * V_{DS} - \Sigma C_{j,i} * V_i \tag{2}$$

where, $M_{j,retained}$ is the mass of element j retained in the bed (g), $C_{j,DS}$ is the concentration of j in the dust suppressant applied to the roadbed (g/L), V_{DS} is the volume of dust suppressant applied to the roadbed (L), $C_{j,i}$ is the concentration of j in each i-th runoff sample (g/L), and V_i is the volume of rainfall during each sampling interval (= 1/24th of storm total; L). If Equation (2) resulted in a negative number (i.e., more mass of an element was present in the runoff than was added by the dust suppressant), that amount was determined to be 'leached' from the roadbed material.

4.5 Dust generation experiments

A detailed description of the laboratory methods to measure dust suppressant efficacy are provided in Stallworth et al. (2020) and Stallworth et al. (2021). A summary of relevant details is provided here. Discs of road aggregate material (6-cm diameter by 1.5-cm depth) were compacted using a modified Proctor test to create a uniform material representative of a dirt and gravel road. The discs were dried and then treated with dust suppressant material at the same application rate as the surface runoff tests. Discs were then dried overnight. The discs were then tumbled in a mechanical drum that was connected to an aerosol monitor (DustTrak II Aerosol Monitor 8530; TSI). This aerosol monitor is the same type as used in field studies. The aerosol monitor measured particulate material smaller than 10 microns (PM10) in size and reported concentrations in units of mg/m^3. Measurements were collected every second for 3 minutes and the average value between 2 and 3 minutes of tumbling was defined as the "Average Maximum Particulate Matter concentration <10-µm", or AM PM10. Replicate measurements for each treatment were collected and the mean and standard deviation of the results are reported. One important modification from the Stallworth method was that the tests in this study were all conducted in an environmental chamber with constant relative humidity of either 20% or 50%.

A relative humidity of 50% is representative of the median humidity above a shaded roadbed in northwest Pennsylvania during the months of May – August. A relative humidity of 20% is representative of the mean humidity above an unshaded roadbed in northwest Pennsylvania during the months of May – August between 11 AM to 5 PM. These relative humidity values were calculated using hourly air temperature and dew point observations from the Warren Venango Regional Airport (KFKL) in Warren County and the Bradford Regional Airport (KBFD) in Bradford County from May 1, 2021 to August 31, 2021 using the Clausius–Clapeyron relation with the August–Roche–Magnus formula to calculate saturation vapor pressure. Unshaded dirt and gravel roadbed surface temperatures commonly reach 125 – 140°F (51.7 – 60°C) in the sun and were conservatively assumed to be 20°C warmer than the observed air temperature in this model (maximum surface temperature used in model was 52.7°C).

Table 4.1 Rainfall totals as a function of time and correlations to time stamps of sampling equipment. ISCO sampler programmed to collect samples from flow-through bucket after every 1/24th of total storm volume. Hannah multimeter programmed to record data every 10-seconds from meter immersed in flow-through bucket.

Time stamp (hr)	Cumulative rainfall (in)	ISCO Sample number	Hannah multimeter Sample number
0.0	0.0	n.a.	0
3.6	0.10	1	1,290
6.2	0.20	2	2,220
8.2	0.31	3	2,940
9.6	0.41	4	3,440
10.5	0.51	5	3,770
11.0	0.61	6	3,970
11.1	0.71	7	4,000
11.2	0.81	8	4,040
11.3	0.92	9	4,080
11.4	1.02	10	4,110
11.5	1.12	11	4,150
11.6	1.22	12	4,180
11.7	1.32	13	4,220
11.8	1.42	14	4,260
11.9	1.53	15	4,290
12.1	1.63	16	4,340
12.4	1.73	17	4,480
12.8	1.83	18	4,620
13.4	1.93	19	4,840
14.4	2.03	20	5,200
15.8	2.14	21	5,700
17.8	2.24	22	6,420
20.8	2.34	23	7,500
24.0	2.44	24	8,640

Table 4.2 Summary of sample handling and analysis of runoff samples.

Analyte(s)	Sample handling	Sample preservation	Analytical instrument	Standard method
Electrical conductivity	none	none	HI98195 Multimeter	
pH	none	none	HI98195 Multimeter	
Anions	Filtered through 0.45-µm syringe filter	Acidified with Nitric Acid, pH<2	Dionex 1100 ICS	EPA 300.1
Dissolved metals	Filtered through 0.45-µm syringe filter	Acidified with Nitric Acid, pH<2	ThermoFisher iCAP 7400 ICP-OES; ThermoFisher iCAP RQ ICP-MS	EPA 6010D; EPA 6020B
Total metals	Unfiltered; Digested with Nitric and Hydrochloric Acids	Acidified with Nitric Acid, pH<2	ThermoFisher iCAP 7400 ICP-OES	EPA 3010A; EPA 6010D
Radioactivity in liquid runoff	Unfiltered	Acidified with Nitric Acid, pH<2	Canberra SAGE gamma spectrometer	
Petroleum hydrocarbons in liquid runoff	Stored in glass bottles	Refrigerated	Pegasus 4D GCxGC-ToFMS	EPA 3510C; EPA 8015C
Chemical oxygen demand	Unfiltered	Acidified with Nitric Acid, pH<2	HACH DRB 200 reactor and HACH DR2800 spectrophotometer	Hach Method 8000
Dissolved organic carbon	Filtered through 0.45-µm syringe filter	Refrigerated	TOC-V CSN	EPA 9060A
Dissolved inorganic carbon	Filtered through 0.45-µm syringe filter	Refrigerated	TOC-V CSN	EPA 9060A
Total Suspended Solids	Unfiltered		HACH DR2800 spectrophotometer	Hach Method 8006

Table 4.3 Summary of sample handling and analysis of roadbed samples.

Analyte(s)	Sample handling	Sample preservation	Analytical instrument	Standard method
Radioactivity in solid roadbed	Sorted to grain size <1.18-mm	Dried, sealed	Canberra SAGE gamma spectrometer	
Petroleum hydrocarbons in solid roadbed	Frozen in plastic until extraction	Frozen	Pegasus 4D GCxGC-ToFMS	EPA 3540C; EPA 8015C

Figure 4.1 Roadbed test frame. 3-feet wide, 9-feet long, stainless-steel lined. Crossed cables used to assist with lifting frame onto steel I-beams. Plastic endpiece removed after roadbed was compacted into test frame. Stainless-steel discharge chute conveyed runoff into flow-through sample bucket.

Figure 4.2 Compaction of gravel aggregate into roadbed test frame. Vibratory plate tamper used to achieve desired % compaction. Nuclear meter used by CMT Labs (State College, PA) to confirm % compaction in relation to number of tamper passes.

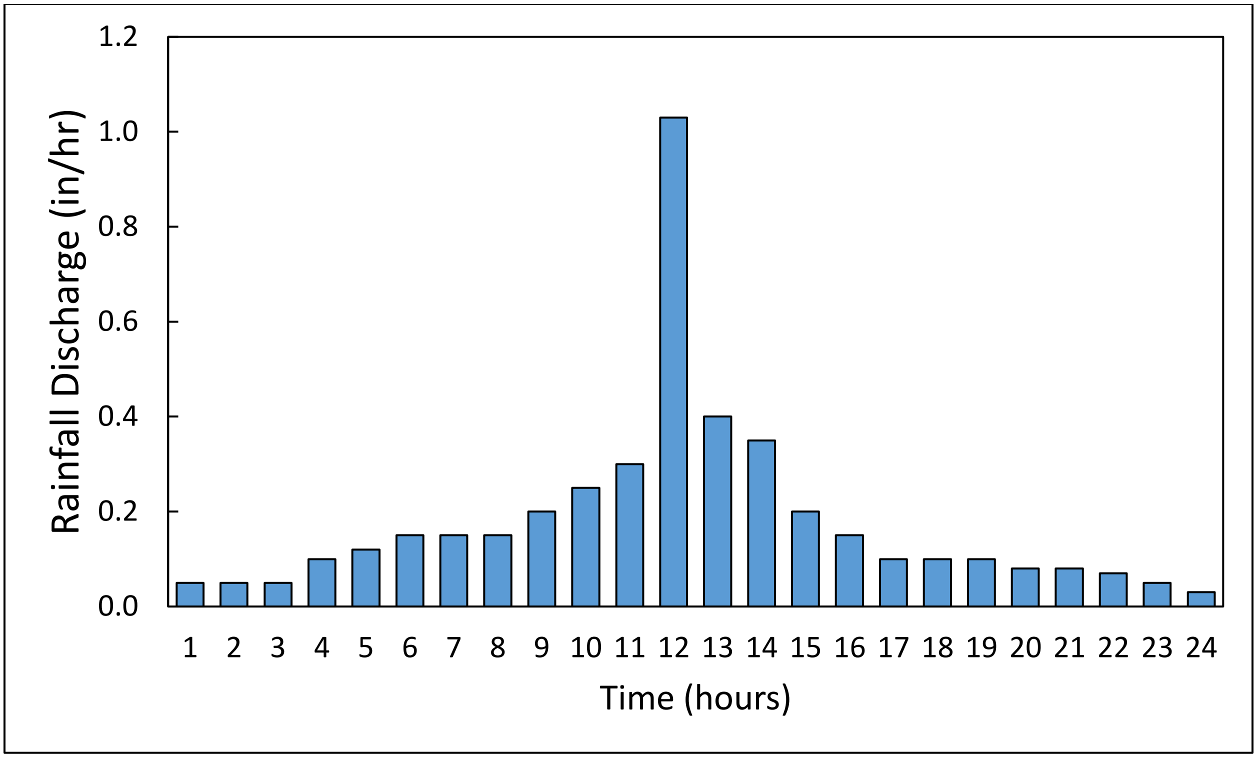

Figure 4.3 Rainfall hyetograph for the storm used for all rainfall-runoff tests in this study. Rainfall pattern matches a 2-year 24-hour rain event for Warren County, PA.

Figure 4.4 Sampling equipment positioned at downstream end of roadbed test frame. 2-gallon plastic bucket was hung onto end of discharge chute. Overflow from bucket was captured in large black plastic tank on floor. Hannah multimeter and ISCO sampling tube were fastened into sampling bucket. Rainfall nozzles positioned inside shower curtain enclosure. Rainfall pumping equipment mounted on scaffold next to test frame.

Figure 4.5 View of rainfall nozzles positioned inside of shower curtain enclosure. Each nozzle delivered synthetic rainwater evenly across a 3-foot by 3-foot square section of the roadbed. Shower curtains contained any over overspray and retained humidity.

5. RESEARCH RESULTS

5.1 Comparisons of dust suppressants

All the dust suppressants were analyzed for a variety of constituents (Table 5.1). All these data are included in a database associated with this report – i.e., every replicate measurement for every analyte for every sample. Some of these analytes were not measured in the soybean oil because it is a nonaqueous phase liquid. Rows in Table 5.1 are organized to present analytes related to salinity (electrical conductivity and total dissolved solids), radioactivity (Ra isotopes), halogens (chloride – iodide), anions (nitrate – sulfate), alkaline earth metals (calcium – barium), alkali metals (sodium – lithium), transition metals (aluminum – lead), metalloids (boron – arsenic), petroleum hydrocarbons (DRO – GRO), organic matter (COD – DOC), inorganic carbon (DIC), and pH. Water quality criteria are included in Table 5.1 for those analytes with a Federal or State standard, limit, or threshold. This report focused on analytes where the concentrations in any one of the dust suppressants divided by the regulatory criteria were much greater than one.

The calcium chloride brine had the highest concentrations of most measured constituents (Table 5.1). The electrical conductivity (EC) of the calcium chloride brine averaged 197 mS/cm, a value approximately four-times higher than seawater (seawater EC = 50 mS/cm), and 65-times higher than the regulatory guideline for irrigation water (USDA, 1997). The total dissolved solids (TDS) of the calcium chloride brine used in the rainfall-runoff experiments averaged 272,000 mg/L TDS. In comparison, seawater commonly contains 35,000 mg/L TDS and the USEPA and PADEP secondary drinking water standard is 500 mg/L TDS. The calcium chloride brine had the highest concentrations of chloride, bromide, nitrate, sulfate, calcium, strontium, potassium, lithium, lead, and boron.

To establish if the Fisher Science Education $CaCl_2$ product used in the rainfall-runoff experiments was compositionally like commercially available $CaCl_2$ dust suppressants, two other products were tested (Commercial Brine 1 and Commercial Brine 2, Table 5.1). Chemical characterizations of these products were consistent with the Fisher Science Education product, especially when normalized to chloride content. These results demonstrate that calcium chloride dust suppressants contain contaminants of interest including chloride, bromide, boron, and radium. One of the commercial products (brine 1) also contained enough sodium to decrease its efficacy as a dust suppressant (section 5.4).

Electrical conductivity (EC) is a measure of water's ability to conduct an electrical current. This ability is related to the concentration of ions in water. High quality distilled-deionized water has a conductivity of about 0.5 µS/cm at 25 °C, typical drinking water is in the range of 200 – 800 µS/cm, while sea water is about 50 mS/cm. The USDA recommends that water with EC greater than 3 mS/cm (= 3,000 µS/cm) not be used for irrigation, or only be used for salt-tolerant crops (USDA, 1997). All the OGPWs included in this study had EC values (118 – 127 mS/cm) 39 to 42-times the criterion for irrigation water. The calcium chloride brine used in this study was the most saline with an average EC value (194 – 200 mS/cm) 65 to 67-times the criterion for irrigation water. The calcium chloride brine used in the rainfall-runoff experiments ranged from 17 – 25% saturation, while the commercially available products used in the dust generation experiments were even more saline. Total dissolved solids (TDS) is a measure of the dissolved combined content of all inorganic and organic substances present in a liquid. In this study, TDS was calculated as the sum of the dissolved concentrations of Ca, Mg, Na, Sr, Ba, Cl, Br, and SO_4. The USEPA and PADEP have established a secondary drinking water standard of 500 mg/L TDS to primarily address aesthetic affects and public acceptance of drinking water. Seawater commonly contains 35,000 mg/L TDS. TDS concentrations in the OGPWs ranged from 81,000 to 84,000 mg/L, while the average TDS for the calcium chloride brine used in the rainfall-runoff experiments averaged 272,000 mg/L, and the TDS of the commercially available $CaCl_2$ dust suppressants used only in the dust generation experiments ranged from 381,000 to 387,000 mg/L. Application of saline dust suppressants to gravel roadbeds led to increased salinity in stormwater runoff (Section 5.2).

Radium is a radioactive alkaline earth metal that occurs naturally in soils and rocks. Radium is a known carcinogen. The USEPA and PADEP established a primary MCL for combined radium (sum of ^{226}Ra plus ^{228}Ra) in public drinking water supplies of 5 picoCuries per liter (pCi/L). The US NRC industrial wastewater discharge limit for combined Ra is 60 pCi/L (Rowan et al., 2011). Combined radium activities in the three OGPWs were 360 (O&G PW1), 84.4 (O&G PW2), and 2,500 pCi/L (O&G PW3; Table 5.1). The higher combined radium activities measured in O&G PW1 and O&G PW3 were consistent with the regional average of 226-radium from conventional oil and gas formations in Pennsylvania. For example, through an analysis of 20 – 25 samples from the USGS Produced Waters Database, the median 226-radium (n = 25), 228-radium (n = 20), and combined radium activities (n = 20) were, respectively, 811, 1,194, and 2,034 pCi/L (Tasker et al., 2020).

The combined radium activities for the calcium chloride brines were elevated and possibly sourced from impurities in the materials. Combined radium activity measured in the calcium chloride used for the rainfall-runoff experiments was 230 pCi/L. This calcium chloride was purchased from Fisher Science Education to prepare large volumes of brine required for the rainfall-runoff experiments. Fisher Science Education reported the purity of its calcium chloride as >95% mass/volume. The abundance of Sr, Na, K, Li, Ba, Fe, Zn, Pb and B in the Fisher Science Education $CaCl_2$ brine (Table 5.1) used in this study suggests that the salt was minimally purified. The elemental composition of this brine was like the commercially available $CaCl_2$ dust suppressants (especially when normalized to chloride concentrations) used in the dust generation experiments. Combined radium activities measured in the commercially available calcium chloride dust suppressants used in the dust generation experiments were 410 and 730 pCi/L. The analysis of these three calcium chloride brines suggest that impurities include contaminants of interest such as radium and boron (Table 5.1).

Combined radium activity in the synthetic rainwater and in the soybean oil were below the instrument's reportable quantification limit (BQL) of 20 pCi/L.

Halogens such as chloride, bromide, and iodide can increase the corrosivity of water and promote the formation of harmful disinfection byproducts in drinking water treatment plants. Bromide in OGPWs is of concern because brominated disinfection byproducts are more toxic than chlorinated disinfection byproducts (Wang et al, 2017). Chloride is the predominant anion in OGPWs. The USEPA and PADEP have established a secondary drinking water standard of 250 mg/L Cl related to taste. Chloride concentrations in the three OGPWs were 192 to 199-times above this limit. Chloride concentrations in the three calcium chloride brines were 706 to 1,070-times above this limit.

Elevated concentrations of metals such as sodium, magnesium, and calcium can affect soil fertility. The USDA established guidelines for irrigation water to protect both crop type and soil health. Sodium concentrations in the three OGPWs were 26-times above the USDA guideline of 920 mg/L Na. Magnesium concentrations in the three OGPWs were 21 to 22-times above the USDA guideline of 61 mg/L Mg. Calcium concentrations in the three OGPWs were 17 to 18-times above the USDA guideline of 401 mg/L Ca. Calcium concentrations in the three calcium chloride brines were 190 to 260-times above the Ca guideline.

The relative concentrations of sodium to calcium plus magnesium (calculated as SAR using Equation (1)) can predict the efficacy of a brine as a dust suppressant (Stallworth et al., 2020). Specifically, a low SAR value (e.g., < 3) would predict that a brine may be an effective dust suppressant (Graber et al., 2019, Stallworth, 2020). SAR values for the three OGPWs ranged from 68 to 69 suggesting that these fluids would not likely be effective dust suppressants (as confirmed by subsequent experiments). In contrast, the SAR value for the calcium chloride brine used in the rainfall-runoff experiments was 1.4. One commercial calcium chloride brine (Commercial Brine 1) used in the dust generation experiments had a SAR value of 17.4 and was the least effective calcium chloride-based product.

OGPWs and brines often contain elevated concentrations of transition metals and metalloids. Based on ratios of concentrations measured in the dust suppressants divided by regulatory standards, strontium, barium, aluminum, manganese, iron, and lead were identified as contaminants of interest.

Organic matter in the dust suppressants was measured in multiple ways. Chemical oxygen demand (COD) measures the amount of oxygen that would be depleted from a body of receiving water (in units of mg/L O_2). COD could not be measured in the OGPWs and calcium chloride brine because chloride concentrations >1,000 mg/L Cl introduce interferences in the analytical method. Dissolved organic carbon (DOC) measures only organic carbon in a sample. Diesel Range Organics (DRO) and Gas Range Organics (GRO) measure hydrocarbons in a sample. The OGPWs had relatively elevated concentrations of DOC and measurable concentrations of both DRO and GRO. O&G PW3 had the highest concentration of DRO (1,650 mg/L C) in all the dust suppressants. As noted on the product label, the soybean oil was 100% oil (>95% total fatty acid) but as a nonaqueous phase liquid, DOC could not be measured.

Table 5.1 Chemical characterization summary of dust suppressants used in the current study.

Analyte	O&G PW1	O&G PW2	O&G PW3	Synthetic Rainwater	$CaCl_2$ Brine	Commercial Brine 1	Commercial Brine 2	Soybean Oil	Regulatory Criteria
EC (mS/cm)	120	120	125	0.023	197	216	180	NA	3.0[g]
TDS* (mg/L)	84,100	82,000	85,300	2.39	272,000	381,000	387,000	0.14	500[b]
Ra-226 (pCi/L)	212	51.5	1,800	BQL	159	641	238	BQL	60[e]
Ra-228 (pCi/L)	148	32.9	696	BQL	71.6	88.9	170	BQL	60[e]
Combined Ra (pCi/L)	360	84.4	2,500	BQL	230	729	408	BQL	5[b]
Chloride (mg/L)	49,700	47,900	49,000	BQL	176,000	251,000	267,000	NA	250[b,i], 230[c]
Bromide (mg/L)	922	753	592	BQL	3,770	3,740	3,430	NA	6[d]
Iodide (mg/L)	13.8	11.2	14.5	0	0.22	47.5	2.58	NA	
Nitrate (mg/L)	324	BQL	BQL	0.7	735	BQL	BQL	NA	10[a,i]
Sulfate (mg/L)	1,480	1,350	2,000	2.14	7,210	BQL	BQL	NA	250[b,i]
Calcium (mg/L)	6,760	6,860	7,150	BQL	78,200	76,200	105,000	0.41	401[g]
Magnesium (mg/L)	1,360	1,310	1,310	BQL	BQL	14,500	896	0.10	61[g]
Strontium (mg/L)	112	112	453	0	1,480	3,070	2,610	BQL	4[f,h,i]
Barium (mg/L)	1.58	4.38	417	0	1.57	--	3.93	BQL	2[a,i]
Sodium (mg/L)	23,600	23,500	24,300	0.14	1,460	20,000	2,500	BQL	20[h], 920[g]
Potassium (mg/L)	117	125	132	0.1	3,120	12,300	5,900	BQL	
Lithium (mg/L)	2.48	2.92	13.3	BQL	57.9	91.4	111	BQL	0.01[f], 0.069[i]
SAR^ (meq/L)$^{1/2}$	68.6	68.1	69.3	BQL	1.4	17.4	2.1	NA	9[g]
Aluminum (mg/L)	BQL	BQL	BQL	BQL	BQL	5.15	5.48	BQL	0.05 to 0.2[b,i]
Manganese (mg/L)	4.06	4.82	4.91	BQL	0.07	1.63	BQL	BQL	0.05[b], 0.3[i]
Iron (mg/L)	15.0,	1.44	43.7	0.02	3.39	4.13	6.52	BQL	0.3[b,i], 1[c]
Nickel (mg/L)	0.09	0.09	0.05	BQL	0.04	BQL	BQL	BQL	0.052[c], 0.1[h,i]
Zinc (mg/L)	1.83	1.93	2.21	0.44	1.84	2.19	3.88	BQL	5[b], 0.12[c], 2[h]
Lead (mg/L)	0.11	0.13	0.11	BQL	0.4	0.1	0.3	BQL	0.015[a], 0.0025[c]
Boron (mg/L)	0.77	0.99	1.26	BQL	22	520	42	BQL	2.4[d], 6[h,i]
Arsenic (mg/L)	0.06	0.05	0.05	BQL	0.02	BQL	BQL	BQL	0.01[a,i], 0.15[c]
DRO (mg/L)	14.7	10.8	1,650	1.1	0.5	NA	NA	6.5	
GRO (mg/L)	1.3	2.6	1.1	BQL	0.6	NA	NA	22.8	
TOC (mg/L)	88.3	81.1	76.6	1.75	8.27	NA	NA	NA	
TIC (mg/L)	1.1	1.5	13.1	0.6	0.6	NA	NA	NA	
pH (std units)	6.42	6.15	6.50	4.29	9.95	4.28	6.32	NA	6.5-8.5[b]

*Calculated as sum of Cl, SO_4, Br, Ca, Mg, Na, K, Sr, Ba concentrations; BQL – below quantification limit; NA – not analyzed; ^Calculated using Equation (1); [a]EPA and DEP Primary Drinking Water Standard; [b]EPA and DEP Secondary Drinking Water Standard; [c]EPA Aquatic Life Criteria; [d]WHO Drinking Water Quality Guideline; [e]Appendix B to 10 CFR Part 20; [f]USGS Human-Based Screening Level; [g]USDA Irrigation Water Quality Guidelines; [h]EPA Drinking Water Health Advisories for lifetime exposures; [i]Medium-Specific Concentrations for Inorganic Regulated Substances in Groundwater 25 PA Code Chapter 250 Appendix A Table 2.

Analyte	O&G PW1	O&G PW2	O&G PW3	Synthetic Rainwater	$CaCl_2$ Brine	Commercial Brine 1	Commercial Brine 2	Soybean Oil	Regulatory Criteria
EC (mS/cm)	120	120	125	0.023	197	216	180	NA	3.0[g]
TDS* (mg/L)	84,100	82,000	85,300	2.39	272,000	381,000	387,000	0.14	500[b]
Ra-226 (pCi/L)	212	51.5	1,800	BQL	159	641	238	BQL	60[e]
Ra-228 (pCi/L)	148	32.9	696	BQL	71.6	88.9	170	BQL	60[e]
Combined Ra (pCi/L)	360	84.4	2,500	BQL	230	729	408	BQL	5[b]
Chloride (mg/L)	49,700	47,900	49,000	BQL	176,000	251,000	267,000	NA	250[b,i], 230[c]
Bromide (mg/L)	922	753	592	BQL	3,770	3,740	3,430	NA	6[d]
Calcium (mg/L)	6,760	6,860	7,150	BQL	78,200	76,200	105,000	0.41	401[g]
Magnesium (mg/L)	1,360	1,310	1,310	BQL	BQL	14,500	896	0.10	61[g]
Strontium (mg/L)	112	112	453	0	1,480	3,070	2,610	BQL	4[f,h,i]
Barium (mg/L)	1.58	4.38	417	0	1.57	--	3.93	BQL	2[a,i]
Sodium (mg/L)	23,600	23,500	24,300	0.14	1,460	20,000	2,500	BQL	20[h], 920[g]
Potassium (mg/L)	117	125	132	0.1	3,120	12,300	5,900	BQL	
Lithium (mg/L)	2.48	2.92	13.3	BQL	57.9	91.4	111	BQL	0.01[f], 0.069[i]
SAR^ (meq/L)$^{1/2}$	68.6	68.1	69.3	BQL	1.4	17.4	2.1	NA	9[g]
Aluminum (mg/L)	BQL	BQL	BQL	BQL	BQL	5.15	5.48	BQL	0.05 to 0.2[b,i]
Manganese (mg/L)	4.06	4.82	4.91	BQL	0.07	1.63	BQL	BQL	0.05[b], 0.3[i]
Iron (mg/L)	15.0,	1.44	43.7	0.02	3.39	4.13	6.52	BQL	0.3[b,i], 1[c]
Nickel (mg/L)	0.09	0.09	0.05	BQL	0.04	BQL	BQL	BQL	0.052[c], 0.1[h,i]
Zinc (mg/L)	1.83	1.93	2.21	0.44	1.84	2.19	3.88	BQL	5[b], 0.12[c], 2[h]
Lead (mg/L)	0.11	0.13	0.11	BQL	0.4	0.1	0.3	BQL	0.015[a], 0.0025[c]
Boron (mg/L)	0.77	0.99	1.26	BQL	22	520	42	BQL	2.4[d], 6[h,i]
Arsenic (mg/L)	0.06	0.05	0.05	BQL	0.02	BQL	BQL	BQL	0.01[a,i], 0.15[c]
DRO (mg/L)	14.7	10.8	1,650	1.1	0.5	NA	NA	6.5	
GRO (mg/L)	1.3	2.6	1.1	BQL	0.6	NA	NA	22.8	
TOC (mg/L)	88.3	81.1	76.6	1.75	8.27	NA	NA	NA	
TIC (mg/L)	1.1	1.5	13.1	0.6	0.6	NA	NA	NA	
pH (std units)	6.42	6.15	6.50	4.29	9.95	4.28	6.32	NA	6.5-8.5[b]

Analyte	O&G PW1	O&G PW2	O&G PW3	Synthetic Rainwater	CaCl$_2$ Brine	Commercial Brine 1	Commercial Brine 2	Soybean Oil	Regulatory Criteria
EC (mS/cm)	120	120	125	0.023	197	216	180	NA	3.0[g]
TDS* (mg/L)	84,100	82,000	85,300	2.39	272,000	381,000	387,000	0.14	500[b]
Ra-226 (pCi/L)	212	51.5	1,800	BQL	159	641	238	BQL	60[e]
Ra-228 (pCi/L)	148	32.9	696	BQL	71.6	88.9	170	BQL	60[e]
Combined Ra (pCi/L)	360	84.4	2,500	BQL	230	729	408	BQL	5[b]
Chloride (mg/L)	49,700	47,900	49,000	BQL	176,000	251,000	267,000	NA	250[b,i], 230[c]
Bromide (mg/L)	922	753	592	BQL	3,770	3,740	3,430	NA	6[d]
Calcium (mg/L)	6,760	6,860	7,150	BQL	78,200	76,200	105,000	0.41	401[g]
Magnesium (mg/L)	1,360	1,310	1,310	BQL	BQL	14,500	896	0.10	61[g]
Strontium (mg/L)	112	112	453	0	1,480	3,070	2,610	BQL	4[f,h,i]
Barium (mg/L)	1.58	4.38	417	0	1.57	--	3.93	BQL	2[a,i]
Sodium (mg/L)	23,600	23,500	24,300	0.14	1,460	20,000	2,500	BQL	20[h], 920[g]
Lithium (mg/L)	2.48	2.92	13.3	BQL	57.9	91.4	111	BQL	0.01[f], 0.069[i]
SAR^ (meq/L)$^{1/2}$	68.6	68.1	69.3	BQL	1.4	17.4	2.1	NA	9[g]
Lead (mg/L)	0.11	0.13	0.11	BQL	0.4	0.1	0.3	BQL	0.015[a], 0.0025[c]
Boron (mg/L)	0.77	0.99	1.26	BQL	22	520	42	BQL	2.4[d], 6[h,i]
pH (std units)	6.42	6.15	6.50	4.29	9.95	4.28	6.32	NA	6.5-8.5[b]

*Calculated as sum of Cl, SO$_4$, Br, Ca, Mg, Na, K, Sr, Ba concentrations; BQL – below quantification limit; NA – not analyzed; ^Calculated using Equation (1); [a]EPA and DEP Primary Drinking Water Standard; [b]EPA and DEP Secondary Drinking Water Standard; [c]EPA Aquatic Life Criteria; [d]WHO Drinking Water Quality Guideline; [e]Appendix B to 10 CFR Part 20; [f]USGS Human-Based Screening Level; [g]USDA Irrigation Water Quality Guidelines; [h]EPA Drinking Water Health Advisories for lifetime exposures; [i]Medium-Specific Concentrations for Inorganic Regulated Substances in Groundwater 25 PA Code Chapter 250 Appendix A Table 2.

Contaminants of interest related to human health include combined radium (^{226}Ra + ^{228}Ra), barium, strontium, lithium, iron, and manganese. Contaminants of interest related to irrigation water include sodium, magnesium, and calcium. Contaminants of interest related to organic-based dust suppressants include chemical oxygen demand and dissolved organic carbon. Contaminants of lesser concern include aluminum, arsenic, lead, nitrate, and sulfate.

5.2 Comparisons of rainfall-runoff concentrations

Runoff samples were collected over the 24-hour storm event to characterize runoff chemistry. A multimeter probe located in the flow-through sampling bucket at the downhill end of the roadbed recorded measurements every 10-seconds yielding 8,640 sampling events per test. A programmable autosampler collected 500-mL samples after every 1/24th of the storm volume. Because of the temporal pattern of the 2-year, 24-hour storm (Figure 4.3), more samples were collected during the peak of the storm as compared to the start or end of the storm. The differences between plotting results as a function of sample number versus as a function of time are illustrated in Figure 5.1. For demonstrative purposes, these comparisons are only shown for one dust suppressant (O&G PW1) but include electrical conductivity (EC; measured by multimeter) and dissolved chloride (measured after collection from automated ISCO sampler bottles). Because EC was measured every 10-seconds, graphs of EC versus multimeter sample number and EC versus time (Figures 5.1A,C) appear similar. These data reflect important stages of the rainfall-runoff test. First, a lag before any rainfall ran off the roadbed into the sampling bucket was observed, then a ‘first flush’ of runoff with the highest measured EC values occurred, then a ‘maximum flush’ period occurred during the heaviest rainfall with the lowest measured EC values (due to rainfall dilution), and then EC values rebounded during the lower-intensity end of the storm.

Because dissolved chloride was measured after every 1/24th of the storm volume, graphs of Cl concentration versus ISCO sample number (Figure 5.1B) and Cl versus time (Figure 5.1D) appear rather different. When plotted versus time (Figure 5.1D), results from the storm peak are compressed and somewhat difficult to resolve. Therefore, for the remainder of this report, results were plotted versus ISCO sample number (hereafter referred to as sample number) for enhanced visual clarity (Figure 5.1B). Time stamps for sample numbers are included in Table 4.1. Sample numbers 1 and 2 correspond to the ‘first flush’ portion of the test while sample numbers 7 and 8 correspond to the ‘maximum flush’ portion of the test. The terms first flush and maximum flush are used in this report to specifically indicate these sample numbers.

Runoff samples were either filtered (0.45-µm) to measure dissolved metals or acid-digested (unfiltered) to measure total metals. A pair-wise analysis of total metal concentrations (y-axis) versus dissolved metal concentrations (x-axis) can resolve whether metals were associated with solids in the runoff or dissolved in solution. Metal concentrations above a 1-to-1 line on such a graph reflect those metals that are associated with particles >0.45-µm in size. Metal concentrations that lie on the 1-to-1 line are completely dissolved in solution. Metal concentrations below the 1-to-1 line could indicate analytical interferences with the digestion solution and/or inaccuracies in sample dilutions because, conceptually, the total concentration cannot be less than the dissolved concentration. Pair-wise analyses for all the dust suppressants are presented in Figure 5.2. Most of the metals measured in the runoff from roadbeds treated with OGPWs and calcium chloride brine were dissolved in solution (Figure 5.2A-D). Because of the elevated metal concentrations in the OGPWs and calcium chloride brine (Table 5.1), most of the metals measured in the runoff from roadbeds treated with OGPWs and calcium chloride brine were sourced from the dust suppressant with a minor contribution from pore fluids in the roadbed.

With synthetic rainwater or soybean oil, magnesium (Mg) and strontium (Sr) in the runoff were associated with particles >0.45-µm in size while the remainder of the metals were dissolved in solution (Figure 5.2E,F). Erosion of a Mg mineral such as magnesium carbonate ($MgCO_3$) coupled with strontium substitution in the $MgCO_3$ could explain these results. Because the synthetic rainwater and soybean oil had low metal concentrations (Table 5.1), the application of these dust suppressants to the roadbed added very little metal mass to the roadbed. Therefore, dissolved metals measured in the runoff in tests with synthetic rainwater and soybean oil were likely sourced from pore fluids in the roadbed and then mobilized by the runoff.

As a dust suppressant, the synthetic rainwater added very little mass of analyzed constituents to the roadbed. Therefore, constituent concentrations measured in the runoff from roadbeds treated with synthetic rainwater effectively represent materials washed from the roadbed and/or from pore fluids in the roadbed. Thus, results from the synthetic rainwater tests represent baseline conditions, except for nitrate and sulfate added to acidify the rainwater.

Salinity and Halogens

The use of brines as road palliatives, either as a deicer or a dust suppressant, raises concerns with respect to episodic salinization of receiving streams. Electrical conductivity (EC) is a reasonable proxy for salinity. (Specific conductivity (SC) is EC temperature-corrected to 25°C.) EC was measured every 10-seconds with the multimeter (Figure 5.3). Except for soybean oil, the shape of the EC versus time curves were similar for all the dust suppressants. The maximum EC values were reached in the 'first flush' of runoff while the minimum EC values were reached in the maximum flush period of heaviest rain. The key difference in the EC versus time curves was the magnitude of the maximum EC. For the

OGPWs, the maximum EC ranged approximately from 17 to 26 mS/cm. For the chloride brine, the maximum EC ranged approximately from 31 to 86 mS/cm. For the synthetic rainwater, the maximum EC ranged approximately from 0.11 to 0.41 mS/cm. The recommended USDA threshold for EC in irrigation water is 3 mS/cm. The chronic aquatic life benchmark value for EC derived from all-year data from West Virginia streams is 0.30 mS/cm (EPA, 2011). Thus, the maximum EC in runoff from roadbeds treated with the OGPWs were 5.7 to 8.7-times above the USDA threshold and 57 to 87-times above the surface water threshold. The maximum EC in runoff from roadbeds treated with calcium chloride brine were 10 to 30-times above the USDA threshold and 100 to 300-times above the surface water threshold.

The maximum values for constituent concentrations measured in the runoff (section 5.2) from the dust suppressant-treated roadbeds are summarized in Table 5.2. Maximum constituent concentrations in the runoff were related and essentially proportional to constituent concentrations in the dust suppressants (Table 5.1). Single entries in Table 5.2 refer to the highest concentration measured in any of the samples from any of the replicate tests. These values represent maximum concentrations coming from the roadbed into an adjacent drainage ditch and do not account for further dilution e.g., from stormwater runoff into the drainage ditch from adjacent un-treated areas.

Maximum constituent concentrations in the runoff were most measured in the first flush samples (e.g., Figures 5.3 – 5.20). For example, the maximum TDS concentration in runoff from the calcium chloride-treated roadbed was 43,000 mg/L TDS (Figure 5.4; Table 5.2) corresponded to an TDS concentration of 272,000 mg/L TDS in the calcium chloride brine (Table 5.1). The maximum TDS concentration in runoff from the OGPW-treated roadbeds ranged from 11,000 to 13,000 mg/L TDS (Figure 5.4; Table 5.2) corresponded to TDS concentrations of 82,000 to 85,000 mg/L TDS in the OGPWs (Table 5.1).

The OGPWs had chloride concentrations of 48,000 – 50,000 mg/L Cl (Table 5.1) while maximum chloride concentrations in the runoff ranged from 5,900 – 12,000 mg/L Cl (Figure 5.5; Table 5.2), amounting to dilution factors of approximately 4 to 8 in the first flush of runoff. The secondary drinking water standard for chloride is 250 mg/L Cl and the surface water chronic exposure standard is 230 mg/L Cl to be protective of aquatic life. Thus, the maximum chloride concentrations in runoff from roadbeds treated with the OGPWs were up to 52-times above the surface water standard. The maximum chloride concentrations in runoff from roadbeds treated with calcium chloride brine exceeded 34,000 mg/L Cl, 148-times above the surface water standard.

Bromide concentrations in the runoff (Figure 5.6) displayed patterns like chloride. The maximum bromide concentrations in the runoff corresponded to the bromide concentrations in the dust suppressants. For example, the calcium chloride brine had an average bromide concentration of 3,770 mg/L Br with a maximum bromide concentration of 760 mg/L in the runoff. The elevated bromide concentration in the calcium chloride brine was surprising because Br generally stays in solution during precipitation of chloride-salts such as NaCl and $CaCl_2$. However, if the $CaCl_2$ was mined from a salt lake deposit, it may have contained additional impurities such as NaBr, KCl, $BaSO_4$ and $SrSO_4$. Indeed, the higher concentrations of Na, Br, K, Ba and Sr indicate the $CaCl_2$ was likely mined from a source with additional impurities. To confirm this, a molar balance was conducted between the elements using their respective atomic mass units (amu) Ca (40 amu), Cl (35 amu) (x2), Na (23 amu), Br (89 amu) and K (39 amu). These calculations revealed that there was enough Na to balance with Br on a mole-to-mole basis in the runoff solutions and the source brine. The OGPWs had bromide concentrations of 590 – 920 mg/L Br while maximum bromide concentrations in the runoff ranged from 65 – 300 mg/L Br.

Radium Isotopes

Due to long count times and relatively low activity, radium in runoff samples were measured only for a subset of dust suppressants (O&G PW3, Calcium Chloride Brine, and Synthetic Rainwater) from select samples (Figure 5.7). Runoff from O&G PW3 contained the two highest activities of all runoff samples measured in runoff samples 1 and 7, which represent the first flush and the maximum flush events, respectively. These are the only reported values above the NRC industrial discharge limit of 60 pCi/L. All other runoff samples from O&G PW3 contained lower radium activities between 10 – 40 pCi/L. Runoff samples collected during the calcium chloride-treated roadbed contained radium activities below 50 pCi/L with the highest values recorded during the first flush event. Runoff samples collected from the synthetic rainwater test also contained radium activities between 30 – 55 pCi/L. The highest values were from samples collected during the maximum flush event. In this case, the low-pH synthetic rainwater likely leached naturally occurring radium from the road aggregate and then mobilized the radium during the maximum flush.

Human Health Concerns

First-flush concentrations of barium, strontium, lithium, iron, and manganese in the runoff exceeded corresponding human-health based criteria (Table 5.1). The EPA and DEP Primary Drinking Water Standard for barium is 2 mg/L Ba. Maximum barium concentrations in the runoff from OGPW-treated roads ranged from 5 – 18 mg/L Ba (Table 5.2; Figure 5.8). Maximum barium concentrations in the runoff from calcium chloride brine-treated roads ranged from 16 – 46 mg/L Ba (up to 23-times above drinking water standard) even though the average barium concentration in the calcium chloride brine was only 1.6 mg/L Ba (Table 5.1). The elevated salinity of the calcium chloride brine likely increased the solubility of barium from the roadbed (Bahadori et al., 2012; Schäfer et al., 2009). Barium may be of concern in the first flush of runoff from roadbeds treated with calcium chloride brine but of lesser concern with OGPWs. Low concentrations of barium (0.04 – 0.1 mg/L Ba) were detected in the runoff from roadbeds treated with soybean oil or synthetic rainwater.

The USGS Human-Based Screening Level for strontium is 4 mg/L Sr (Table 5.1). HBSLs are benchmarks to provide perspective on potential risks to human health for measured contaminants in natural waters. Strontium concentrations in the runoff were highest from roadbeds treated with calcium chloride brine (Table 5.2) corresponding to higher concentrations in the calcium chloride brine (Table 5.1). Maximum strontium concentrations in the runoff from calcium chloride brine-treated roads ranged from 150 – 310 mg/L Sr (Figure 5.9). Maximum strontium concentrations in the runoff from OGPW-treated roads ranged from 10 – 32 mg/L Sr. As noted above, strontium was an impurity in the calcium chloride brine. The calcium chloride brine used in the rainfall-runoff experiments was compositionally like the two other commercially available calcium chloride dust suppressants used in the dust generation experiments (when normalized to chloride concentration). Thus, impurities in calcium chloride brines may be common.

The USGS Human-Based Screening Level for lithium is 0.01 mg/L Li (Table 5.1). Lithium concentrations in the runoff were highest from roadbeds treated with calcium chloride brine (Table 5.2). Maximum lithium concentrations in the runoff from calcium chloride brine-treated roads ranged from 4.6 – 11 mg/L Li (up to 1,100-times above the standard; Figure 5.10). Maximum lithium concentrations in the runoff from OGPW-treated roads ranged from 0.18 – 1.3 mg/L Li (up to 130-times the standard). Low concentrations of lithium (0.0017 – 0.0045 mg/L Li) were detected in the runoff from roadbeds treated with soybean oil or synthetic rainwater.

The EPA and DEP Primary Drinking Water Standard for iron is 0.3 mg/L Fe (Table 5.1). Iron concentrations in the runoff were highest from roadbeds treated with calcium chloride brine (Table 5.2). Maximum iron concentrations in the runoff from calcium chloride brine-treated roads ranged from 0.30 – 0.80 mg/L Fe (only up to 2.7-times above the standard). Iron may be of minor concern in the first flush of runoff from roadbeds treated with calcium chloride brine but of little concern with OGPWs (Figure 5.11).

The DEP Regulated Substances in Groundwater Standard for manganese is 0.3 mg/L Mn and the EPA and DEP Secondary Drinking Water Standard is 0.05 mg/L Mn (Table 5.1). Maximum manganese concentrations in the runoff from calcium chloride brine-treated roads ranged from 0.46 – 1.1 mg/L Mn. Maximum manganese concentrations in the runoff from OGPW-treated roads ranged from 0.23 – 0.82 mg/L Mn. Manganese may be of some concern in the runoff from roadbeds treated with calcium chloride brine or with OGPWs (Figure 5.12). Low concentrations of manganese (0.018 – 0.047 mg/L Mn) were detected in the runoff from roadbeds treated with soybean oil or synthetic rainwater.

Irrigation Water Concerns

Concentrations of sodium, magnesium, and calcium in the runoff exceeded corresponding USDA Irrigation Water Quality Guidelines (Table 5.1). The USDA Guideline for sodium is 920 mg/L Na and the EPA Drinking Water Health Advisory for lifetime exposures is 20 mg/L Na (for individuals on a low-sodium diet). Maximum sodium concentrations in the runoff from OGPW-treated roads ranged from 1,400 – 4,500 mg/L Na (up to 4.9-times the USDA Guideline; Figure 5.13) reflecting the higher Na concentrations in the dust suppressants (Table 5.1). Maximum sodium concentrations in the runoff from calcium chloride brine-treated roads ranged from 130 – 310 mg/L Na. Maximum sodium concentrations in the runoff from roadbeds treated with soybean oil were 4.9 – 17 mg/L Na and 3.7 – 25 mg/L Na with synthetic rainwater (Table 5.2). Sodium concentrations in the runoff from all tests dropped to low concentrations shortly after the ‘maximum flush’ period of the rain event.

The USDA Irrigation Water Quality Guideline for magnesium is 61 mg/L Mg (Table 5.1). Maximum magnesium concentrations in the runoff from OGPW-treated roads ranged from 120 – 400 mg/L Mg (up to 6.6-times the USDA Guideline; Figure 5.14). Maximum magnesium concentrations in the runoff from calcium chloride brine-treated roads ranged from 120 – 310 mg/L Mg. Maximum magnesium concentrations in the runoff from roadbeds treated with soybean oil were 6.1 – 6.2 mg/L Mg and 2.7 – 9.7 mg/L Mg from roadbeds treated with synthetic rainwater.

The USDA Irrigation Water Quality Guideline for calcium is 401 mg/L Ca (Table 5.1). Maximum calcium concentrations in the runoff from calcium chloride brine-treated roads ranged from 9,200 – 21,000 mg/L Ca (up to 52-times the USDA Guideline; Figure 5.15). Maximum calcium concentrations in the runoff from OGPW-treated roads ranged from 750 – 2,200 mg/L Ca (up to 5.5-times the USDA

Guideline). Maximum calcium concentrations in the runoff from roadbeds treated with soybean oil or synthetic rainwater were 21 – 52 mg/L Ca and sourced from the road or in the roadbed pore fluids.

Constituents of Lesser Concern

Concentrations of aluminum, lead, arsenic, nitrate, sulfate, and pH in the runoff from roadbeds treated with any of the dust suppressants rarely were above any corresponding regulatory criteria. The EPA and DEP Primary Drinking Water Standards range from 50 to 200 µg/L Al and runoff concentrations never exceeded the upper range (Figure 5.16). The EPA and DEP Primary Drinking Water Standards for lead is 15 µg/L Pb and runoff concentrations never exceeded this standard (Figure 5.17). The EPA and DEP Primary Drinking Water Standards for arsenic is 10 µg/L As and runoff concentrations never exceeded this standard (Figure 5.18). The EPA and DEP Primary Drinking Water Standards for nitrate is 10 mg/L NO_3-N and only the 'first flush' from $CaCl_2$-treated roadbeds exceed this standard (Figure 5.19). The EPA and DEP Secondary Drinking Water Standards for sulfate is 250 mg/L SO_4 and only the 'first flush' from $CaCl_2$-treated roadbeds exceed this standard (Figure 5.20). The EPA and DEP Secondary Drinking Water Standards for pH is within 6.5 to 8.5 and most exceedances occurred with the synthetic rainwater tests and during the 'maximum flush' portion of the rain event (Figure 5.21).

Organic Compounds

Dissolved organic compounds were measured as COD (Figure 5.22) and DOC and DRO (Figure 5.23). Taken together, these results demonstrated that organic compounds from OGPWs and calcium chloride brine likely pose minor environmental impacts to receiving streams. In contrast, dissolved organic compounds from organics-based dust suppressants like soybean oil may impact receiving streams. Biodegradable portions of the COD or DOC may create an oxygen demand in the receiving stream that leads to decreased dissolved oxygen concentrations. DRO may exert toxicity on aquatic species in the receiving stream. However, while DRO is operationally-defined as 'diesel', organics derived from soybean oil would not be classified as petroleum hydrocarbons. Organics from soybean oil may be less toxic than organics from petroleum-based products.

COD concentrations in the runoff (Figure 5.22) varied for the different dust suppressants. For soybean oil, COD concentrations were highest in the first flush of runoff (sample number 1) but then peaked again during the maximum flush of runoff (sample numbers 7 and 8). Maximum COD concentrations in the runoff from soybean oil-treated roadbeds ranged from 1,500 – 2,200 mg/L O_2. For soybean oil-treated roadbeds the COD concentrations in the runoff suggest that a portion of the oil was miscible in the first flush and another portion of the oil was mobilized in the maximum flush.

Table 5.2 Maximum concentrations of water quality analytes in collected runoff samples.

Analyte	Max Runoff Concentration					
	O&G PW1	**O&G PW2**	**O&G PW3**	**$CaCl_2$ Brine**	**Soybean Oil**	**Synthetic Rainwater**
EC (mS/cm)	31.3	23.8	30.5	86.1	0.186	0.482
TDS* (mg/L)	19,300	12,100	12,700	57,500	102	68
Ra-226 (pCi/L)	NA	NA	59.6	27.9	NA	28.9
Ra-228 (pCi/L)	NA	NA	42.7	39.2	NA	24.3
Combined Ra (pCi/L)	NA	NA	82.3	47.8	NA	51.5
Chloride (mg/L)	11,80	7,550	10,000	34,300	14	3
Bromide (mg/L)	296	82	134	757	BQL	BQL
Iodide (mg/L)	1.31	1.70	1.92	0.10	0.01	0.06
Nitrate (mg/L)	159	16	42	74	8	11
Sulfate (mg/L)	449	122	301	447	31	33
Calcium (mg/L)	2,200	1,360	1,590	20,700	36	32
Magnesium (mg/L)	402	224	257	310	6	4
Strontium (mg/L)	17	10	32	305	BQL	BQL
Barium (mg/L)	5.09	4.84	18.1	45.9	BQL	0.05
Sodium (mg/L)	4,540	2,730	2,650	310	17	4
Potassium (mg/L)	36	16	32	296	2	2
Lithium (mg/L)	0.24	0.18	1.29	11.2	0.00	0.00
Aluminum (mg/L)	0.08	0.18	0.03	0.14	0.17	0.23
Manganese (mg/L)	0.82	0.41	0.43	1.13	0.05	0.01
Iron (mg/L)	0.11	0.05	0.11	0.80	0.21	0.18
Zinc (mg/L)	0.04	0.03	0.03	0.10	0.02	0.04
Boron (mg/L)	0.08	0.08	0.10	2.37	0.02	0.02
DRO (mg/L)	NA	2.0	35.7	NA	NA	2.4
COD (mg/L)	276	244	182	270	2236	193
DOC (mg/L)	NA	18.7	NA	NA	57.8	10.0
DIC (mg/L)	14.6	14.3	16.7	7.7	31.1	17.7

NA – not analyzed

BQL – below quantification limit

Analyte	O&G PW1	O&G PW2	O&G PW3	CaCl$_2$ Brine	Soybean Oil	Synthetic Rainwater
EC (mS/cm)	31.3	23.8	30.5	86.1	0.186	0.482
TDS* (mg/L)	19,300	12,100	12,700	57,500	102	68
Ra-226 (pCi/L)	NA	NA	59.6	27.9	NA	28.9
Ra-228 (pCi/L)	NA	NA	42.7	39.2	NA	24.3
Combined Ra (pCi/L)	NA	NA	82.3	47.8	NA	51.5
Chloride (mg/L)	11,80	7,550	10,000	34,300	14	3
Bromide (mg/L)	296	82	134	757	BQL	BQL
Calcium (mg/L)	2,200	1,360	1,590	20,700	36	32
Magnesium (mg/L)	402	224	257	310	6	4
Strontium (mg/L)	17	10	32	305	BQL	BQL
Barium (mg/L)	5.09	4.84	18.1	45.9	BQL	0.05
Sodium (mg/L)	4,540	2,730	2,650	310	17	4
Potassium (mg/L)	36	16	32	296	2	2
Lithium (mg/L)	0.24	0.18	1.29	11.2	0.00	0.00

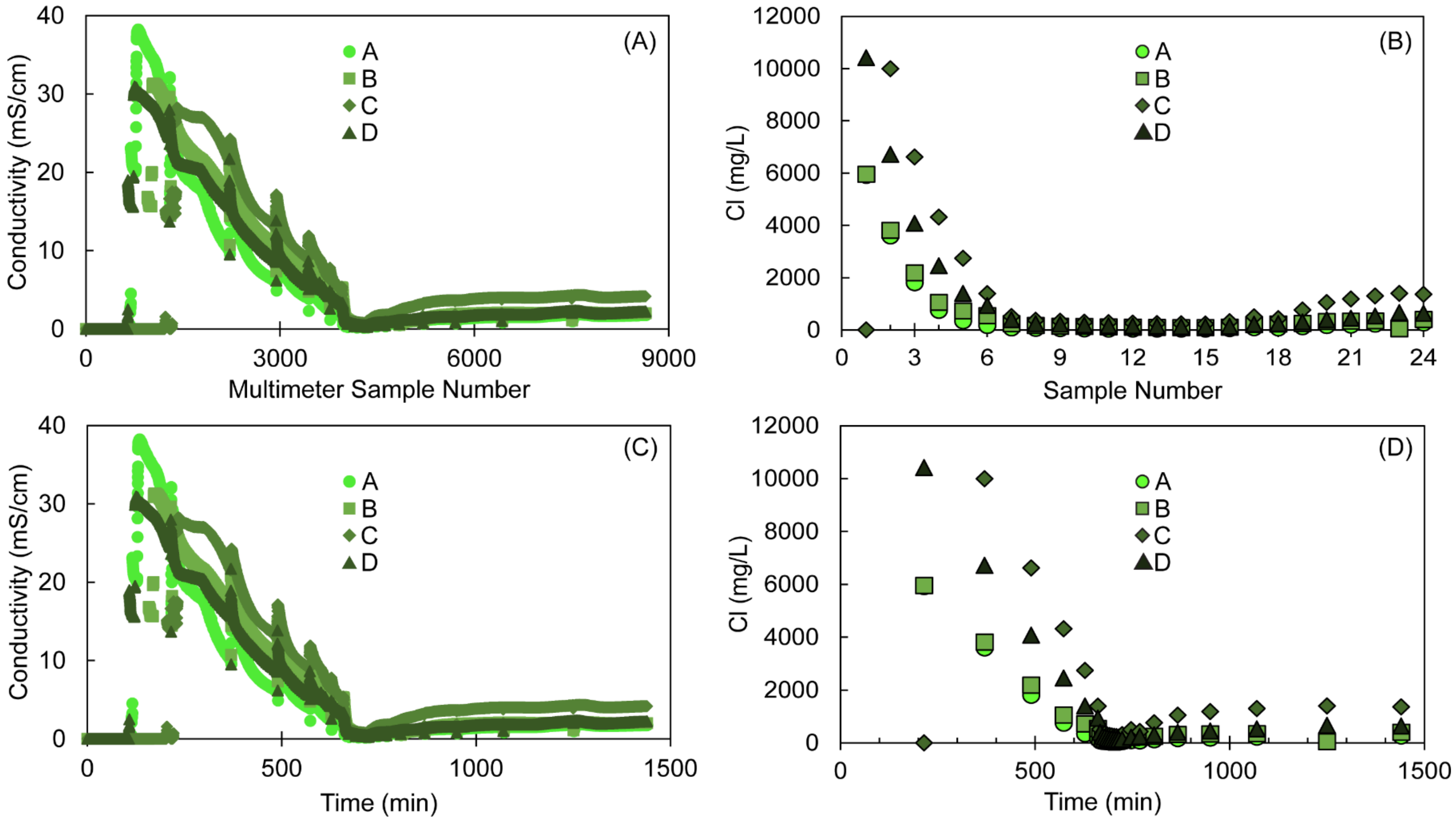

Figure 5.1 Electrical conductivity (A and C) and dissolved chloride concentrations (B and D) measured in runoff from gravel roadbeds treated with Oil & Gas Produced Water 1. Different letters refer to replicate tests. Panels A and C are used to show comparisons between plotting data as a function of sample number versus experimental run time for an analyte recorded every 10-seconds with the Hanna multimeter. Panels B and D are used to show comparisons between plotting data as a function of sample number versus experimental run time for an analyte collected with the ISCO sampler after every 1/24th of the storm volume.

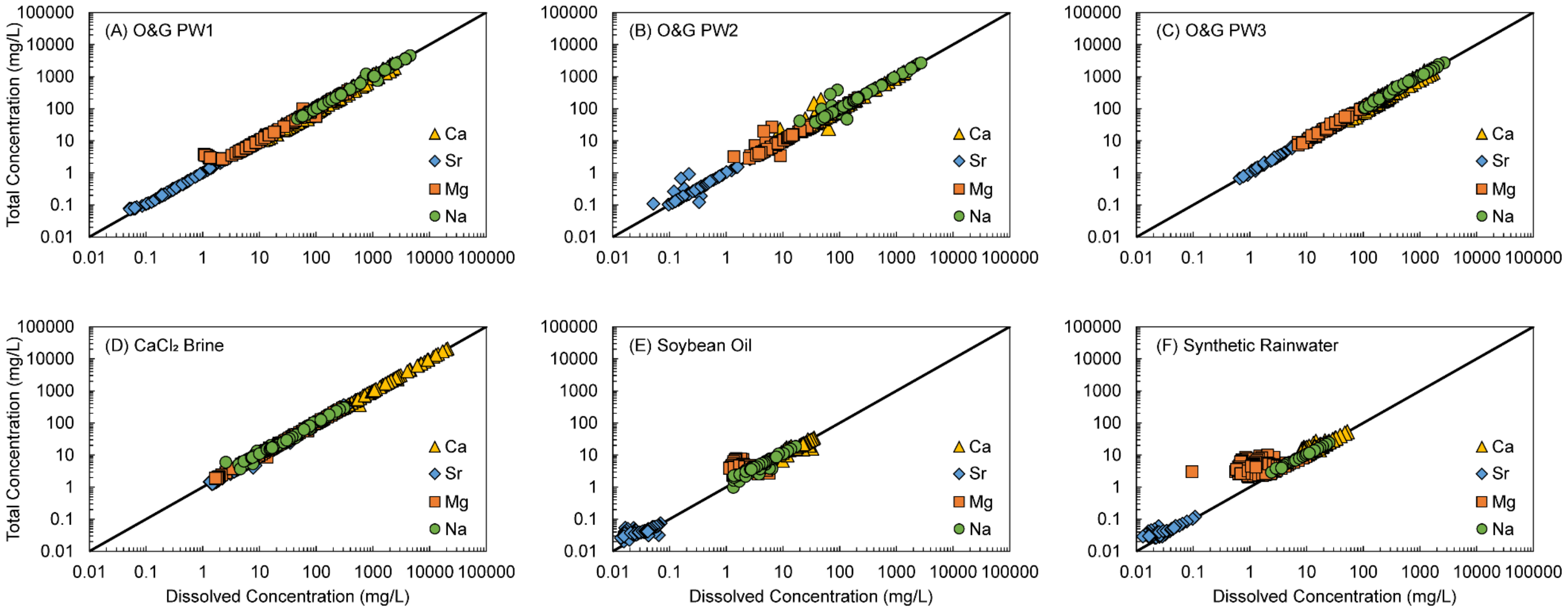

Figure 5.2 Comparisons of dissolved (0.45-µm filtered) and total (unfiltered and digested in nitric + hydrochloric acids) metal concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Solid line in each panel shows 1-to-1 correspondence. For each dust suppressant all results from all replicate tests are combined and different symbols refer to individual base cations.

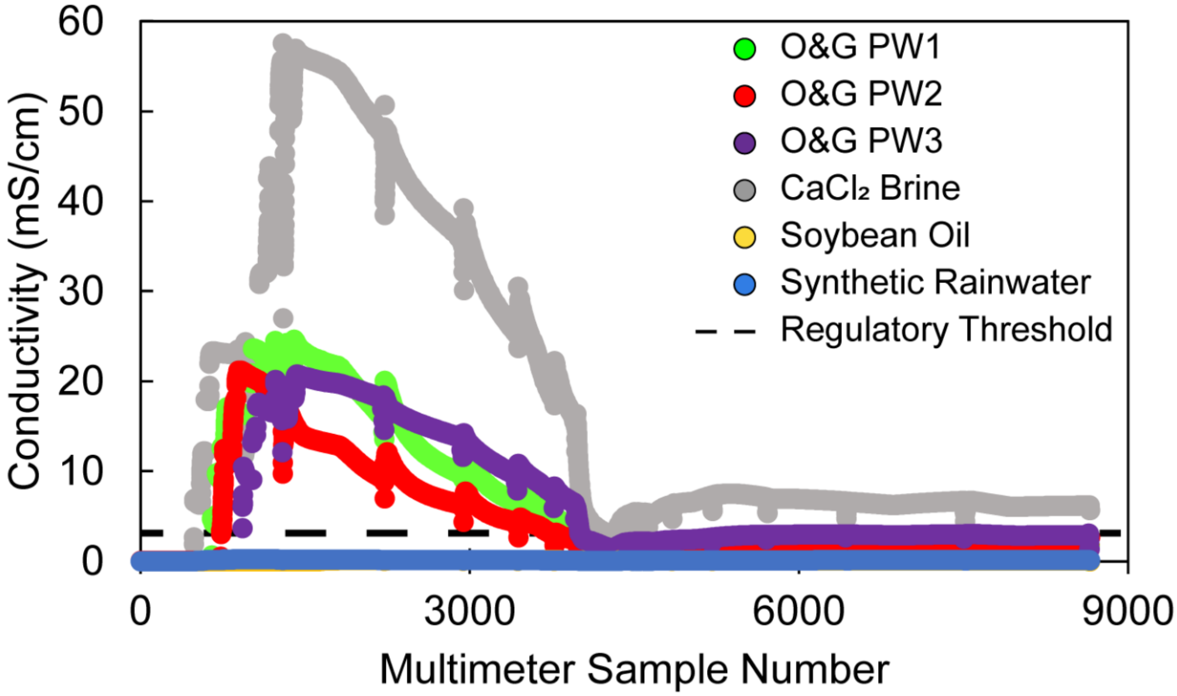

Figure 5.3 Comparisons of electrical conductivity measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Measurements were recorded every 10-seconds of the 24-hour storm. The Regulatory Threshold shown is 3.0 mS/cm from USDA Irrigation Water Quality Guidelines. The chronic aquatic life benchmark value for conductivity in central Appalachian streams is 0.30 mS/cm.

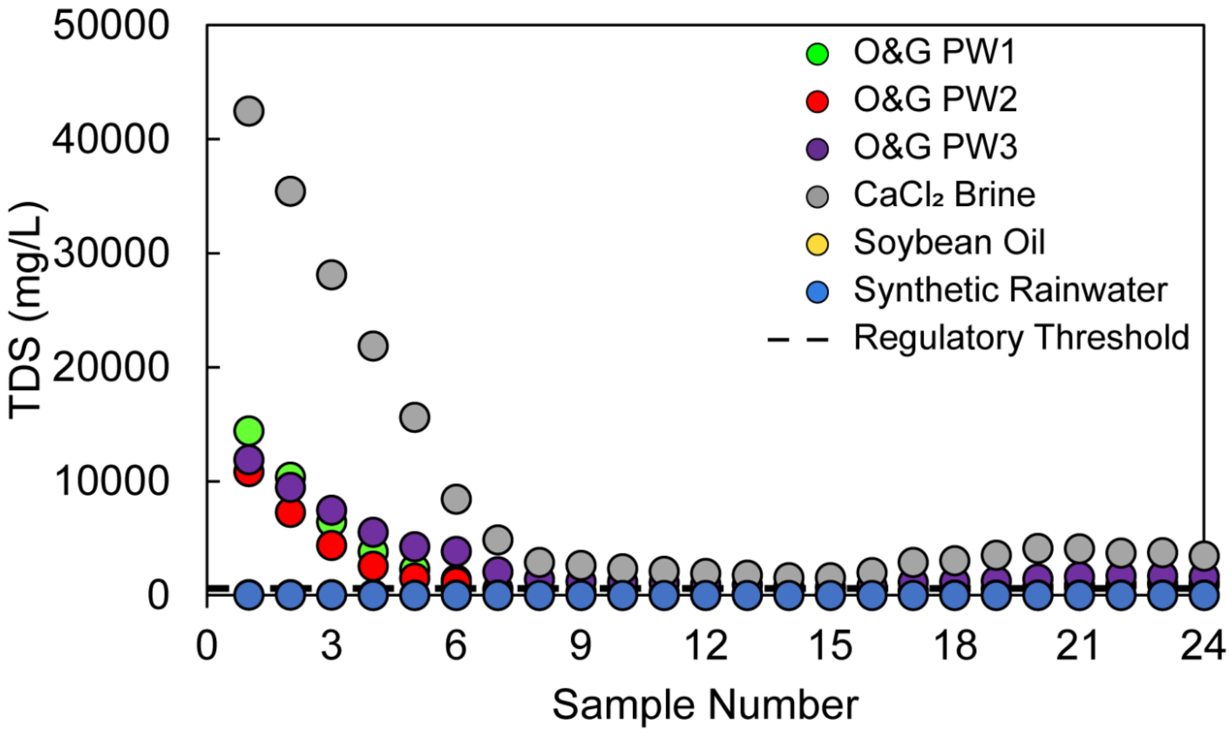

Figure 5.4 Comparisons of total dissolved solids (TDS) concentrations calculated in runoff from gravel roadbeds treated with the six dust suppressants used in this study. TDS was calculated as the sum of measured Cl, SO_4, Br, Ca, Mg, Na, K, Sr, Ba concentrations. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 500 mg/L TDS from EPA and DEP Secondary Drinking Water Standards.

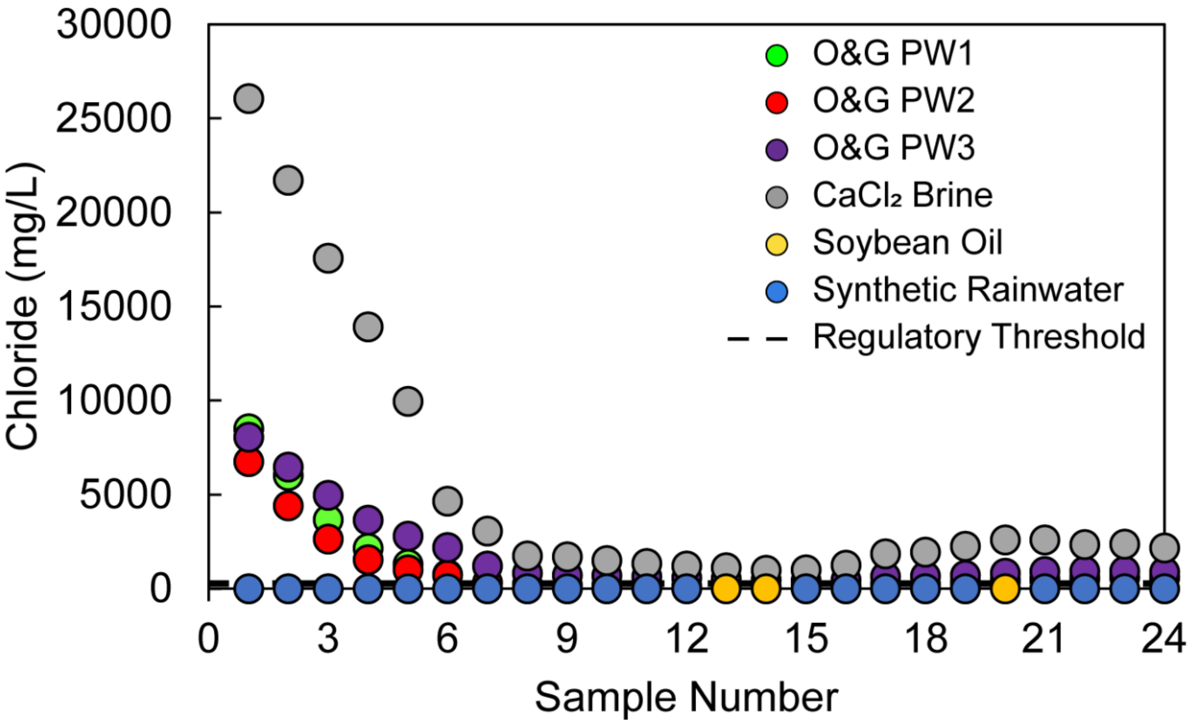

Figure 5.5 Comparisons of dissolved chloride (Cl) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 250 mg/L Cl from EPA and DEP Secondary Drinking Water Standards. The EPA chronic aquatic life benchmark value for chloride is 230 mg/L Cl.

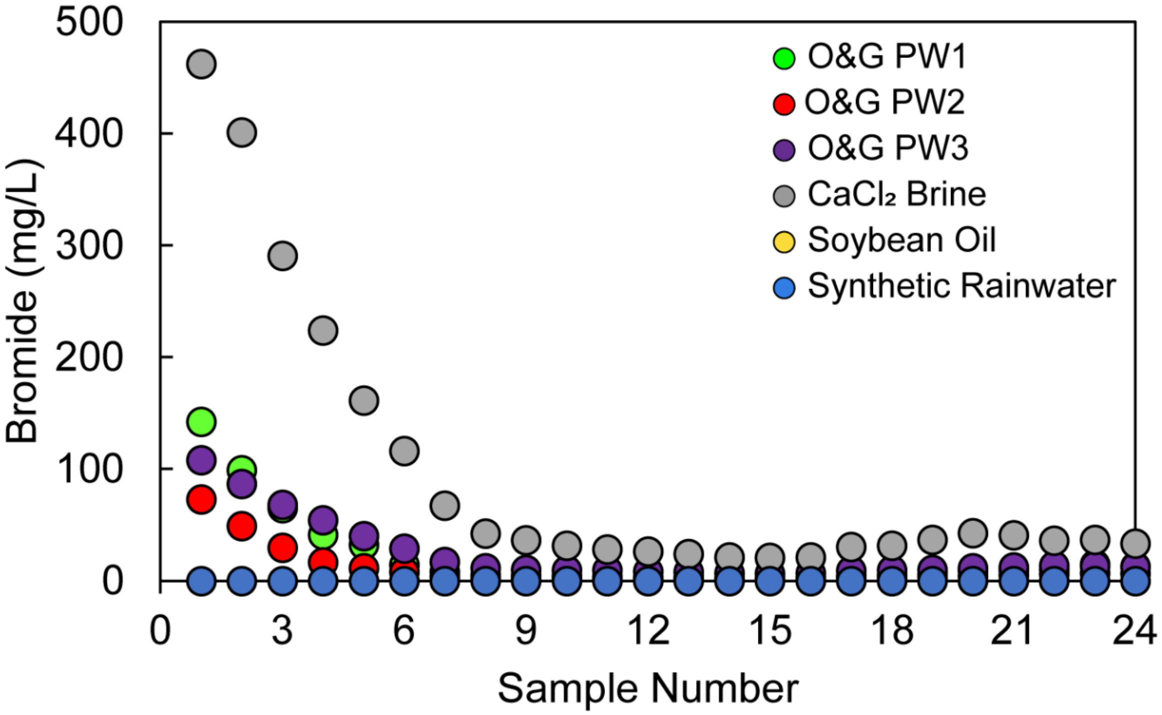

Figure 5.6 Comparisons of dissolved bromide (Br) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples collected after every 1/24th of the storm volume. There are no US regulatory thresholds for bromide, however, bromide leads to formation of disinfection byproducts (DBPs) in drinking water treatment plants. Influent bromide concentrations of 0.050 mg/L Br have shown to lead to increased formation of DBPs (Landis et al., 2016) while concentrations <0.080 mg/L Br may be protective for human health (Wang et al., 2017).

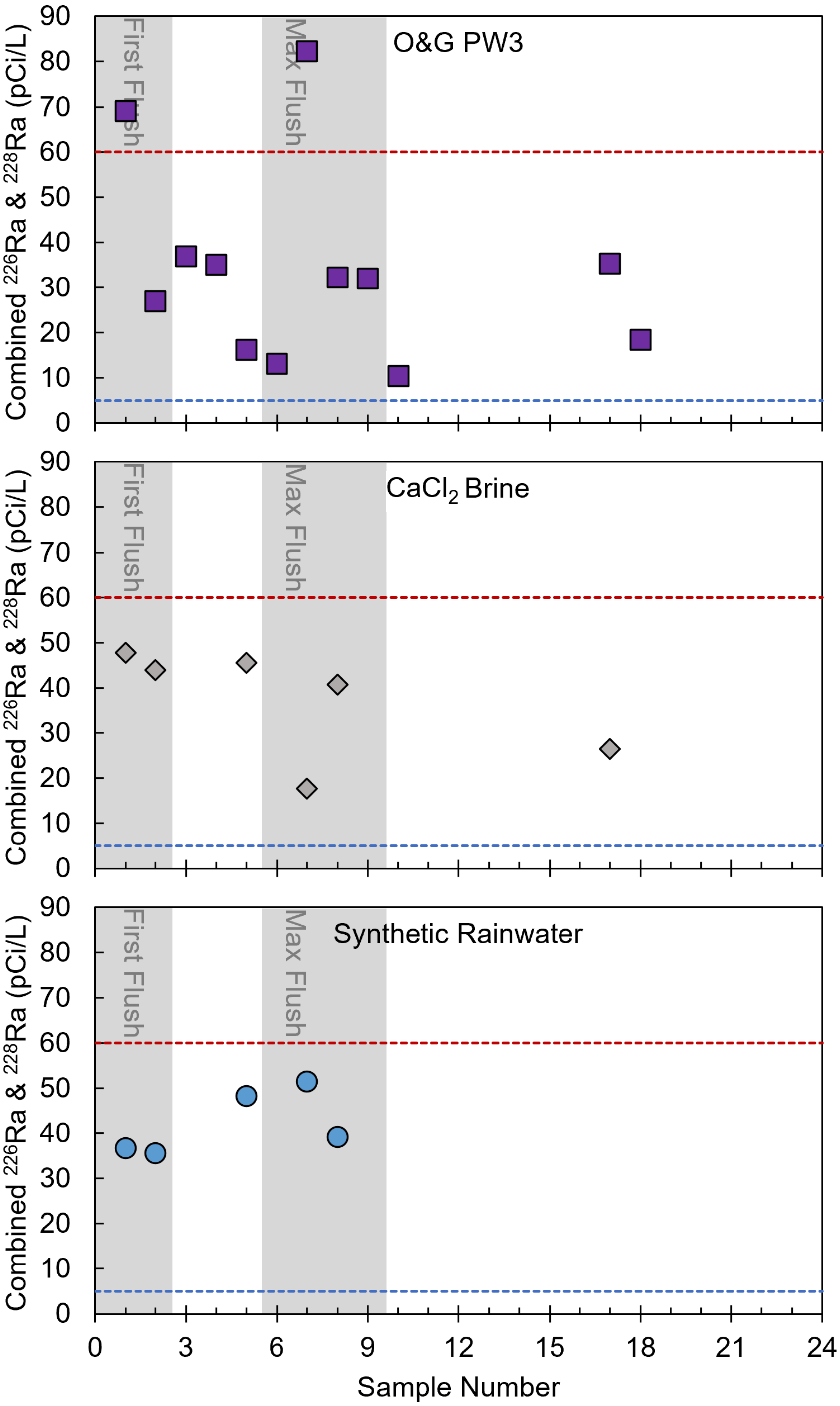

Figure 5.7 Comparisons of combined radium activities (^{226}Ra + ^{228}Ra) measured in runoff from gravel roadbeds treated with three of the dust suppressants used in this study. Results shown are from single tests. (top) Oil & Gas Produced Water 3, (middle) Calcium Chloride Brine, and (bottom) Synthetic Rainwater. Sample numbers 1 and 2 correspond to the first flush of runoff while sample numbers 7 and 8 correspond to the maximum flush of runoff. The NRC industrial wastewater discharge standard for combined radium activity is 60 pCi/L (red dashed line). The EPA and DEP Primary Drinking Water Standard for combined radium activity is 5.0 pCi/L (blue dashed line).

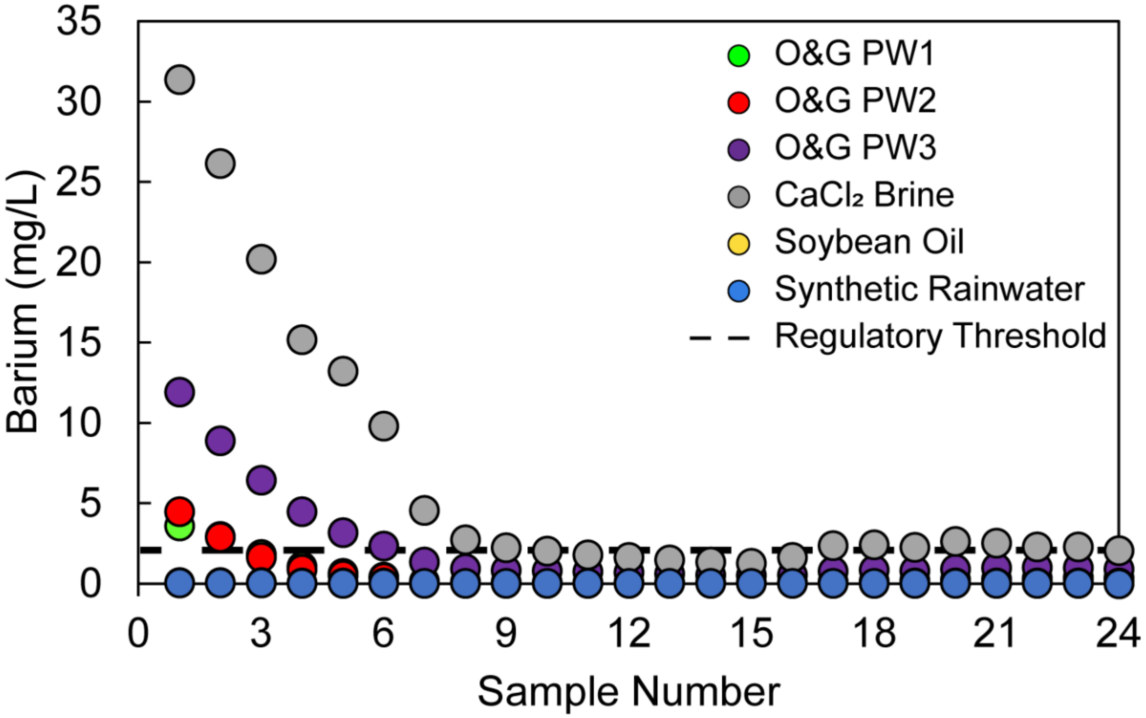

Figure 5.8 Comparisons of dissolved barium (Ba) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 2 mg/L Ba from EPA and DEP Primary Drinking Water Standards.

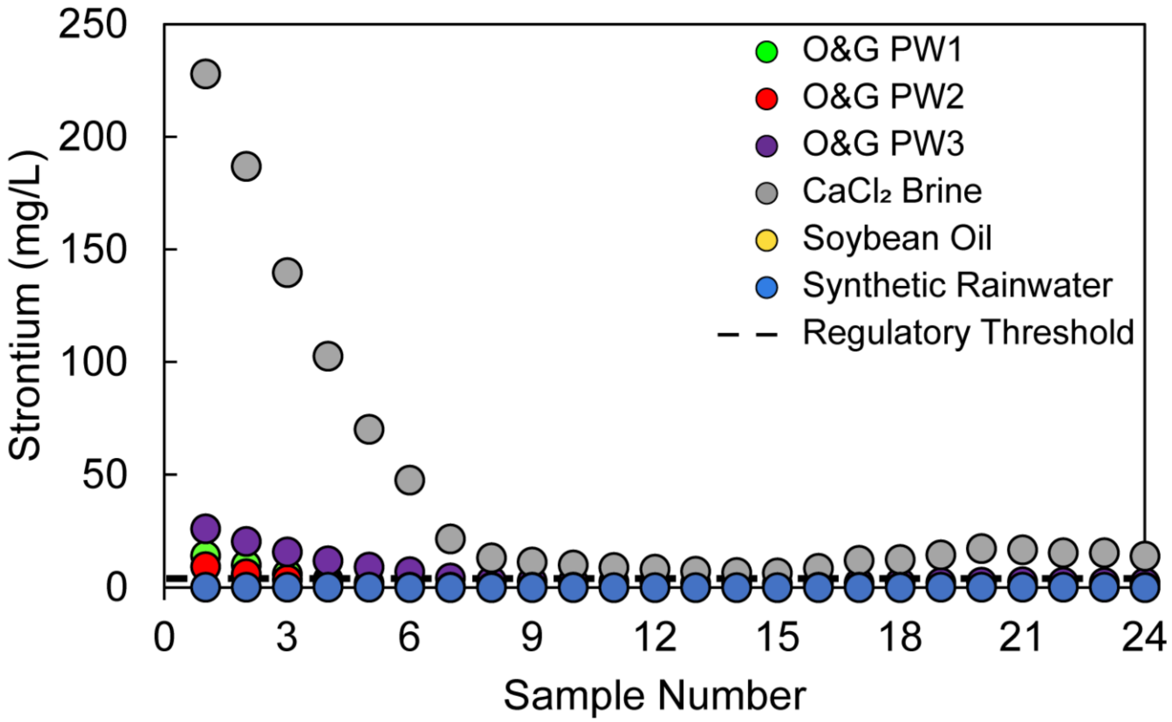

Figure 5.9 Comparisons of dissolved strontium (Sr) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 4 mg/L Sr from USGS Human-Based Screening Levels.

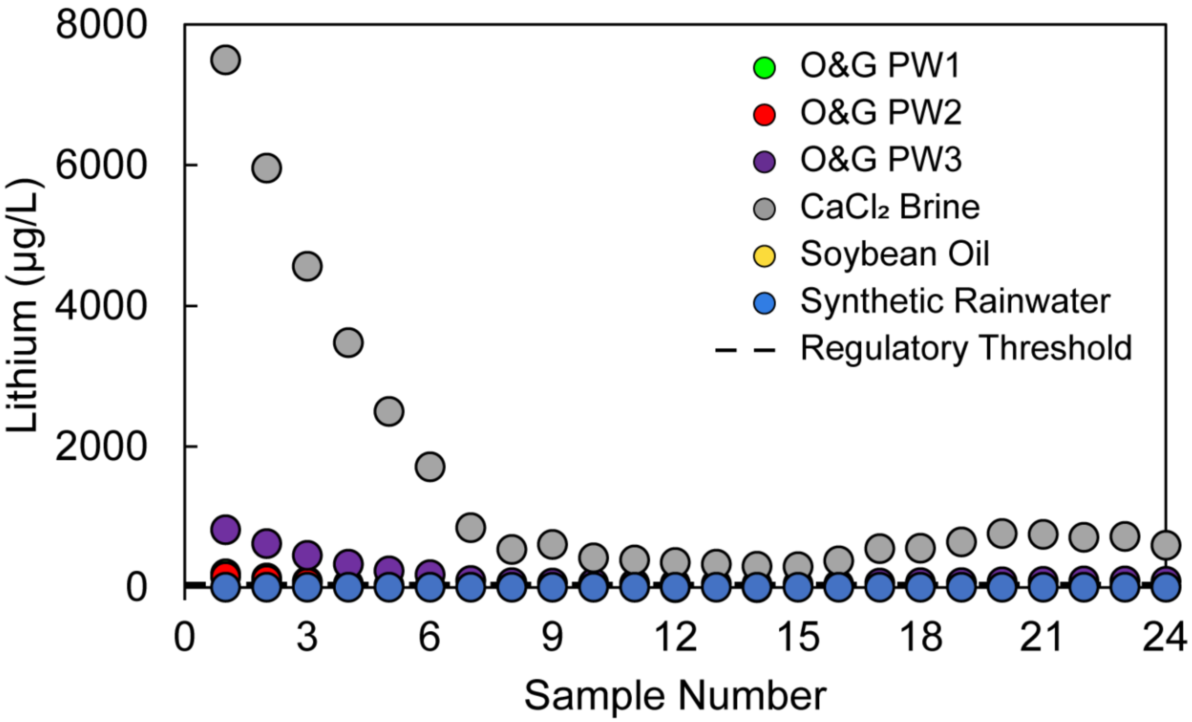

Figure 5.10 Comparisons of dissolved lithium (Li) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 0.01 mg/L Li (= 10 µg/L) from USGS Human-Based Screening Levels.

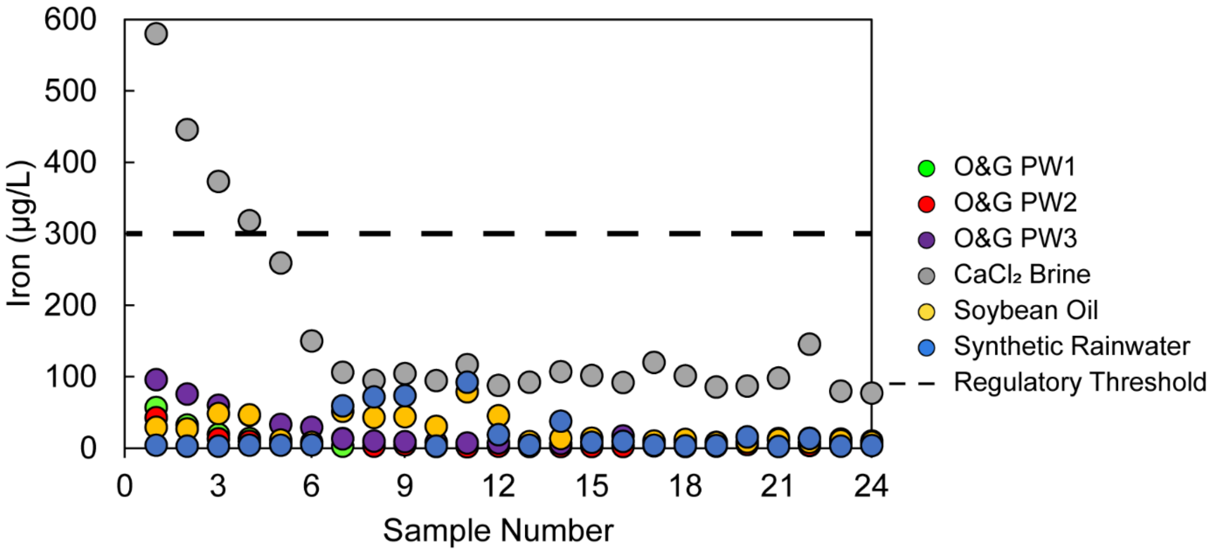

Figure 5.11 Comparisons of dissolved iron (Fe) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 0.3 mg/L Fe (= 300 µg/L) from EPA and DEP Primary Drinking Water Standards.

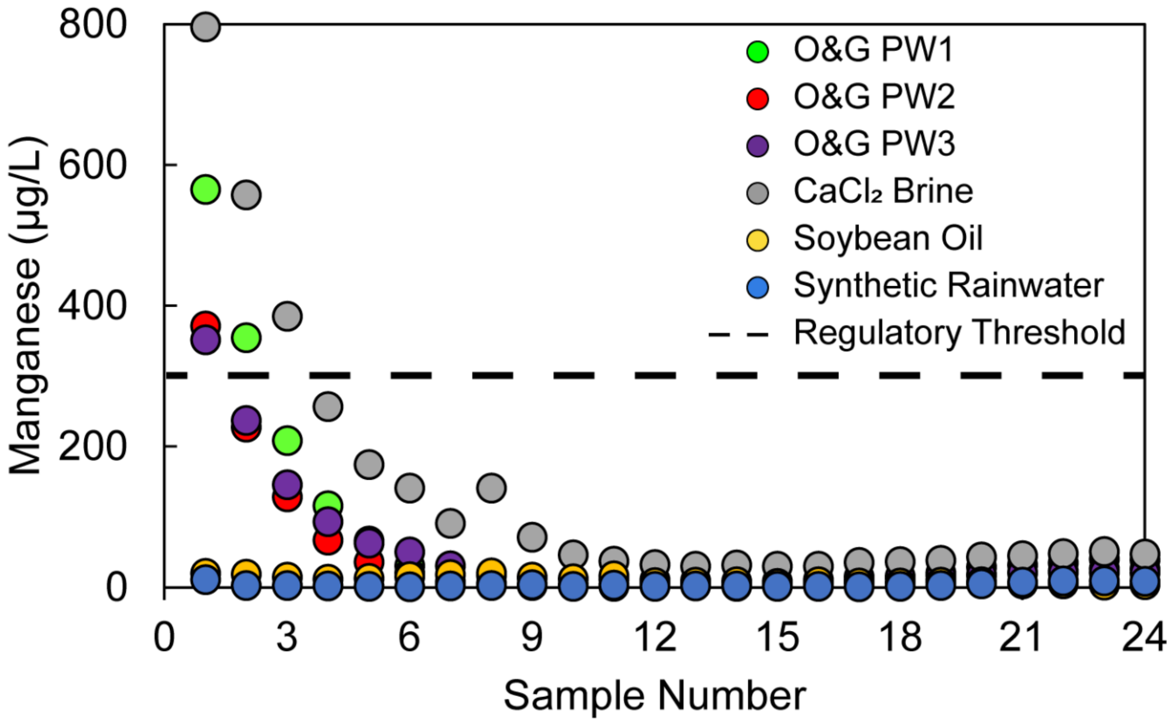

Figure 5.12 Comparisons of dissolved manganese (Mn) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 0.3 mg/L Mn (= 300 µg/L) from DEP Regulated Substances in Groundwater Standards. The EPA and DEP Secondary Drinking Water Standards is 50 µg/L Mn.

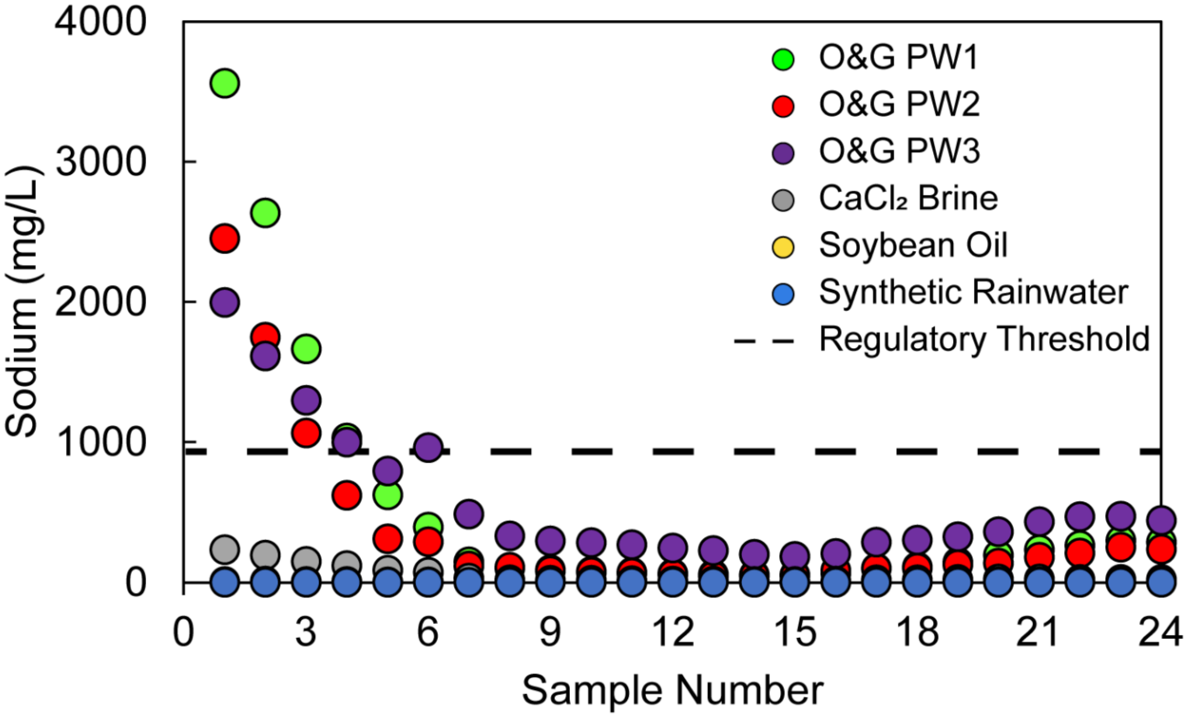

Figure 5.13 Comparisons of dissolved sodium (Na) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 920 mg/L Na from USDA Irrigation Water Quality Guidelines. The EPA Drinking Water Health Advisories for lifetime exposures is 20 mg/L Na.

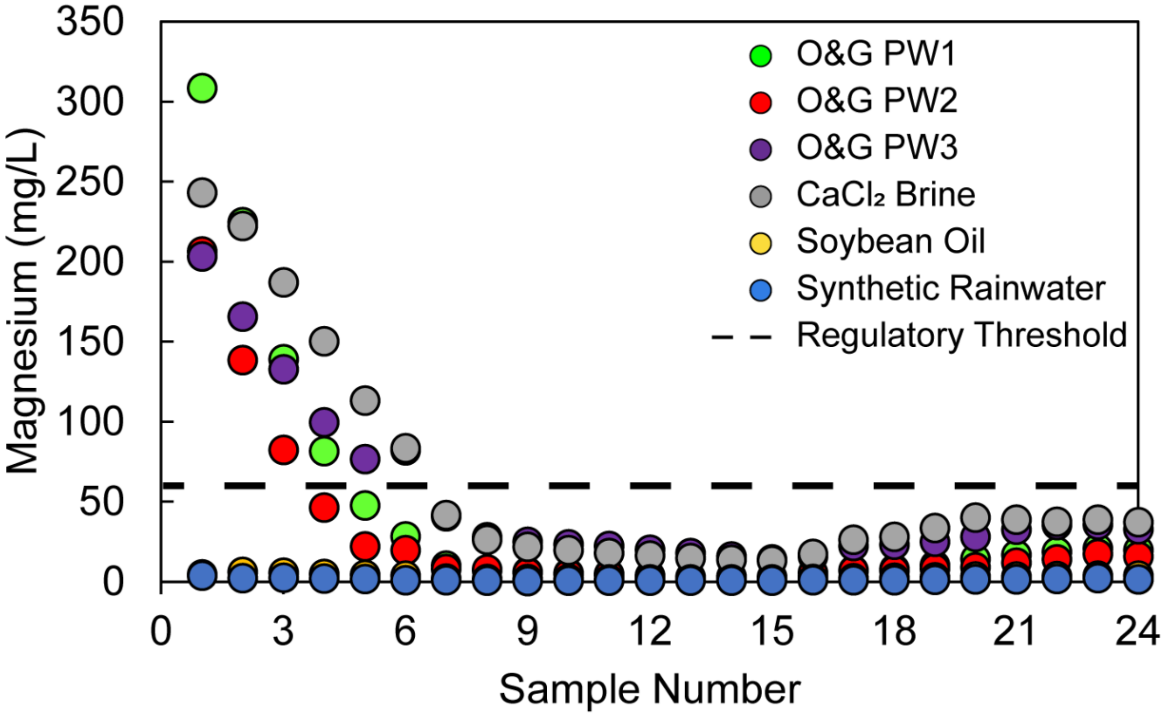

Figure 5.14 Comparisons of dissolved magnesium (Mg) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 61 mg/L Mg from USDA Irrigation Water Quality Guidelines.

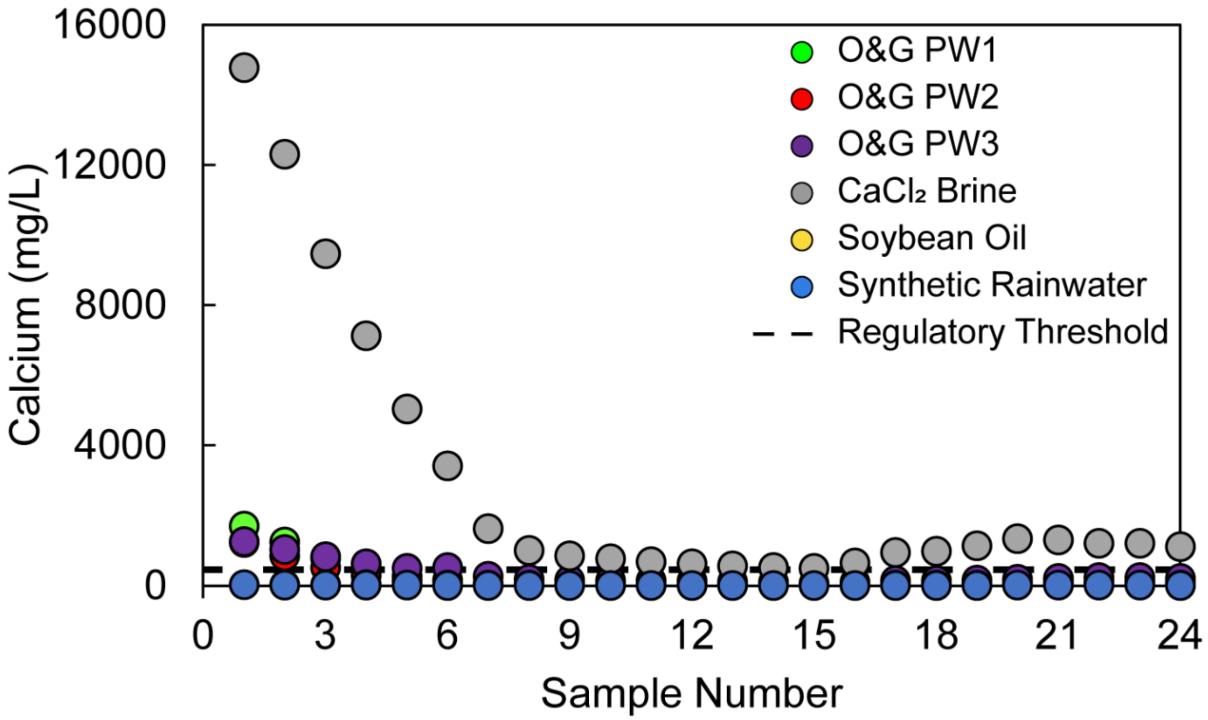

Figure 5.15 Comparisons of dissolved calcium (Ca) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 401 mg/L Ca from USDA Irrigation Water Quality Guidelines.

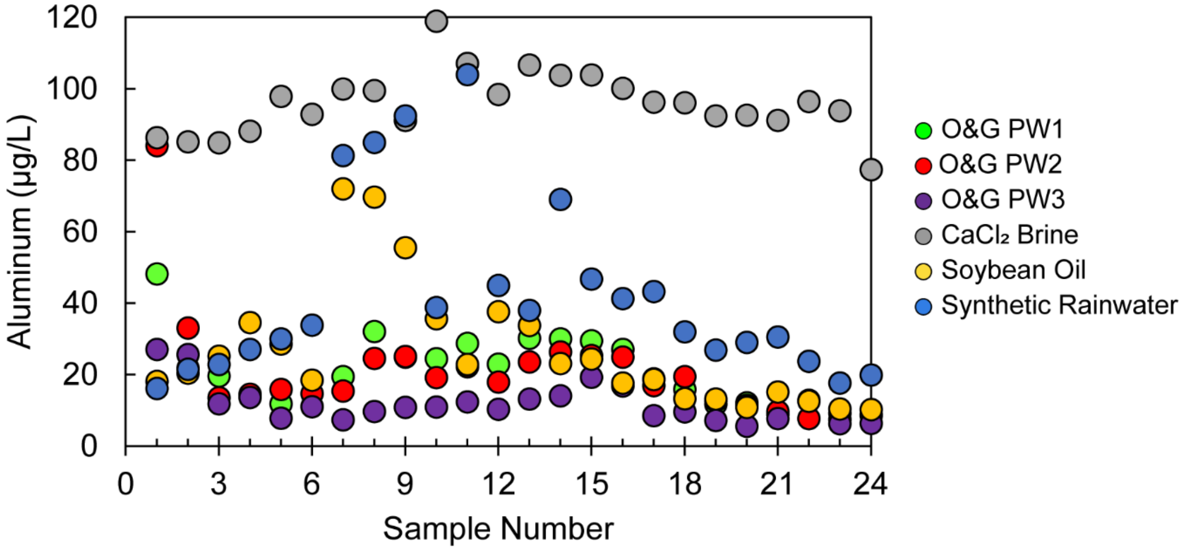

Figure 5.16 Comparisons of dissolved aluminum (Al) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The EPA and DEP Primary Drinking Water Standards range from 50 to 200 µg/L Al.

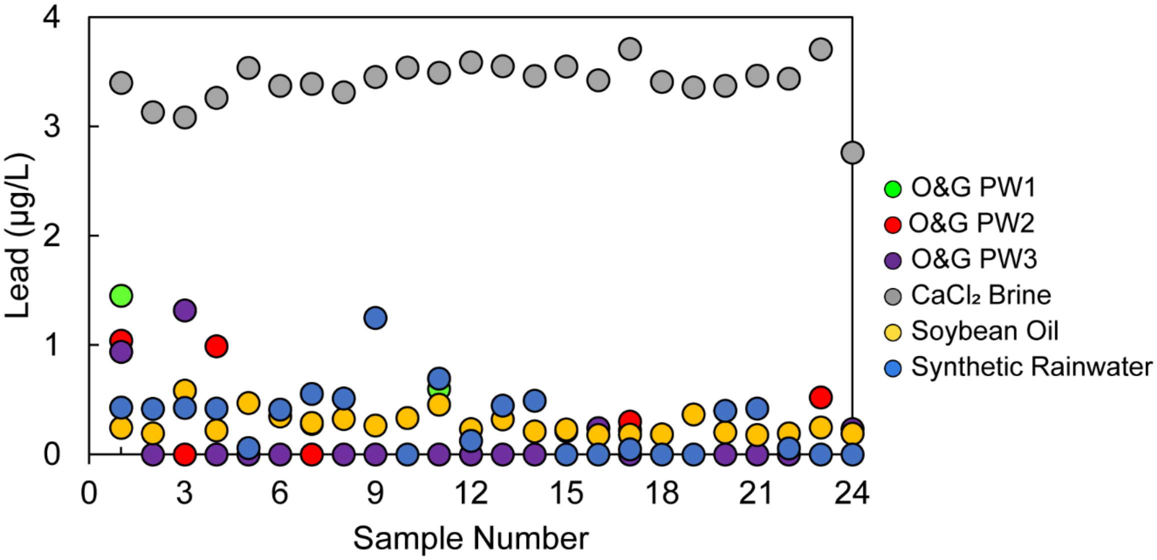

Figure 5.17 Comparisons of dissolved lead (Pb) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The EPA and DEP Primary Drinking Water Standards for lead is 0.015 mg/L Pb (= 15 μg/L).

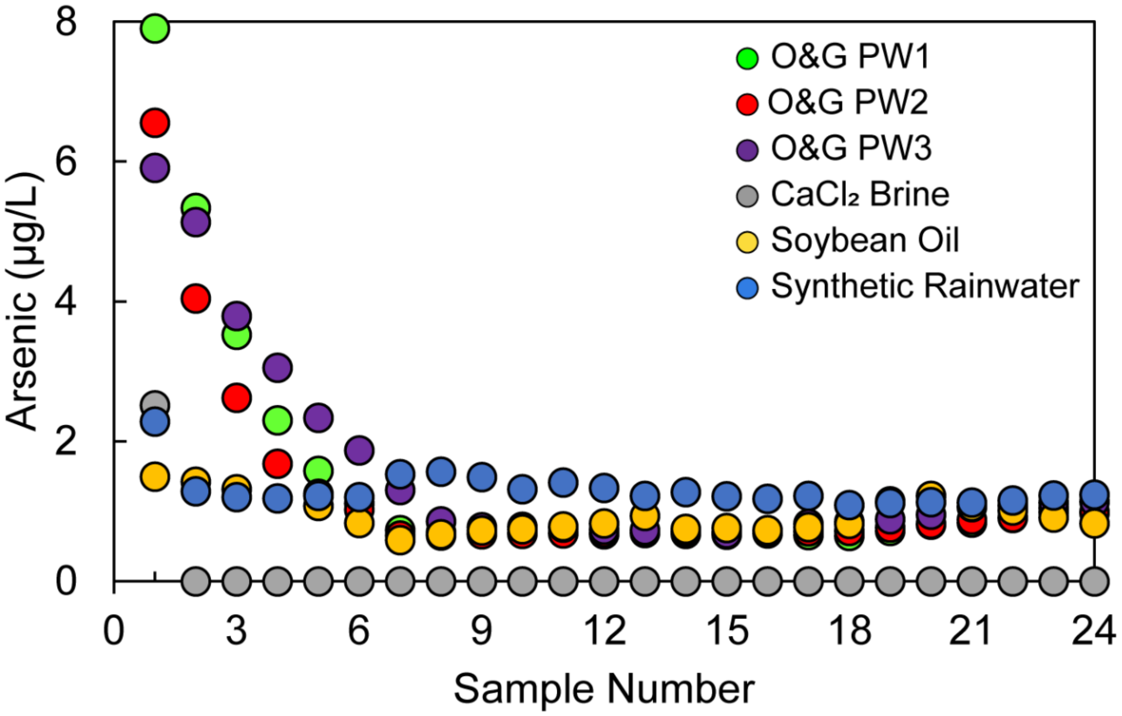

Figure 5.18 Comparisons of dissolved arsenic (As) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The EPA and DEP Primary Drinking Water Standards for arsenic is 0.01 mg/L As (= 10 µg/L).

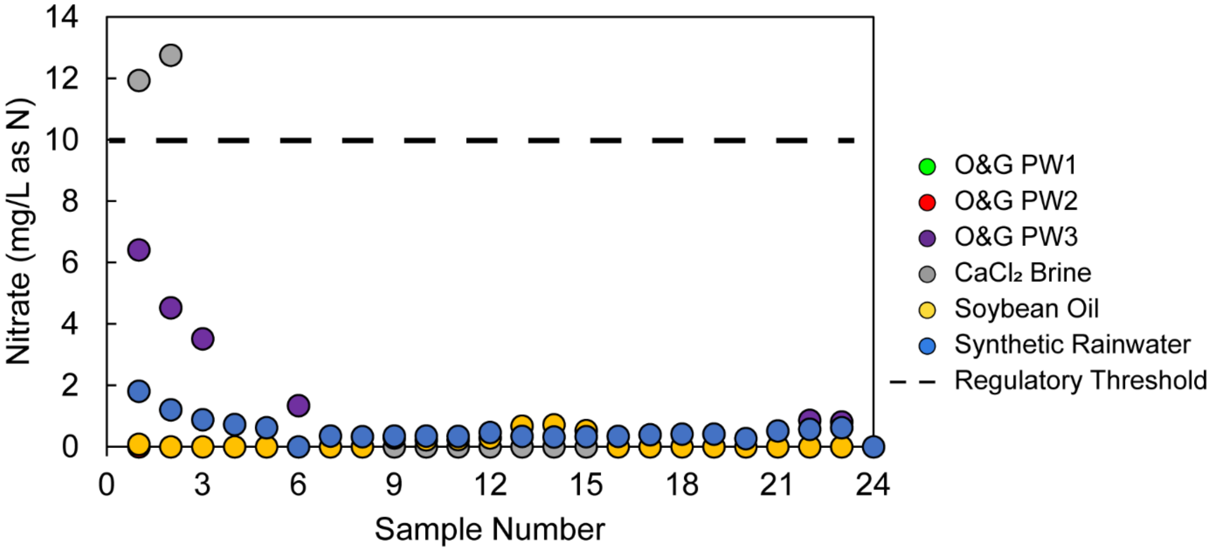

Figure 5.19 Comparisons of dissolved nitrate (NO_3^-) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 10 mg/L NO_3-N from EPA and DEP Primary Drinking Water Standards.

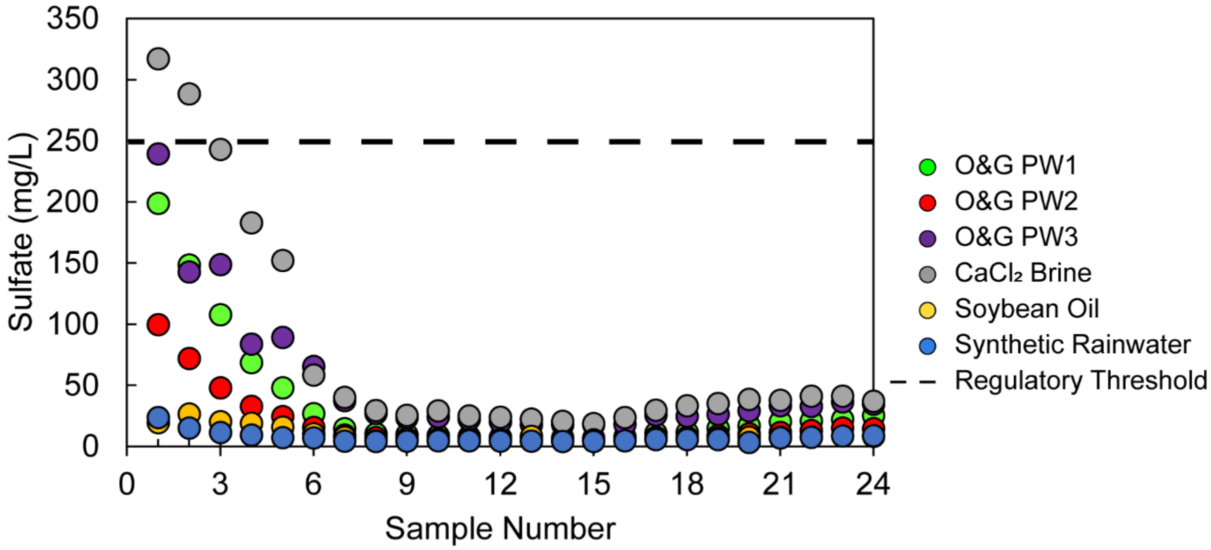

Figure 5.20 Comparisons of dissolved sulfate (SO_4^{2-}) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume. The Regulatory Threshold shown is 250 mg/L SO_4 from EPA and DEP Secondary Drinking Water Standards.

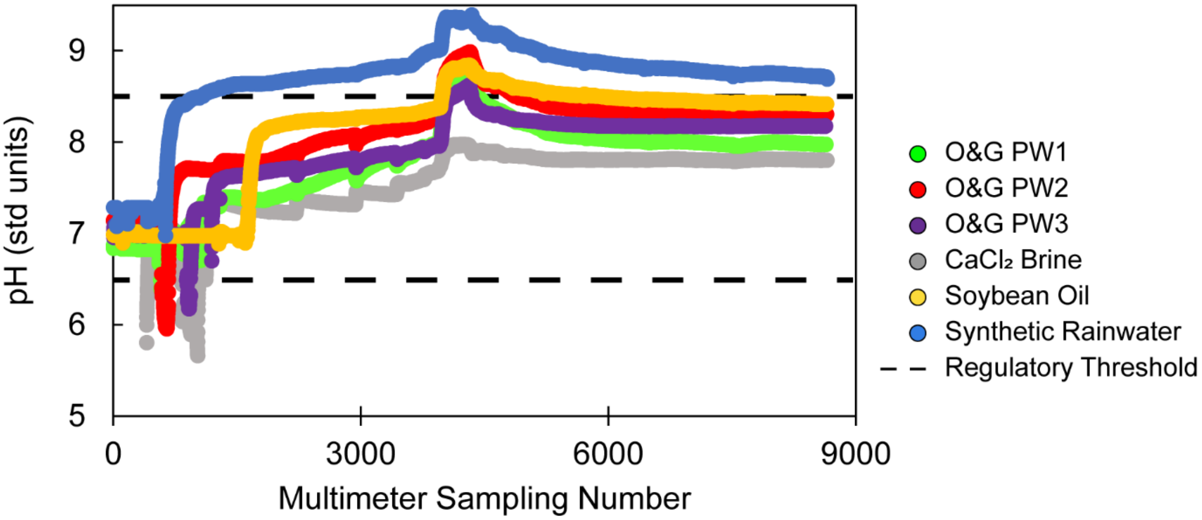

Figure 5.21 Comparisons of pH measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Measurements were recorded every 10-seconds of the 24-hour storm. The Regulatory Thresholds shown are pH 6.5 to pH 8.5 from EPA and DEP Secondary Drinking Water Standards.

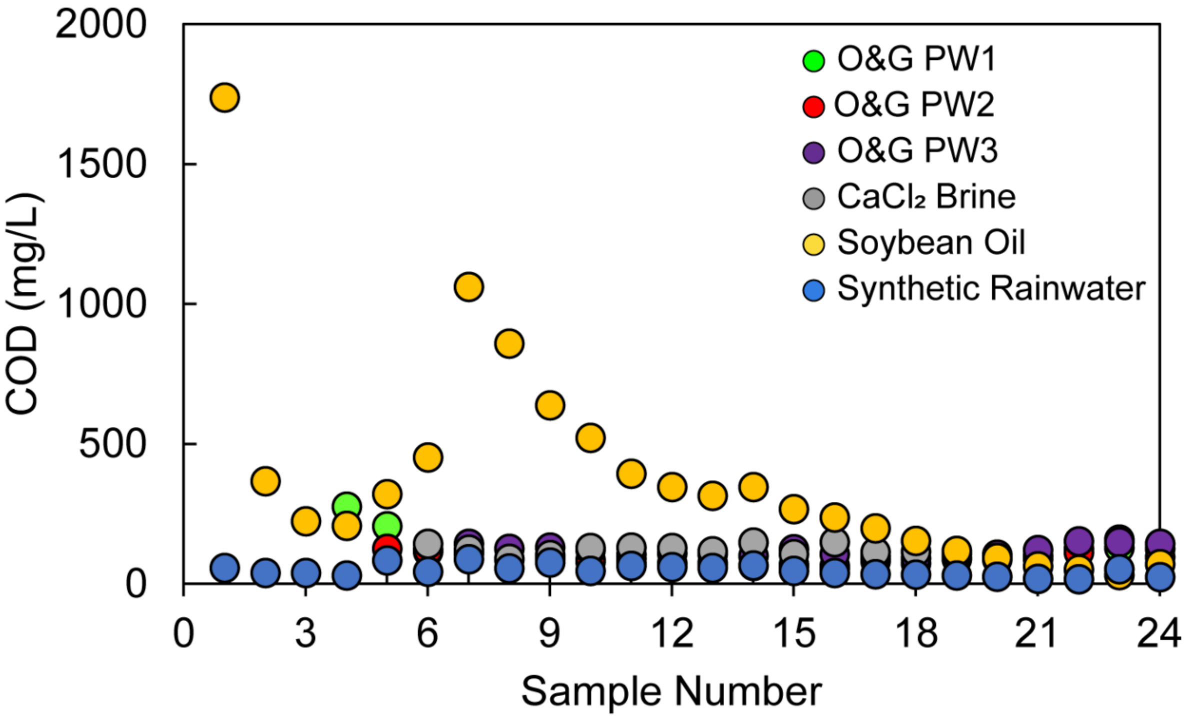

Figure 5.22 Comparisons of chemical oxygen demand (COD) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples were collected after every 1/24th of the storm volume.

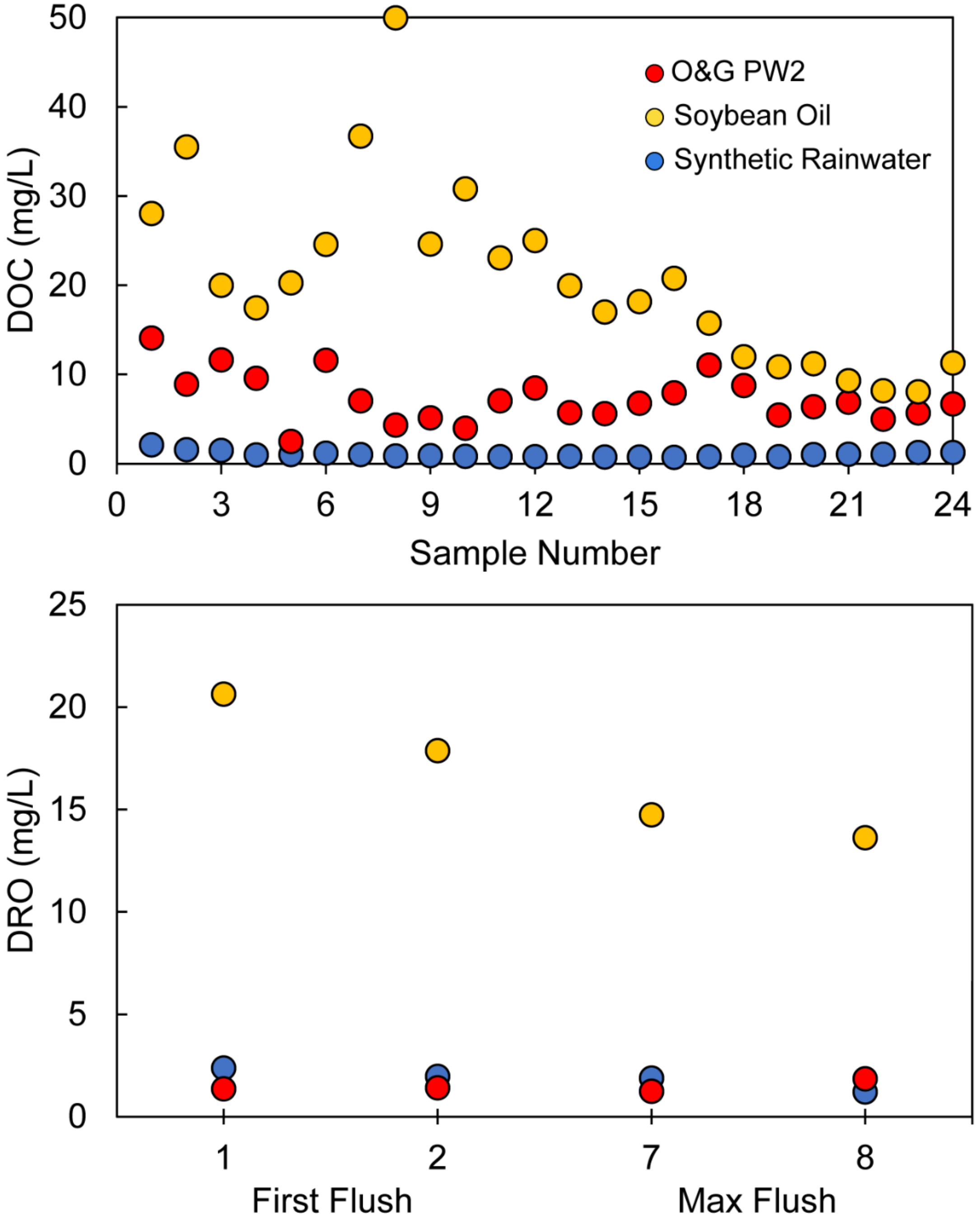

Figure 5.23 Comparisons of dissolved organic carbon (DOC) and diesel range organics (DRO) concentrations measured in runoff from gravel roadbeds treated with three of the six dust suppressants used in this study. Results shown are averaged from replicate tests for each dust suppressant except for single measurements for synthetic rainwater.

5.3 Comparisons of final roadbed concentrations

Constituent concentrations retained in the roadbeds were calculated based on mass balances or directly measured (radium and DRO) at the conclusion of the rainfall-runoff experiments. Elemental mass applied to the roadbed was calculated based on the measured concentration in the dust suppressants (Table 5.1) multiplied by the total volume of dust suppressant applied to the road. Elemental mass flushed off the road was calculated based on the measured concentrations in the runoff samples multiplied by the incremental volume of each sampling interval (equal to 1/24th of the total storm volume using Equation (2). Elemental mass retained in the roadbed was calculated by difference according to (Equation (3)):

$$\text{Retained mass} = \text{Applied mass} - \text{Flushed mass} \tag{3}$$

Elemental mass leached out of the roadbed was defined for elements measured in runoff samples that were not measured in the applied suppressant. In this case, leached mass was calculated based on the measured concentrations in the runoff samples multiplied by the incremental volume of each sampling interval.

Based on relatively low activities of combined radium measured in the roadbeds at the conclusion of the rainfall-runoff experiments (Figure 5.24), especially compared to the control conditions measured with synthetic rainwater, most of the radium applied to the roadbeds with the dust suppressants was flushed off in the runoff. The highest radium activity measured in roadbed samples was collected from a roadbed treated with O&G PW3. This measured activity was slightly above the solid-phase combined radium activity limit of 5 pCi/g for handling the material as a radioactive waste.

Diesel range organics (DRO) were measured in roadbed samples collected from the gravel pile and from roadbeds treated with synthetic rainwater, O&G PW2, and soybean oil (Figure 5.25). Elevated concentrations of DRO were only detected in the roadbeds treated with soybean oil.

While chloride concentrations were elevated in runoff samples from roadbeds treated with calcium chloride and OGPWs (Figure 5.5), masses of chloride were retained in the roadbeds at the conclusion of the rainfall-runoff experiments (Figure 5.26). Similar results were obtained with bromide suggesting that the continued flushing of both chloride and bromide could occur with subsequent rainfalls. Sulfate and nitrate were retained to even greater extents than chloride and bromide. Sulfate (Figure 5.20) and nitrate (Figure 5.19) concentrations measured in the runoff were not elevated relative to regulatory standards. It is expected that subsequent rain events would produce even lower runoff concentrations of these constituents.

Sodium was retained in the roadbeds treated with OGPWs (Figure 5.27). As noted above, sodium tends to destabilize dirt and gravel roads. Retention of sodium from OGPWs may increase the duration of destabilization. Calcium tended to be better flushed from roadbeds treated with OGPWs or calcium chloride. Leached concentrations of magnesium and barium were only measured with calcium chloride-treated roadbeds. This leaching may be promoted by elevated TDS runoff that increases mineral solubility.

Lead and iron in OGPWs were completely retained in the roadbeds (Figure 5.28). consistent with Tasker et al. (2018). calcium chloride, SB and SRW promoted the leaching of arsenic and manganese. Elevated TDS in calcium chloride would enhance solubility of these elements. Organic-metal complexes formed by SB could enhance solubility of these elements. A potentially lower pH during the ‘resting’ of the roadbed could have enhanced solubility of these elements.

Roadbed aggregate was collected prior to application of dust suppressants, following application of dust suppressants, and following the 24-hour rainfall event. The road aggregate samples were sieved to isolate the silt and clay size fraction (<45 um) that could be mobilized as dust or TSS. Combined radium activity of road aggregate samples prior to the start of all tests was ca. 4 pCi/gram. Following application of O&G PW 1 and O&G PW3 the <45-µm size fractions contained higher activities, reflecting the added radium from the dust suppressants. However, following the rain event, the small size fractions of the road aggregate were again 4 pCi/g. This suggests that following a 24-hour 2-year rain event, the radium activity that was added with a dust suppressant will be flushed off the gravel road. This is consistent with the results of the runoff that showed elevated activity in the runoff samples of O&G PW3. Road aggregate treated with both synthetic rainwater and calcium chloride brine showed reduced radium activity relative to untreated road aggregate. Following the rain event, the activity of the road aggregate in the synthetic rainwater experiment decreased relative to the initial pre-treatment concentration. This result is consistent with the rainfall runoff experiment that showed that radium was mobilized to the runoff from leaching of the road aggregate.

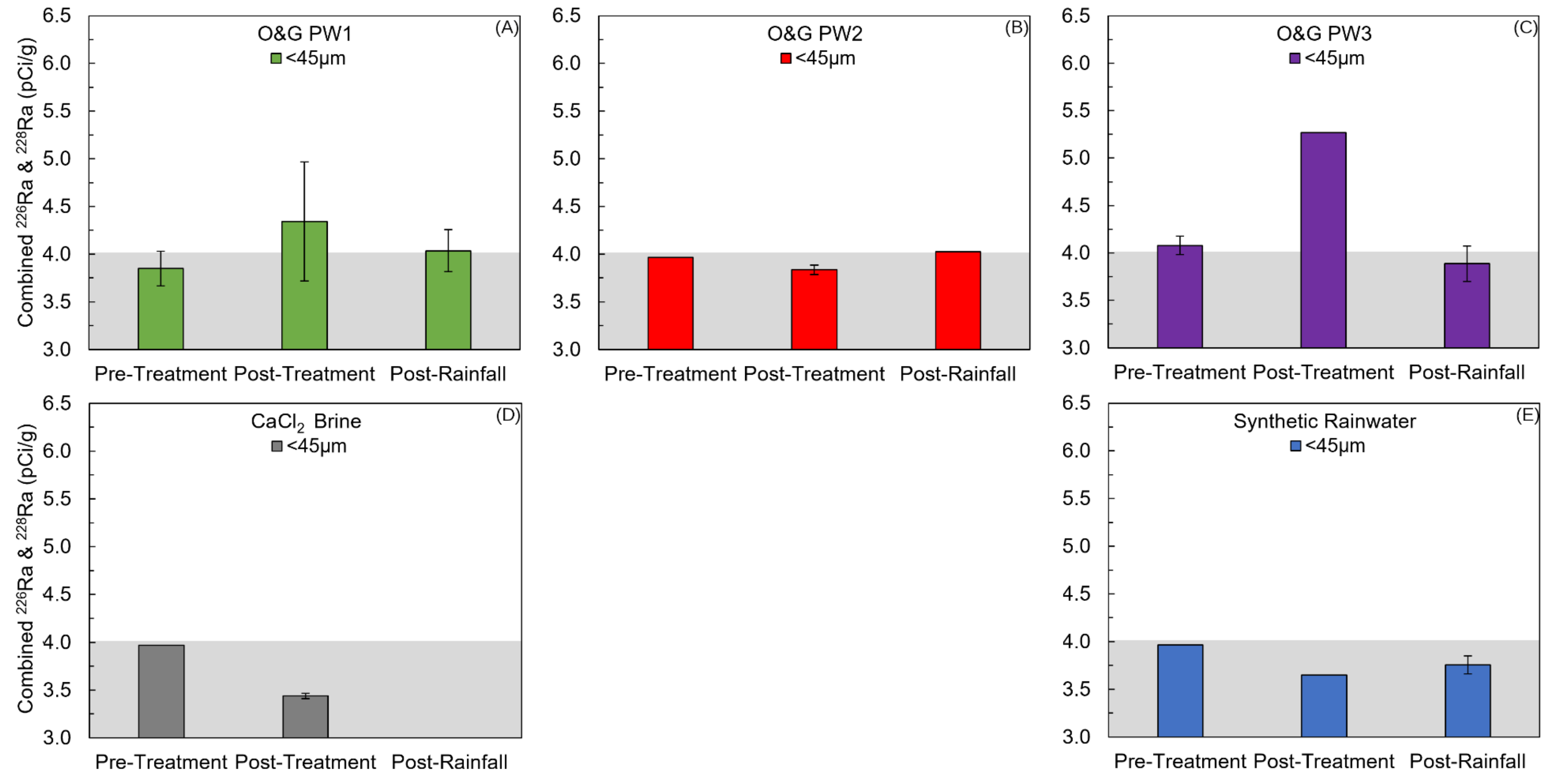

Figure 5.24 Comparisons of activities of combined radium measured in gravel roadbed samples collected after the rainfall-runoff tests for roadbeds treated with five of the dust suppressants used in this study – A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, and E) Synthetic Rainwater. Results are shown for triplicate samples collected from the roadbed of one replicate test. Samples were sieved to smaller than 45 microns before activity measurements. Note the results in relation to the grey shaded background which represents the average activity of untreated roadbed material, 3.997 pCi/g. No post-rainfall samples were collected for the Calcium Chloride Brine tests.

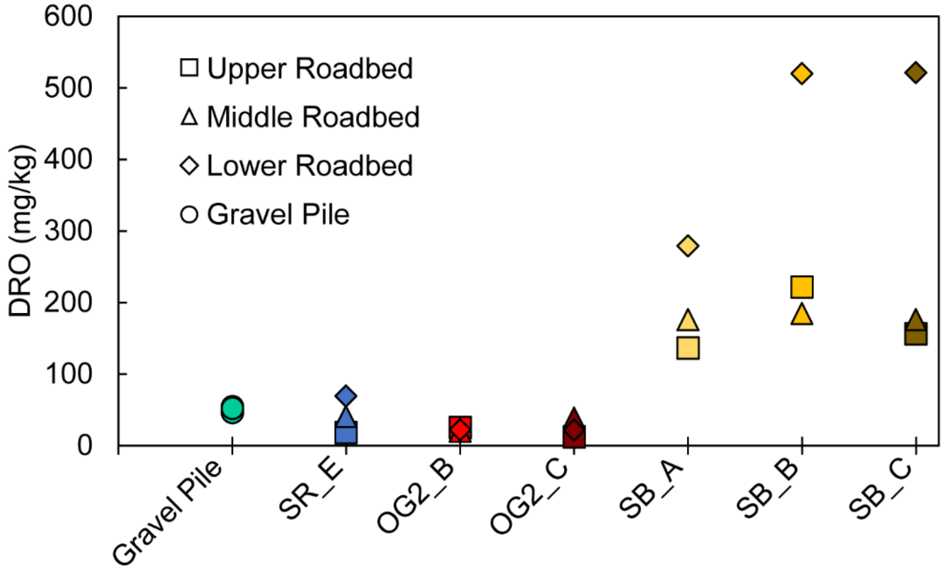

Figure 5.25 Comparisons of concentrations of diesel range organics (DRO) measured in gravel roadbed samples collected after the rainfall-runoff tests. The Gravel Pile was located outside the CITEL facility. SR_E refers to Synthetic Rainwater replicate E. OG2_B and OG2_C refer to Oil & Gas Produced Water 2 replicates B and C. SB_A, SB_B, and SB_C refer to Soybean Oil replicates A, B and C. Results are shown for triplicate samples collected from the roadbed of one replicate test.

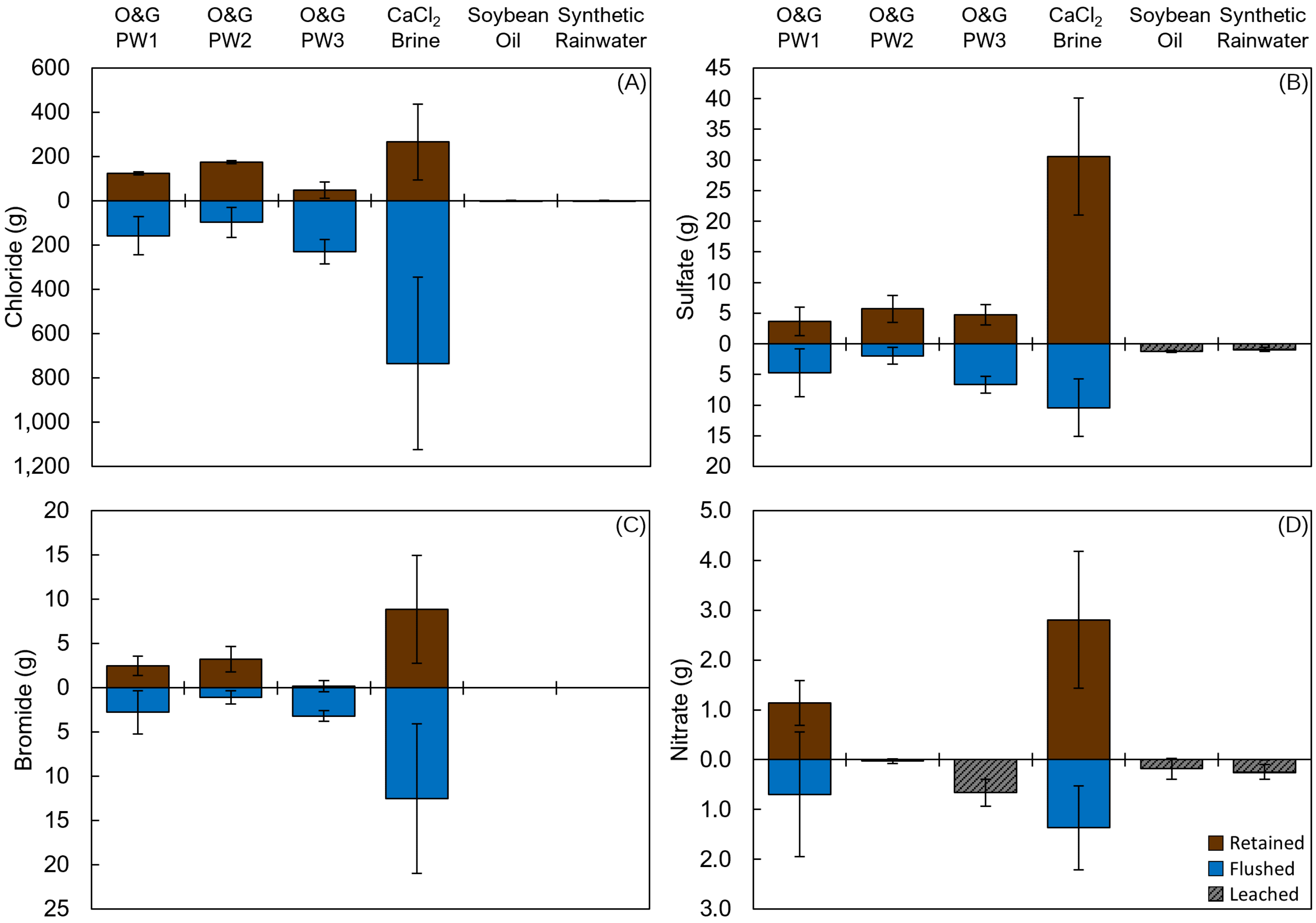

Figure 5.26 Mass balance analyses for anions retained, flushed, or leached from gravel roadbeds treated with six different dust suppressants. A) Chloride, B) Sulfate, C) Bromide, and D) Nitrate. Flushed masses were calculated from runoff concentrations. Retained masses were calculated according to Equation 3. Leached masses were mobilized from the roadbeds.

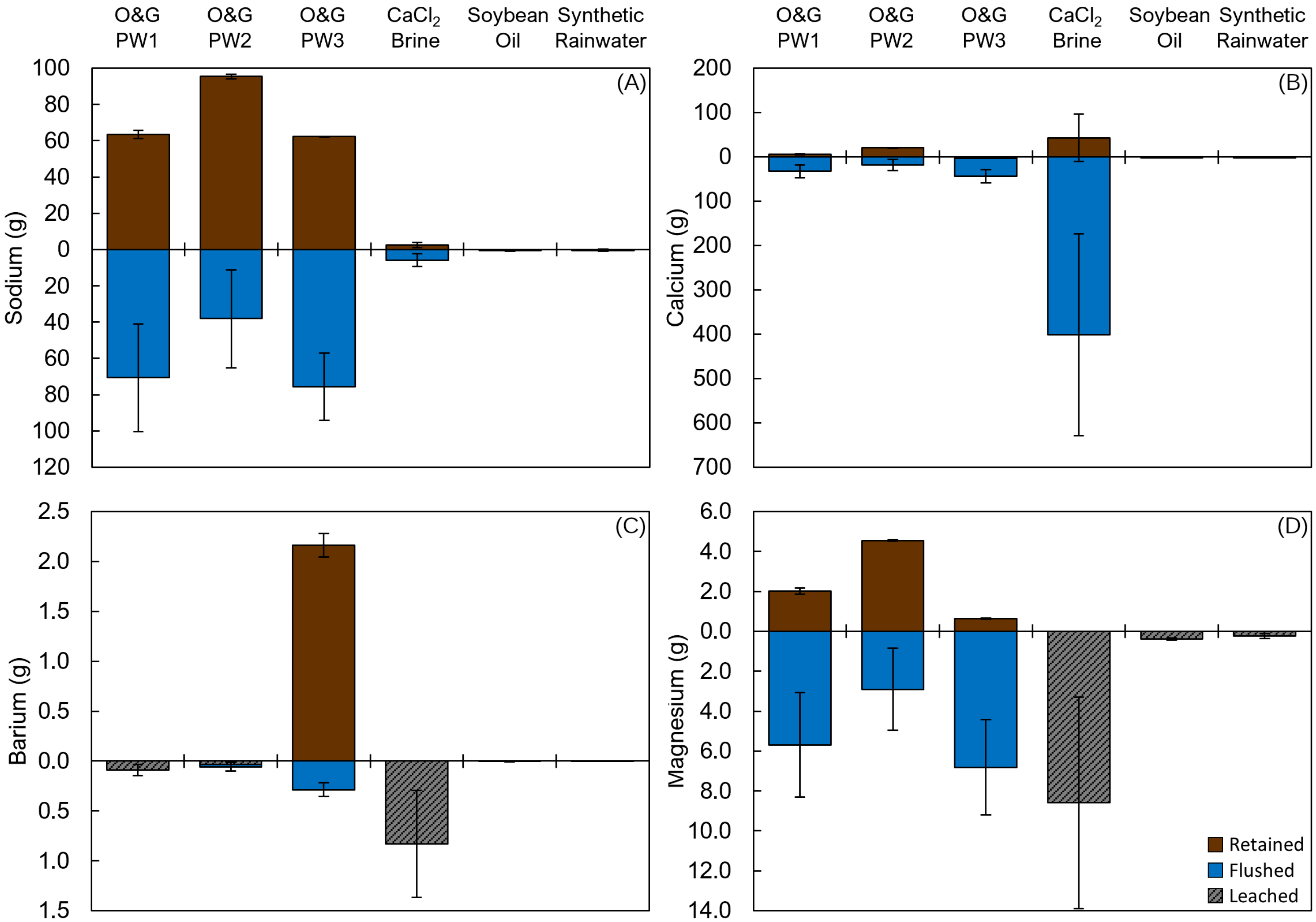

Figure 5.27 Mass balance analyses for cations retained, flushed, or leached from gravel roadbeds treated with six different dust suppressants. A) Sodium, B) Calcium, C) Barium, and D) Magnesium. Flushed masses were calculated from runoff concentrations. Retained masses were calculated according to Equation 3. Leached masses were mobilized from the roadbeds.

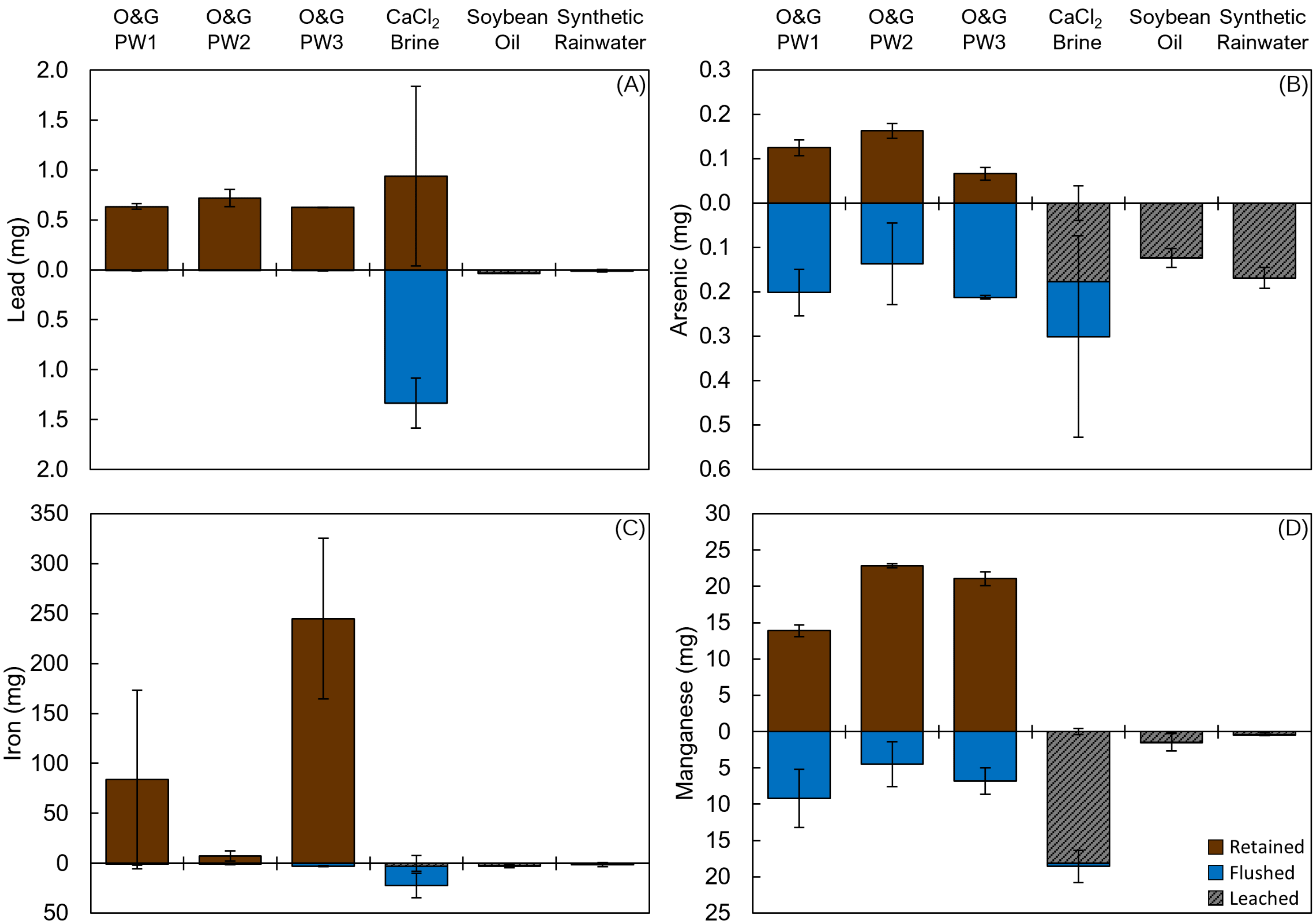

Figure 5.28 Mass balance analyses for trace elements retained, flushed, or leached from gravel roadbeds treated with six different dust suppressants. A) Lead, B) Arsenic, C) Iron, and D) Manganese. Flushed masses were calculated from runoff concentrations. Retained masses were calculated according to Equation 3. Leached masses were mobilized from the roadbeds.

5.4 Comparisons of dust suppression efficacy

Results from dust generation tests are summarized in Table 5.3. Eight dust suppressants (including synthetic rainwater) were tested under two conditions that mimic summer relative humidity (RH) conditions expected in northwestern Pennsylvania in dry sunny conditions (20% RH) or dry shaded conditions (50% RH). Dust concentrations were measured and recorded every second over a three-minute period. The average maximum PM_{10} (AM PM_{10}) dust concentrations were averaged from the last minute of the tests.

Under dry sunny conditions (20% RH), dust generated from road aggregate treated with the OGPWs saturated the dust sampler's detector (Figure 5.29A). Under these conditions the AM PM_{10} was reported as >400 mg/m^3 (Table 5.3), equivalent to the upper detection limit of the test. Under these conditions, OGPWs were no more effective than synthetic rainwater with respect to controlling dust generation. Dust generated from road aggregate treated with calcium chloride brines ranged from 4.9 to 13 mg/m^3. Dust generated from road aggregate treated with soybean oil was 0.20 mg/m^3. Low AM PM10 concentrations demonstrate that calcium chloride brines and soybean oil can suppress dust. Elevated AM PM10 concentrations demonstrate that OGPWs and synthetic rainwater cannot suppress dust under these dry sunny conditions.

Under dry shaded conditions (50% RH), dust generated from road aggregate treated with the OGPWs did not saturate the dust sampler's detector (Figure 5.29B). Dust generated from road aggregate treated with the three OGPWs was 340, 385, and 313 mg/m^3 as compared to >400 mg/m^3 for road aggregate treated with synthetic rainwater. Dust generated from road aggregate treated with calcium chloride brines ranged from 0.11 to 0.75 mg/m^3. Dust generated from road aggregate treated with soybean oil was 0.60 mg/m^3. The OGPWs and calcium chloride brines controlled dust better under higher relative humidity. However, even under higher relative humidity, two of the three OGPWs were little more effective than synthetic rainwater with respect to controlling dust generation and all the OGPWs were substantially less effective than calcium chloride brines and soybean oil.

Total suspended solids (TSS) in runoff samples may reflect efficacy of the dust suppressants to stabilize the roadbed (Figure 5.30). Unlike EC (Figures 5.3) and dissolved chloride (Figures 5.5), TSS peaked during the maximum flush period. The maximum rainfall intensity and maximum water velocities discharging off the roadbed at this time likely led to the maximum scour of the roadbed. Higher concentrations of TSS in runoff samples may reflect lesser efficacy for roadbed stabilization.

Calcium chloride brine was shown to be the most effective dust suppressant for roadbed stabilization based maximum TSS concentrations in the runoff. Calcium chloride brine was the only dust suppressant that significantly reduced TSS in runoff samples compared to the synthetic rainwater control ($p < 0.1$, Table 5.3, Figure 5.30). This result is consistent with widespread marketing and use of calcium chloride as a soil stabilizer and additive for dirt and gravel road full-depth reclamation projects. All the other dust suppressants produced maximum TSS concentrations not significantly different than synthetic rainwater. None of the OGPWs greatly improved road stabilization or decreased dust generation as compared to synthetic rainwater.

From previous lab-scale testing, the sodium adsorption ratio (SAR; Equation 1) used in combination with the TDS has proven useful in predicting a brine's efficacy for suppressing dust on dirt and gravel roads (Stallworth et al., 2020). SAR represents the equivalent ratio of monovalent sodium cations to divalent calcium and magnesium cations. This ratio is important because divalent cations are capable of bridging negatively-charged clay particles together and physically stabilizing gravel roads. In contrast, sodium cations tend to disperse clays and destabilize gravel roads. Calcium chloride, magnesium chloride, and sodium chloride salts are also hygroscopic, meaning they adsorb water from the humidity in the air. Moist roads tend to produce less dust. Based on the TDS concentrations of the OGPWs used in this study (ca. 82,000 mg/L TDS), brines with SAR values greater than about 3 are predicted to be relatively ineffective as dust suppressants. Therefore, based only on SAR values (Table 5.3) and compared to synthetic rainwater, one would predict that only the calcium chloride brine would be effective and that the OGPWs would be ineffective. SAR is not applicable to soybean oil because it is a nonaqueous phase liquid that suppresses dust by other mechanisms.

Table 5.3 Summary of efficacy metrics for roadbed stabilization and dust suppression for dust suppressants used in the current study and other commercial brines.

Dust Suppressant	Max [TSS] (mg/L) Mean	±std	n	AM PM10 (mg/m^3)# 20% RH	AM PM10 (mg/m^3)# 50% RH	SAR
O&G PW1	4580 A*	703	4	>400	341	68.6
O&G PW2	5327 A	107	3	>400	386	68.1
O&G PW3	4543 A	1083	3	>400	313	69.3
$CaCl_2$ Brine (Fisher)	2915 B	586	4	5.8	0.11	1.4
Commercial Brine 1	n.t		-	3.4	0.53	17.4
Commercial Brine 2	n.t.		-	9.1	0.82	2.1
Soybean Oil	4457 A	633	3	0.2	0.60	--
Synthetic Rainwater	4350 A	1521	3	>400	>400	--

* Different letters denote statistically significant values based on unpaired, one-tailed Student T-tests at $p \leq 0.1$.

AM PM10 = average maximum 10-µm particulate matter measured according to Stallworth et al. (2021). Maximum measurable dust concentration was 400 mg dust/m^3 air.

n.t. = not tested in rainfall-runoff experiment

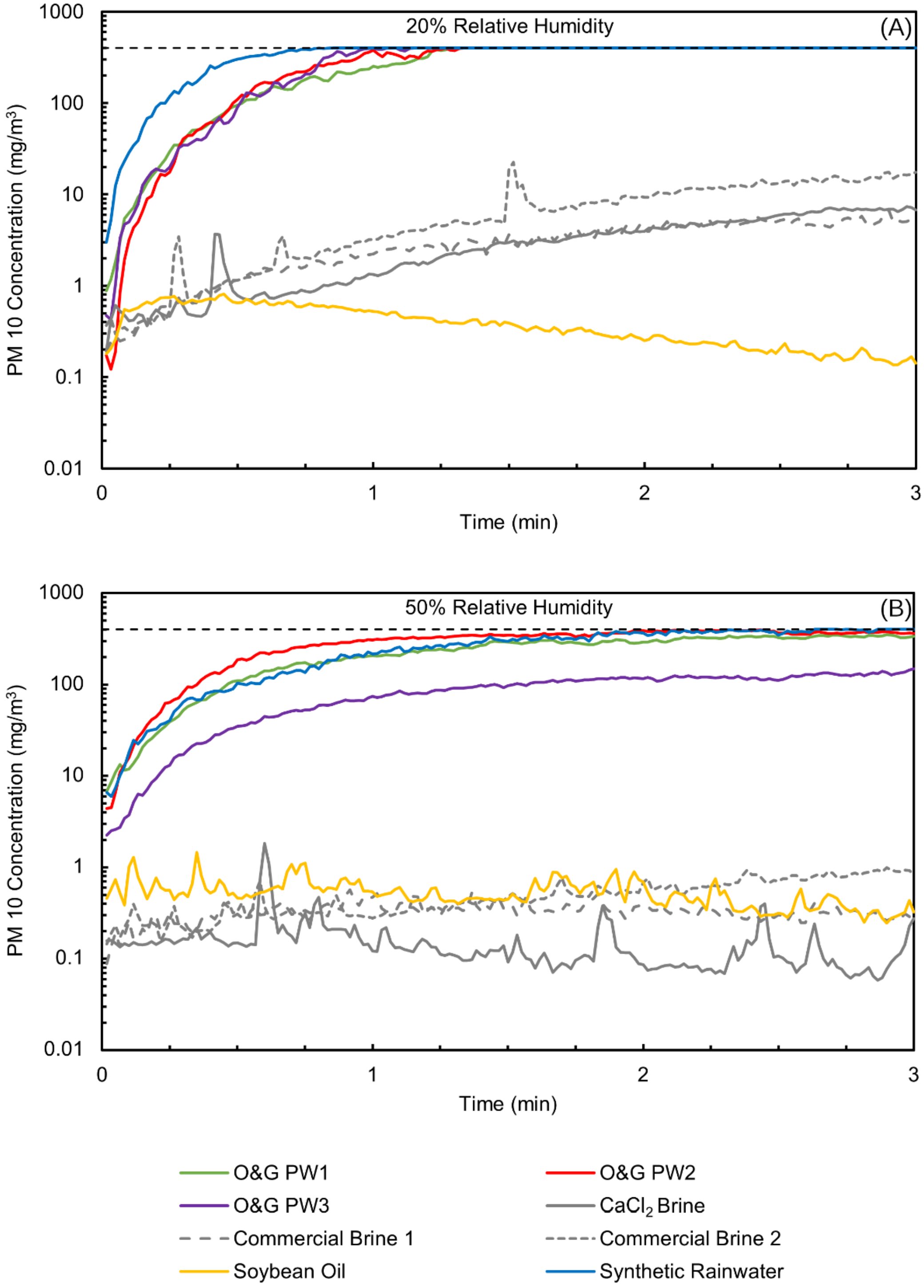

Figure 5.29 Comparison of average dust generated (PM 10 in mg/m^3) over time for dust suppressants used in this study. A) Tests conducted at 20% relative humidity. B) Tests conducted at 50% relative humidity. Results are presented for replicate dust tests. Note the instrument detection limit of 400 mg/m^3 represented by the horizontal dashed black line.

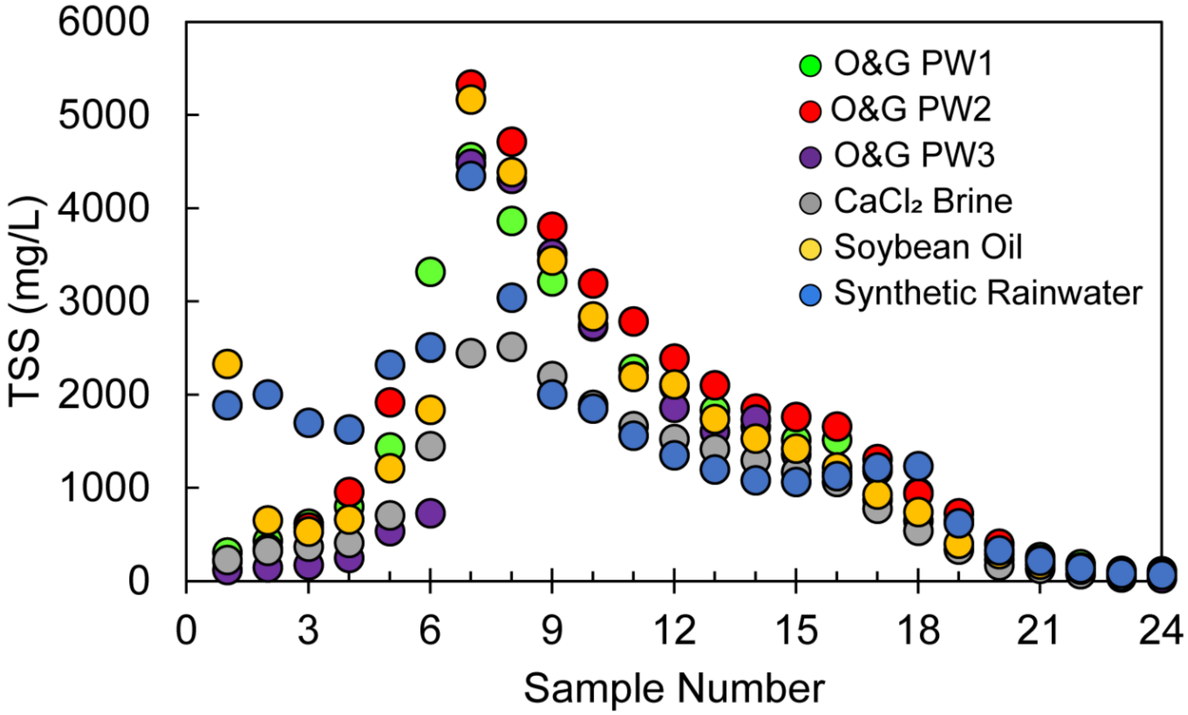

Figure 5.30 Comparisons of total suspended solids (TSS) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. Results shown are averaged from all replicate tests for each dust suppressant. Samples collected after every 1/24th of the storm volume.

6. CONCLUSIONS

A series of laboratory-scale experiments were conducted to evaluate the environmental impacts of several dust suppressants, including oil and gas produced waters. Two types of experiments were conducted, rainfall-runoff and dust efficacy. Rainfall-runoff experiments were conducted using a 3-foot wide by 9-foot long gravel roadbed treated with each dust suppressant and then subject to a controlled rain event. Runoff water samples were collected over the course of the rain event and an extensive suite of analytes were measured. Dust generation experiments were conducted with compacted 'pucks' of gravel road material treated with each dust suppressant and subjected to controlled abrasion to simulate tire wear on roadbed material. Air-borne concentrations of particulate matter were measured during abrasion. All experimental materials were selected to match conditions representative of northwestern Pennsylvania.

When applied as a dust suppressant, oil and gas produced waters were little to no more effective than rainwater. This result is consistent with previous studies conducted both in the laboratory (Stallworth et al., 2020) and in the field (Graber et al., 2019). Oil and gas produced waters are likely ineffective dust suppressants because of their elevated concentrations of sodium relative to calcium and magnesium. Sodium is a monovalent cation that does not effectively bridge clay particles (the size-fraction most likely to be mobilized as road dust) to promote dust suppression. Instead, sodium can destabilize gravel roads and increase long-term road maintenance costs. Calcium and magnesium are divalent cations that can bridge clay particles together. Calcium chloride brines and magnesium chloride brines are commonly marketed as commercial dust suppressants. Calcium chloride brines used in this study were shown to be highly effective dust suppressants.

Based on dust generation experiments, only the $CaCl_2$-based brines and the organic-based soybean oil were effective dust suppressants. The oil and gas produced waters were little to no more effective than synthetic rainwater with respect to controlling dust generation. Based on rainfall-runoff experiments, the $CaCl_2$-based brines led to the lowest concentrations of total suspended solids (TSS) washed off the roadbeds indicating enhanced roadbed stability. There was no difference in the amounts of TSS washed off the roadbeds treated with OGPWs as compared to synthetic rainwater.

Chemical analyses of brine-based dust suppressants can be used to predict their efficacy. The sodium adsorption ratio (SAR) is a measure of sodium to calcium plus magnesium (Equation 1). In the current study, brines with a SAR value of < 3 were shown to be effective dust suppressants, consistent with previous studies (Graber et al., 2019, Stallworth, 2020). SAR values for the three OGPWs ranged from 68 to 69 suggesting that these fluids would not be effective dust suppressants as confirmed by subsequent experiments. DEP should consider setting a low SAR value for any brines proposed for dust suppression.

Maximum concentrations in the runoff were related and essentially proportional to concentrations in the dust suppressants. Contaminants of interest related to salinization of freshwater resources include electrical conductivity, TDS, chloride, and bromide. Contaminants of interest related to human health include combined radium (^{226}Ra + ^{228}Ra), barium, strontium, lithium, iron, and manganese. Contaminants of interest related to irrigation water include sodium, magnesium, and calcium. Contaminants of interest related to organic-based dust suppressants include chemical oxygen demand and dissolved organic carbon. Contaminants of lesser concern include aluminum, arsenic, lead, nitrate, and sulfate. Contaminants of lesser concern in this study were so designated only because they were not elevated in the dust suppressants themselves. DEP should consider requiring measurements for contaminants of interest and contaminants of lesser concern when evaluating a proposed dust suppressant.

Through mass balance analysis of material applied to, washed from, and retained by the roadbed, most contaminants of interest were washed from the roadbed. An important exception occurred with roadbeds treated with oil and gas produced waters. For these OGPWs, the roadbeds retained radium, sodium, iron, and manganese. Sodium is of concern because it likely leads to the destabilization of dirt and gravel roads. Radium retained in the roadbed was associated with fine materials and could be subject to remobilization in dust.

Runoff from $CaCl_2$ brine-treated roadbeds contained the highest concentrations of most contaminants of interest – including TDS, electrical conductivity, chloride, bromide, barium, strontium, lithium, iron, manganese, sodium, magnesium, and chloride. Roadbeds treated with calcium chloride brine produced runoff with elevated TDS (up to 57,000 mg/L) and chloride concentrations (up to 34,000 mg/L Cl) and elevated activities of combined radium (up to 48 pCi/L). Aside from calcium and chloride, most of the contaminants of interest were likely sourced from impurities in the brine. Therefore, DEP may want to request measurements for these contaminants of interest for currently-approved calcium chloride-based and magnesium chloride-based dust suppressants.

OGPWs-treated roadbeds led to the highest concentrations of combined radium in the runoff. Combined radium activities in the three OGPWs when applied to the roadbeds ranged from 84 to 2,500 pCi/L, within the anticipated range for OGPWs from western Pennsylvania. Combined radium activities in runoff from the OGPW-treated roadbeds exceeded 60 pCi/L, the effluent standard for industrial wastewater discharges, during both the ‘first flush’ and the ‘maximum flush’ parts of the rain event. Roadbeds treated with OGPWs also produced runoff with elevated TDS (up to 19,000 mg/L), chloride (up to 12,000 mg/L Cl), and bromide (up to 300 mg/L Br) concentrations. DEP should consider setting a low standard for combined radium activity for any brines proposed for dust suppression.

7. DATA REPOSITORY

Data generated for this project is packaged as a Microsoft Access Database (.accdb) with tables for most test analytes (e.g., table CL_A_TOC includes all the TOC data for Calcium Chloride Brine Test A). Summary tables for each test are also included (e.g., SR_E includes all data collected in the database for Synthetic Rainwater Test E).

Dust testing results and radium testing results are summarized in comma separated value files (.csv).

The database, dust testing results, and radium testing results are available at:

https://pennstateoffice365-my.sharepoint.com/:f:/g/personal/wdb3_psu_edu/EptcFMGBeeROtvuqMEDPTFIBKQ60cM8qlDeOqGB92JnHMg?e=DPoC2F

8. REFERENCES

Bahadori, A., Zahedi, Gholamreza, Z., Zendehboudi, S. 2012. Estimation of Potential Barium Sulfate (Barite) Precipitation in Oilfield Brines Using a Simple Predictive Tool. *Environmental Progress and Sustsainable Energy*, 32, 860-865.

EPA. 1994. SW-846 Test Method 1312: Synthetic Precipitation Leaching Procedure. https://www.epa.gov/hw-sw846/sw-846-test-method-1312-synthetic-precipitation-leaching-procedure.

EPA. 1996. SW-846 Test Method 3510C: Separatory Funnel Liquid-Liquid Extraction. https://www.epa.gov/hw-sw846/sw-846-test-method-3510c-separatory-funnel-liquid-liquid-extraction

EPA. 1996. Method 3540C, Revision 3, December 1996, Final Update III to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.

Graber, K., C. L. M. Hargiss, J. E. Norland, and T. DeSutter. Is Oil-Well Produced Water Effective in Abating Road Dust? Water, Air, and Soil Pollution, 2017. https://doi.org/10.1007/s11270-017-3640-x.

Graber, K., Hargiss, C. L. M., DeSutter, T., He, Y., and Norland, J. E. 2019. Dispersion of Gravel Road Fine-Fractions as Influenced by Oil-Well Produced Water and Simulated Solutions of Various SAR, EC, and Ca/Mg Ratios. *Water, Air, and Soil Pollution*, *230*(61):1-10. https://doi.org/10.1007/s11270-019-4111-3.

He, C., Li, M., Liu, W., Barbot, E., and Vidic, R. D. 2014. Kinetics and Equilibrium of Barium and Strontium Sulfate Formation in Marcellus Shale Flowback Water. *J. Environ. Eng.*, *140*(5):B4014001-1–9. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000807.

Kunz, B. K., and E. E. Little. Dust Control Products at Hagerman National Wildlife Refuge, Texas. Transportation Research Record: Journal of the Transportation Research Board, Vol. 2472, No. 1, 2015, pp. 64–71. https://doi.org/10.3141/2472-08.

Landis, M., Kamal, A., Kovalcik, K., Croghan, D., Norris, G., and Bergdale, A. 2016. The impact of commercially treated oil and gas produced water discharges on bromide concentrations and modeled brominated trihalomethane disinfection byproducts at two downstream municipal drinking water plants in the Upper Allegheny River, Pennsylvania, USA. *Sci. Total Environ.*, 542, 505–520.

Payne, B. F. Oil and Gas Well Brines for Dust Control on Unpaved Roads – Part 1: Ineffectiveness. European Scientific Journal, ESJ, Vol. 14, No. 27, 2018, p. 398.

Rowan, E.L., Engle, M.A., Kirby, C.S., Kraemer, T.F. Radium Content of Oil- and Gas-Field Produced Waters in the Northern Appalachian Basin (USA): Summary and Discussion of Data. US Geological Survey. 2011.

Schäfer, J., Norra, S., Klein, D., Blanc, G. 2009. Mobility of trace metals associated with urban particles exposed to natural waters of various salinities from the Gironde Estuary, France. *J Soils Sediments*, 9, 374-392.

Stallworth, A. M., Chase, E. H., Burgos, W. D., and Warner, N. R. 2020. Laboratory Method to Assess Efficacy of Dust Suppressants for Dirt and Gravel Roads. *Transportation Research Record*, 2674 (6), 188-199.

Stallworth, A., Marak, K., McDevitt, B., Laporte, G., Chase E., Freedman, M., Taylor-Wilson, R., Burgos, W.D., and Warner, N. R. 2021. Changes in Road Dust Generation and Composition following Treatment with Oil and Gas Wastewater Produced Water. *Science of The Total Environment*, 799, 10, 149347.

Tasker, T. L., Burgos, W. D., Piotrowski, P., Castillo-Meza, L., Blewett, T. A., Ganow, K. B., Stallworth, A., Delompré, P. L. M., Goss, G. G., Fowler, L. B., Vanden Heuvel, J. P., Dorman, F., and Warner, N. R. 2018.

Tasker, T.L., Warner, N., Burgos, W.D. 2020. Geochemical and isotope analysis of produced water from the Utica/Point Pleasant Shale, Appalachian Basin. *Environmental Sciences: Processes and Impacts*, 22, 1224-1232.

Environmental and Human Health Impacts of Spreading Oil and Gas Wastewater on Roads. *Environ. Sci. Technol.*, *52*(12):7081–7091. https://doi.org/10.1021/acs.est.8b00716.

The Pennsylvania Department of Transportation (2015), PennDOT Drainage Manual, March 2015 Edition.

United States Department of Agriculture (1986). Urban Hydrology for Small Watersheds. Technical Release 55.

Method 1312, September 1994, Final Update IIB to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.

Method 3010A, Revision 1, July 1992, Final Update I to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.

U.S. EPA. 1997. “Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography,” Revision 1.0. Cincinnati, OH.

Wang, Y., Small, M., VanBriesen, J.M. (2017) “Assessing the risk associated with increasing bromide in drinking water sources in the Monongahela River, Pennsylvania,” ASCE Journal of Environmental Engineering. Vol 143: Issue 3. J. Environ. Eng., 2017, 143(3): 04016089

Wu, Shimin and Yu, Wenjuan. “Liquid-liquid extraction of polycyclic aromatic hydrocarbons in four different edible oils from China.” Food Chemistry, 135, 2012.

9. Appendix:

EVALUATION OF ENVIRONMENTAL IMPACTS FROM DUST SUPPRESSANTS USED ON GRAVEL ROADS

PRESENTED TO	PRESENTED BY
Pennsylvania Department of Environmental Protection, Office of Oil and Gas Management Harrisburg, PA	**William D. Burgos** Penn State University University Park, PA

Release date:

May 26, 2022

Prepared by:

William Burgos, Ph.D.

Nathaniel Warner, Ph.D.

Xiaofeng Liu, Ph.D.

Eric Chase

Andrew Kearney

James Farnan

Andrew Eck

Hassan Ismail

Table A.1 Chemical characterization summary of dust suppressants used in the current study.

Dust Suppressant	**O&G PW1**		**O&G PW2**		**O&G PW3**		**Synthetic Rainwater**		**Regulatory Criteria**
Analyte	**Avg.**	**St.Dev.**	**Avg.**	**St.Dev.**	**Avg.**	**St.Dev.**	**Avg.**	**St.Dev.**	
EC (mS/cm)	120	1.39	120	1.13	125	1.5	0.023	0.009	3.0[g]
TDS* (mg/L)	84073	988	81967	1090	85307	6606	2.39	0.05	500[b]
Ra-226 (pCi/L)	212.0	117.9	51.5	1.9	1797.6	929.0	--	--	60[e]
Ra-228 (pCi/L)	148.4	88.0	32.9	6.0	695.6	455.3	--	--	60[e]
Combined Ra (pCi/L)	360.4	147.1	84.4	6.3	2514.4	1034.6	--	--	5[b]
Chloride (mg/L)	49683	1246	47941	1327	48951	6629	--	--	250[b], 230[c]
Bromide (mg/L)	922	188	753	253	592	110	--	--	6[d]
Iodide (mg/L)	13.8	0.37	11.2	1.3	14.5	0.72	0	0	
Nitrate (mg/L)	324	78.7	--	--	--	--	0.7	0.02	10[a]
Sulfate (mg/L)	1478	407	1348	389	2004	291	2.14	0.06	250[b]
Calcium (mg/L)	6757	116	6861	47.9	7153	65.9	--	--	401[g]
Magnesium (mg/L)	1359	25.5	1313	7.69	1311	4.6	--	--	61[g]
Strontium (mg/L)	112	1.85	112	2.09	453	3.59	0	0	4[f,h]
Barium (mg/L)	1.58	0.14	4.38	0.1	417	19.2	0	0	2[a]
Sodium (mg/L)	23643	405	23511	233	24278	30.6	0.14	0.01	20[h], 920[g]
Potassium (mg/L)	117	1.62	125	2.33	132	8.82	0.1	0.01	
Lithium (mg/L)	2.48	0.12	2.92	0.08	13.3	0.13	--	--	0.01[f]
SAR^ (meq/L)$^{1/2}$	68.6	0.58	68.1	0.46	69.3	0.17	--	--	9[g]
Aluminum (mg/L)	--	--	--	--	--	--	--	--	0.05 to 0.2[b]
Manganese (mg/L)	4.06	0.14	4.82	0.05	4.91	0.51	0	0	0.05[b]
Iron (mg/L)	15	15.7	1.44	0.89	43.7	42.5	0.02	0	0.3[b], 1[c]
Nickel (mg/L)	0.09	0.04	0.09	0.01	0.05	0.01	0	0	0.052[c], 0.1[h]
Zinc (mg/L)	1.83	0.09	1.93	0.19	2.21	0.15	0.44	0.02	5[b], 0.12[c], 2[h]
Lead (mg/L)	0.11	0	0.13	0.02	0.11	0	0	0	0.015[a], 0.0025[c]
Boron (mg/L)	0.77	0.11	0.99	0.15	1.26	0.01	0	0	2.4[d], 6[h]
Arsenic (mg/L)	0.06	0	0.05	0	0.05	0	--	--	0.01[a], 0.15[c]
DRO (mg/L)	14.7	3.2	10.8	0.2	1654.1	322.2	1.1	0.9	
GRO (mg/L)	1.3	0.04	2.6	0.08	1.1	0.27	0	0	
TOC (mg/L)	88.3	8.33	81.1	11.7	76.6	14.5	1.75	.50	
TIC (mg/L)	1.1	0.5	1.5	0.9	13.1	8.3	0.6	0.7	
pH (std units)	6.42	0.16	6.15	0.14	6.50	0.04	4.29	0.10	6.5-8.5[b]

*Calculated from Cl, SO_4, Br, Ca, Mg, Na, K, Sr, Ba concentrations; ^Calculated using equation (1)

[a] EPA and DEP Primary Drinking Water Standard

[b] EPA and DEP Secondary Drinking Water Standard

[c] EPA Aquatic Life Criteria

[d] WHO Drinking Water Quality Guideline

[e] Appendix B to 10 CFR Part 20

[f] US EPA Human-Based Screening Level

[g] USDA Irrigation Water Quality Guidelines

[h] EPA Drinking Water Health Advisories for lifetime exposures

Table A.1 (cont.) Chemical characterization summary of dust suppressants used in the current study.

Dust Suppressant	**$CaCl_2$ Brine**		**Commercial Brine 1**		**Commercial Brine 2**		**Soybean Oil**		**Regulatory Criteria**
Analyte	**Avg.**	**St.Dev.**	**Avg.**	**St.Dev.**	**Avg.**	**St.Dev.**	**Avg.**	**St.Dev.**	
EC (mS/cm)	197	4	216	--	180	--	--	--	3.0[g]
TDS* (mg/L)	271668	41742	381032	--	386848	--	0.14	0.02	500[b]
Ra-226 (pCi/L)	158.5	41.9	640.5	--	238.2	--	--	--	60[e]
Ra-228 (pCi/L)	71.6	41.7	88.9	--	170.1	--	--	--	60[e]
Combined Ra (pCi/L)	230.0	59.1	729.4	--	408.3	--	--	--	5[b]
Chloride (mg/L)	176402	30148	251127	--	266714	--	--	--	250[b], 230[c]
Bromide (mg/L)	3769	1071	3741	--	3429	--	--	--	6[d]
Iodide (mg/L)	0.22	0.04	47.50	--	2.58	--	--	--	
Nitrate (mg/L)	735	242	--	--	--	--	--	--	10[a]
Sulfate (mg/L)	7211	1681	--	--	--	--	--	--	250[b]
Calcium (mg/L)	78229	9441	76245	--	104788	--	0.41	--	401[g]
Magnesium (mg/L)	--	--	14535	--	896	--	0.10	0.004	61[g]
Strontium (mg/L)	1475	113	3070	--	2613	--	--	--	4[f,h]
Barium (mg/L)	1.57	0.87	--	--	3.93	--	--	--	2[a]
Sodium (mg/L)	1458	265	20014	--	2499	--	--	--	20[h], 920[g]
Potassium (mg/L)	3123	547	12301	--	5904	--	--	--	
Lithium (mg/L)	57.9	9.3	91.4	--	111.4	--	--	--	0.01[f]
SAR^ $(meq/L)^{1/2}$	1.4	0.18	17.4	--	2.1	--	--	--	9[g]
Aluminum (mg/L)	--	--	5.15	--	5.48	--	--	--	0.05 to 0.2[b]
Manganese (mg/L)	0.07	0.07	1.63	--	--	--	--	--	0.05[b]
Iron (mg/L)	3.39	1.41	4.13	--	6.52	--	--	--	0.3[b], 1[c]
Nickel (mg/L)	0.04	0.01	--	--	--	--	--	--	0.052[c], 0.1[h]
Zinc (mg/L)	1.84	0.75	2.19	--	3.88	--	--	--	5[b], 0.12[c], 2[h]
Lead (mg/L)	0.4	0.63	0.1	--	0.3	--	--	--	0.015[a], 0.0025[c]
Boron (mg/L)	22	3.65	520	--	42	--	--	--	2.4[d], 6[h]
Arsenic (mg/L)	0.02	0.01	--	--	--	--	--	--	0.01[a], 0.15[c]
DRO (mg/L)	0.5	0	--	--	--	--	6.5	0.7	
GRO (mg/L)	0.6	0.06	--	--	--	--	22.8	6.98	
TOC (mg/L)	8.27	1.29	--	--	--	--	--	--	
TIC (mg/L)	0.6	0.02	--	--	--	--	--	--	
pH (std units)	9.95	0.19	4.28	--	6.32	--	--	--	6.5-8.5[b]

*Calculated from Cl, SO_4, Br, Ca, Mg, Na, K, Sr, Ba concentrations; ^Calculated using equation (1)

[a] EPA Primary Drinking Water Standard

[b] EPA Secondary Drinking Water Standard

[c] EPA Aquatic Life Criteria

[d] WHO Drinking Water Quality Guideline

[e] Appendix B to 10 CFR Part 20

[f] US EPA Human-Based Screening Level

[g] USDA Irrigation Water Quality Guidelines

[h] EPA Drinking Water Health Advisories for lifetime exposures

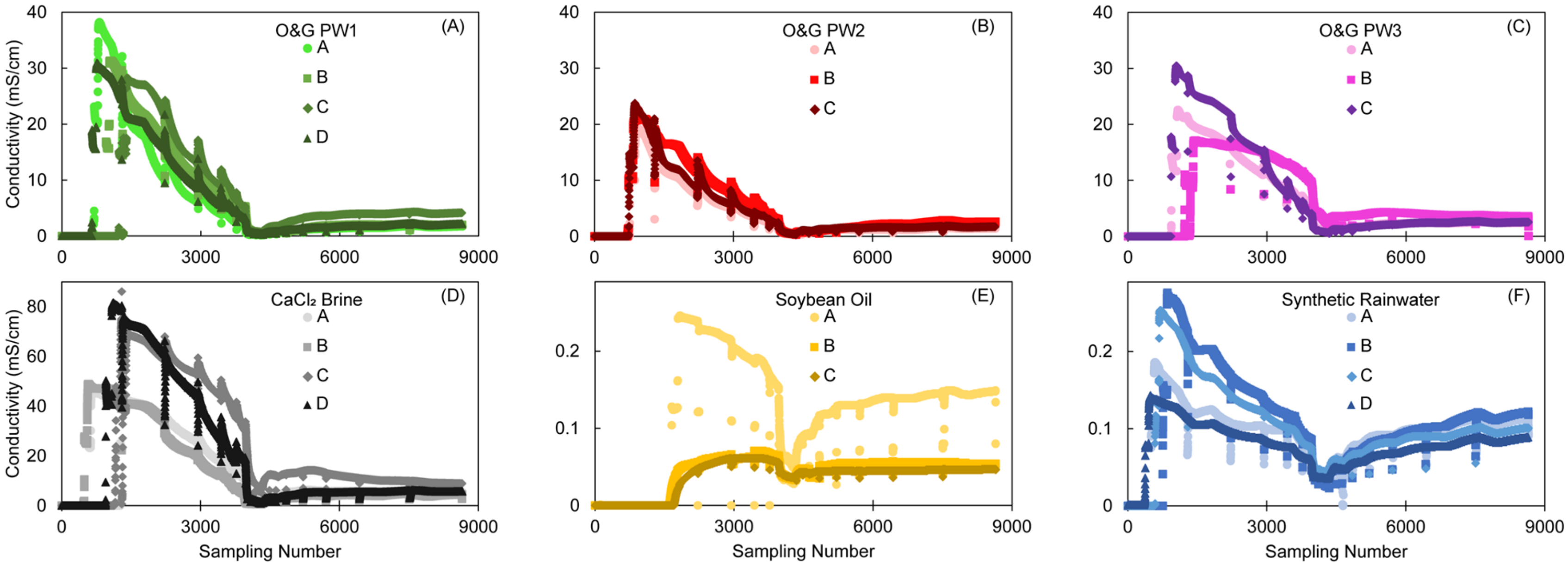

Figure A.1 Comparisons of electrical conductivity measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected every 10-seconds of the 24-hour storm. Note different y-axis scales used in each panel. A Regulatory Threshold for conductivity is 3.0 mS/cm from USDA Irrigation Water Quality Guidelines. The chronic aquatic life benchmark value for conductivity in central Appalachian streams is 0.30 mS/cm (EPA, 2011).

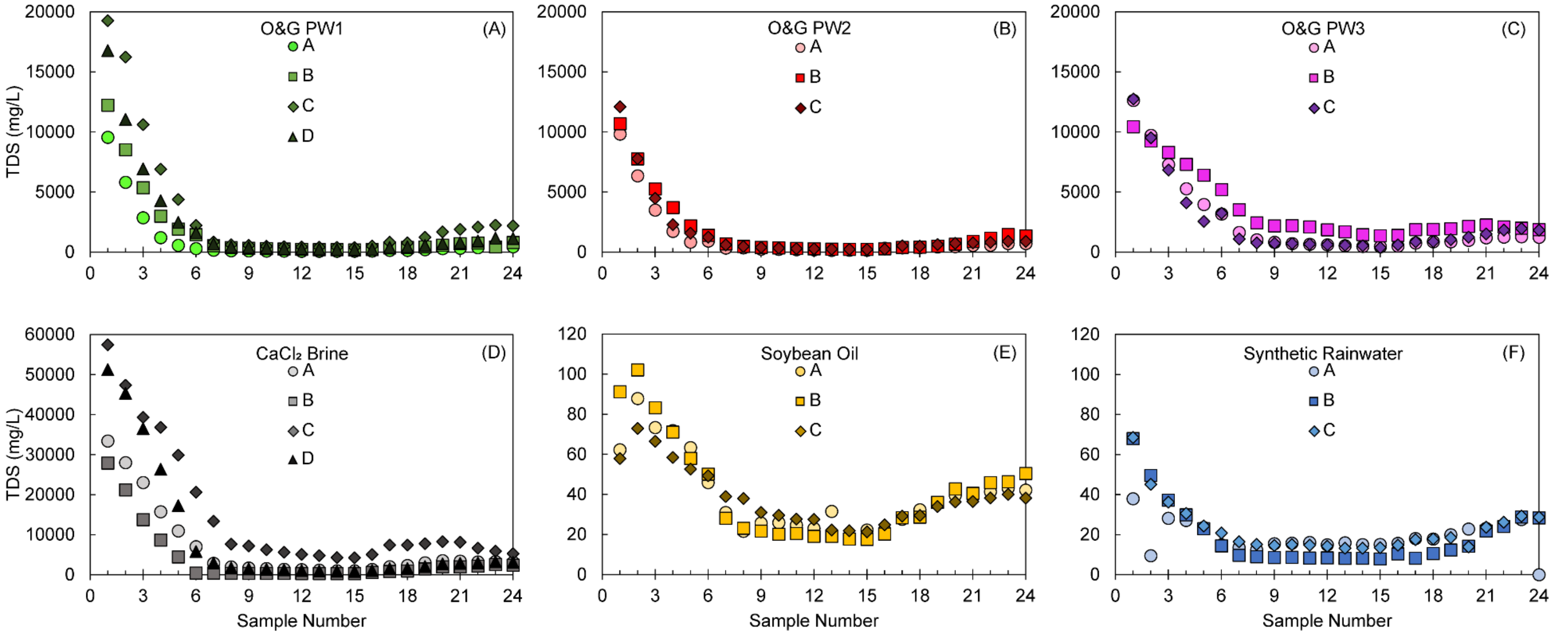

Figure A.2 Comparisons of total dissolved solids (TDS) concentrations calculated in runoff from gravel roadbeds treated with the six dust suppressants used in this study. TDS was calculated as the sum of measured Cl, SO_4, Br, Ca, Mg, Na, K, Sr, Ba concentrations. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. A Regulatory Threshold for TDS is 500 mg/L from EPA and DEP Primary Drinking Water Standards.

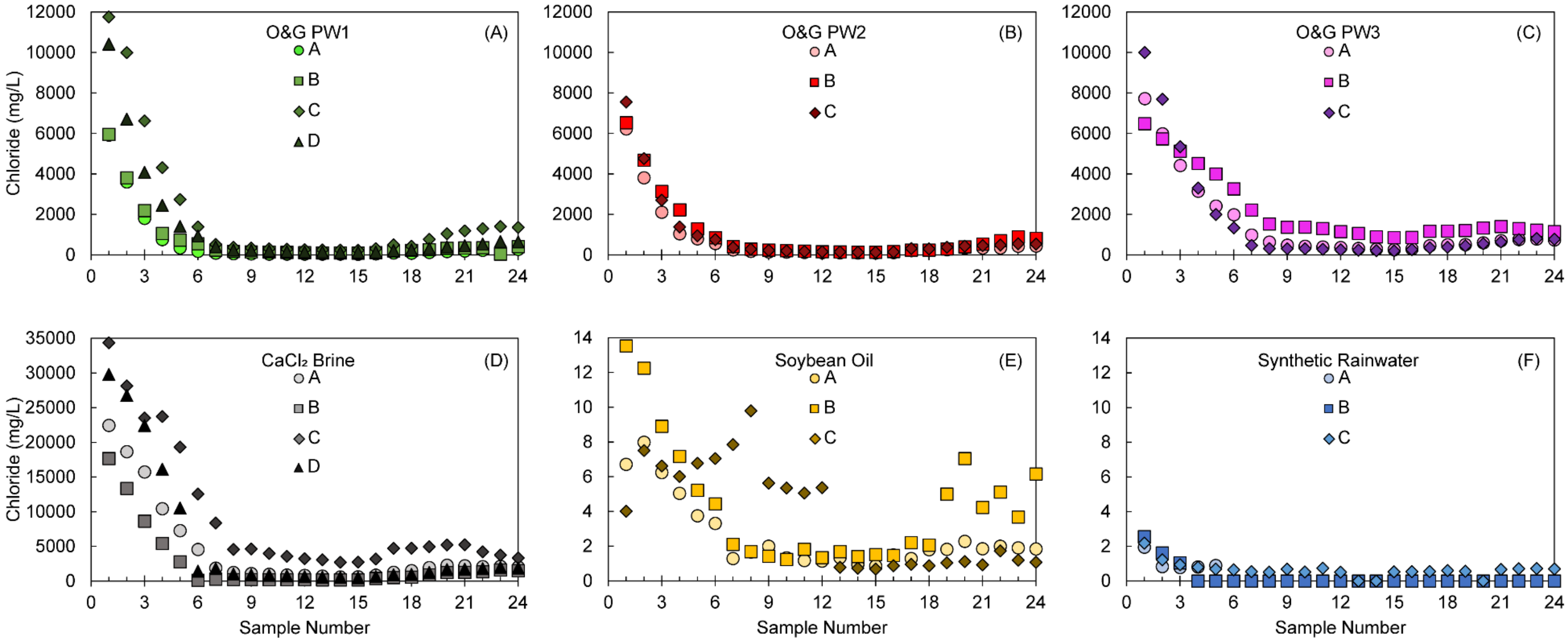

Figure A.3 Comparisons of dissolved chloride (Cl) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. A Regulatory Threshold is 250 mg/L Cl from EPA and DEP Secondary Drinking Water Standards.

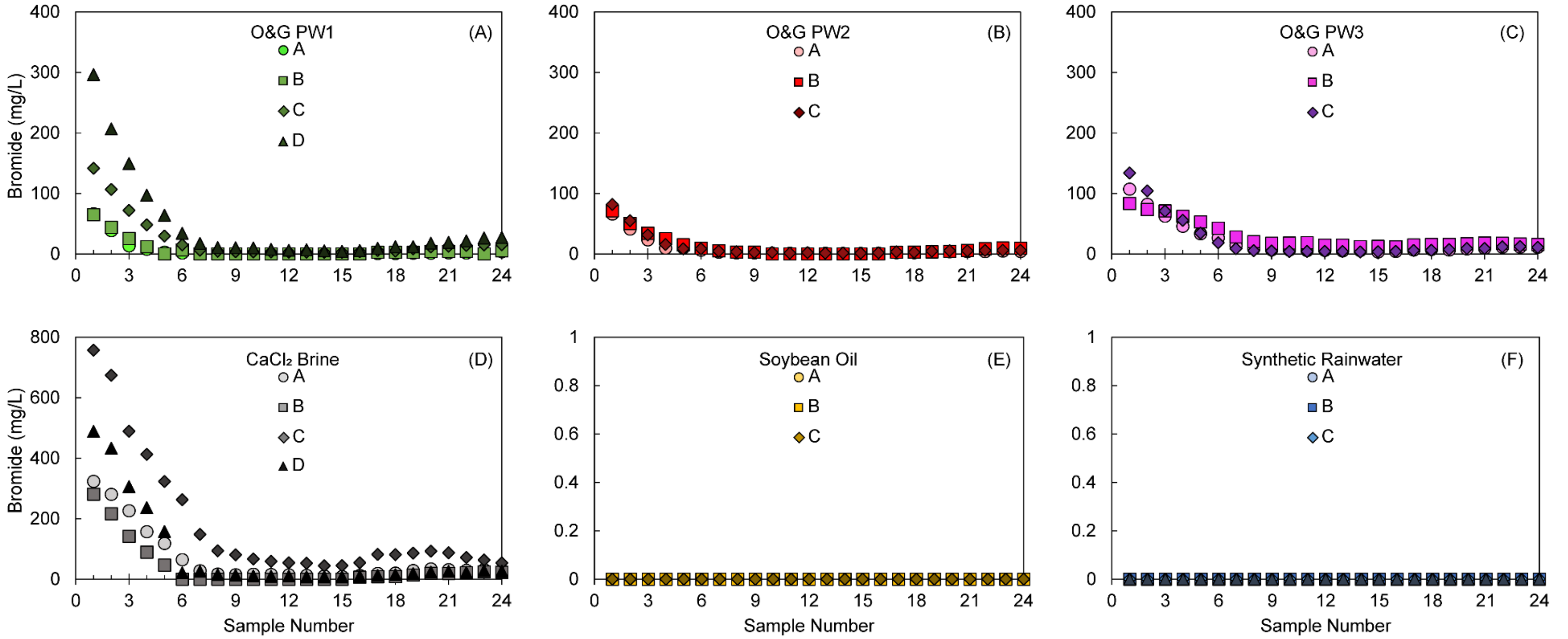

Figure A.4 Comparisons of dissolved bromide (Br) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. There are no regulatory thresholds for bromide, however, bromide leads to formation of disinfection byproducts (DBPs) in drinking water treatment plants. Influent bromide concentrations of 0.050 mg/L Br have shown to lead to increased formation of DBPs (Landis et al., 2016) while concentrations <0.080 mg/L Br may be protective for human health (Wang et al., 2017).

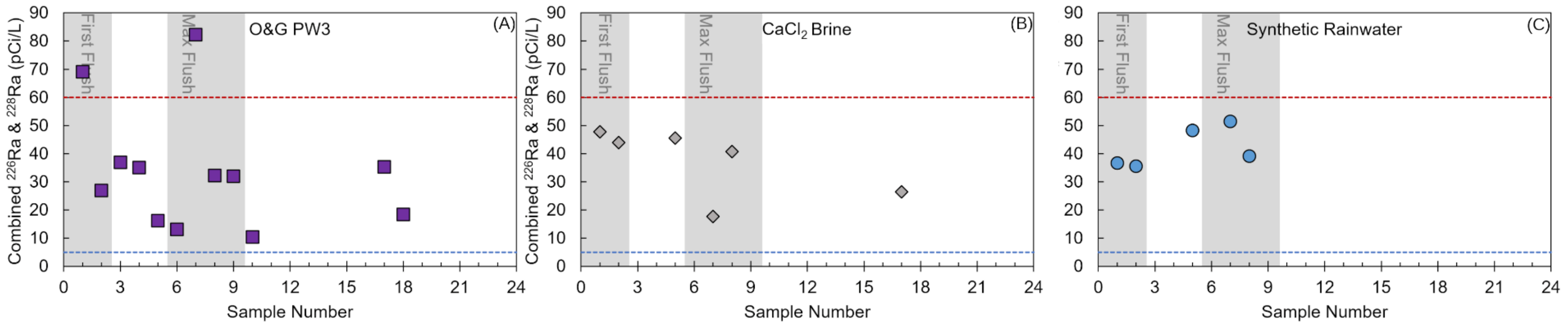

Figure A.5 Comparisons of combined radium activities (^{226}Ra + ^{228}Ra) measured in runoff from gravel roadbeds treated with three of the dust suppressants used in this study. Results shown are from single tests. (A) Oil & Gas Produced Water 3, (B) Calcium Chloride Brine, and (C) Synthetic Rainwater. Sample numbers 1 and 2 correspond to the first flush of runoff while sample numbers 7 and 8 correspond to the maximum flush of runoff. The NRC industrial wastewater discharge standard for combined radium activity is 60 pCi/L (red dashed line). The EPA and DEP primary drinking water standard for combined radium activity is 5.0 pCi/L (blue dashed line).

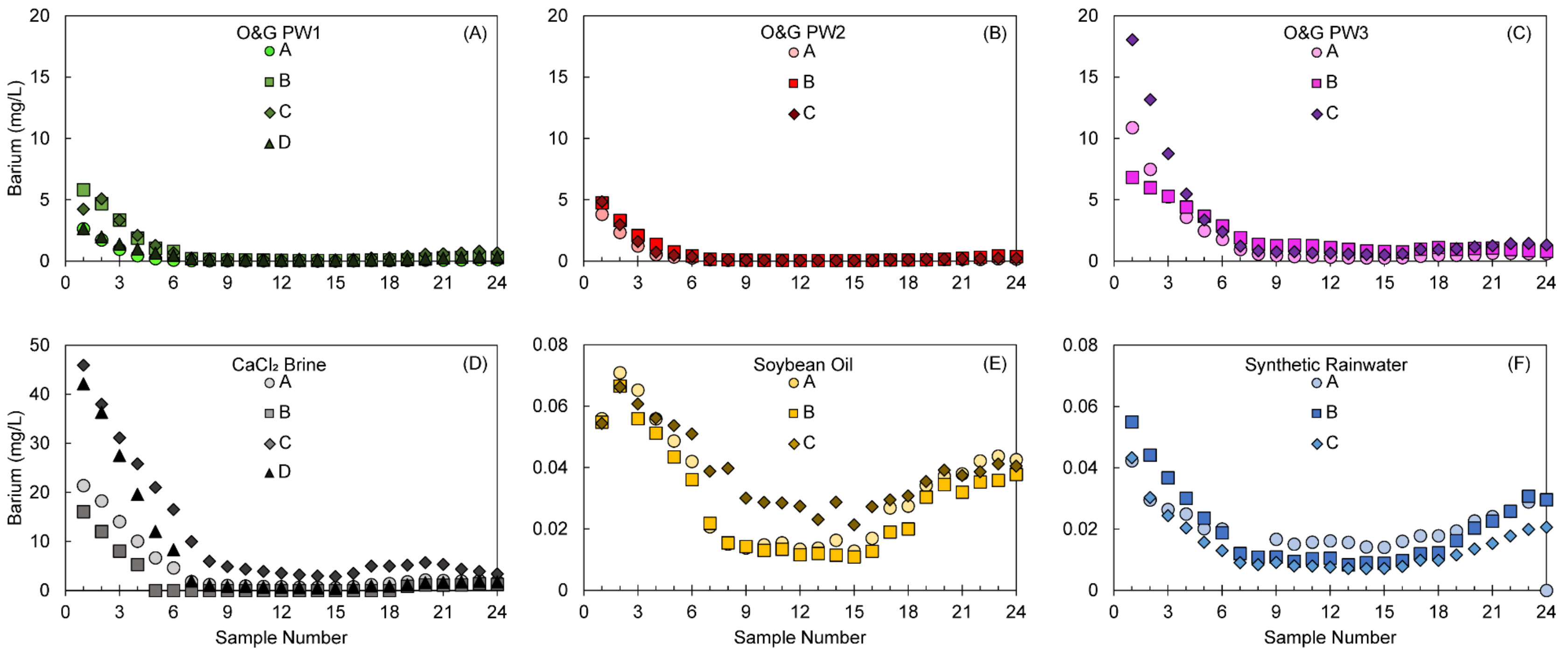

Figure A.6 Comparisons of dissolved barium (Ba) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The EPA and DEP primary drinking water standard for barium is 2 mg/L Ba.

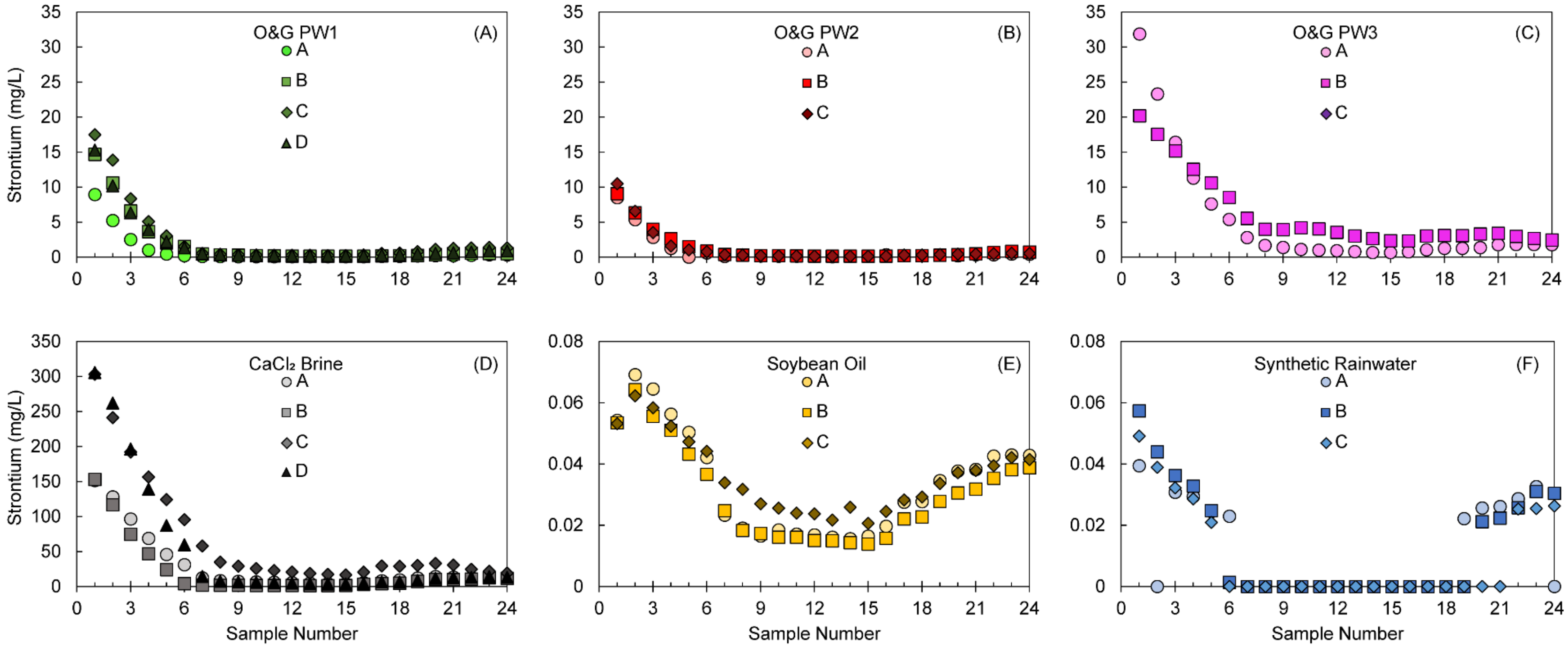

Figure A.7 Comparisons of dissolved strontium (Sr) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. A Regulatory Threshold is 4 mg/L Sr from EPA Human-Based Screening Levels.

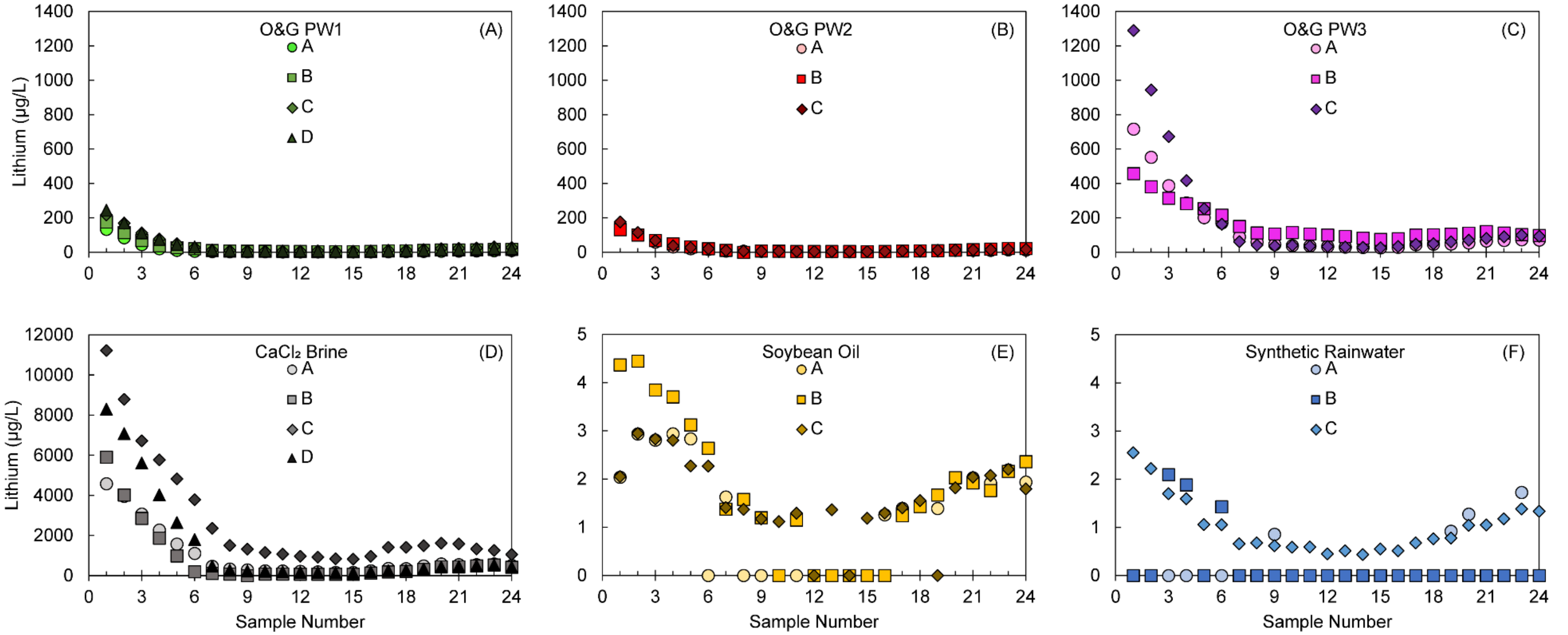

Figure A.8 Comparisons of dissolved lithium (Li) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The EPA Human-Based Screening Level for lithium is 0.01 mg/L (= 10 µg/L).

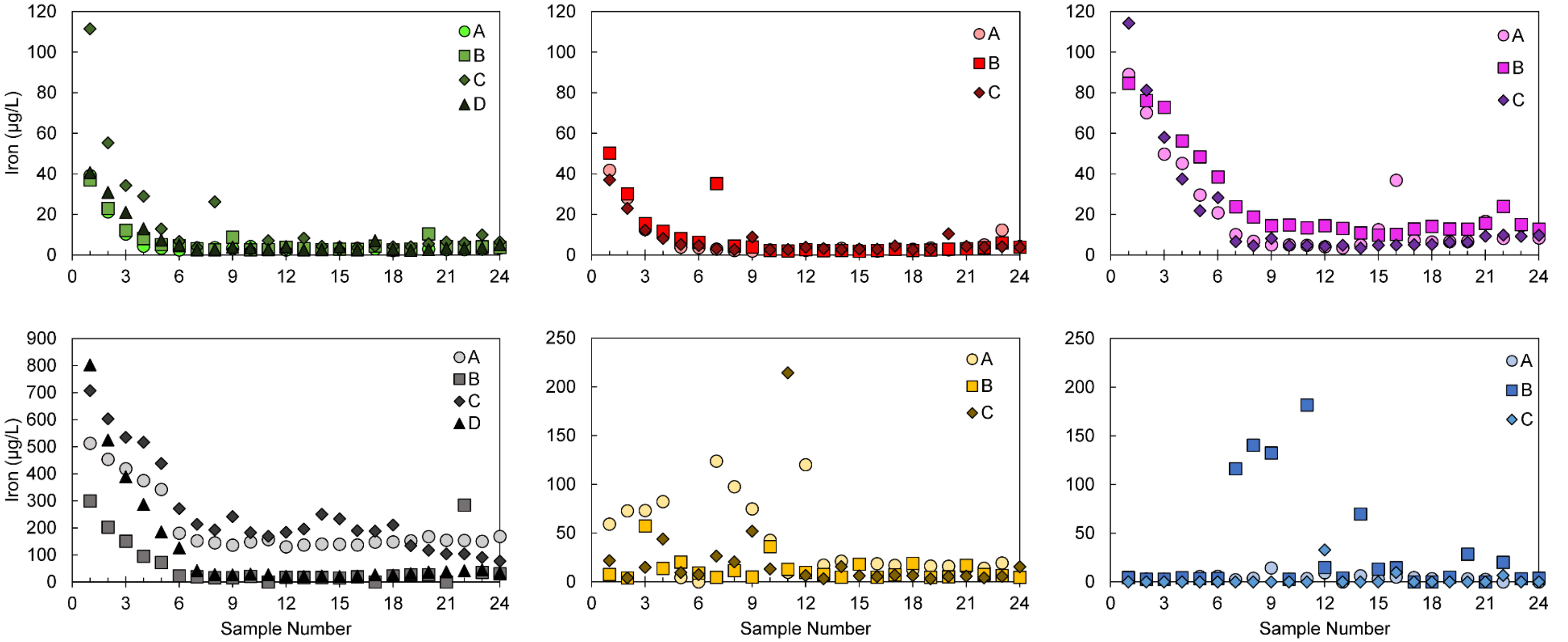

Figure A.9 Comparisons of dissolved iron (Fe) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The Pennsylvania water quality criteria for iron is 0.3 mg/L dissolved Fe and 1.5 mg/L total Fe.

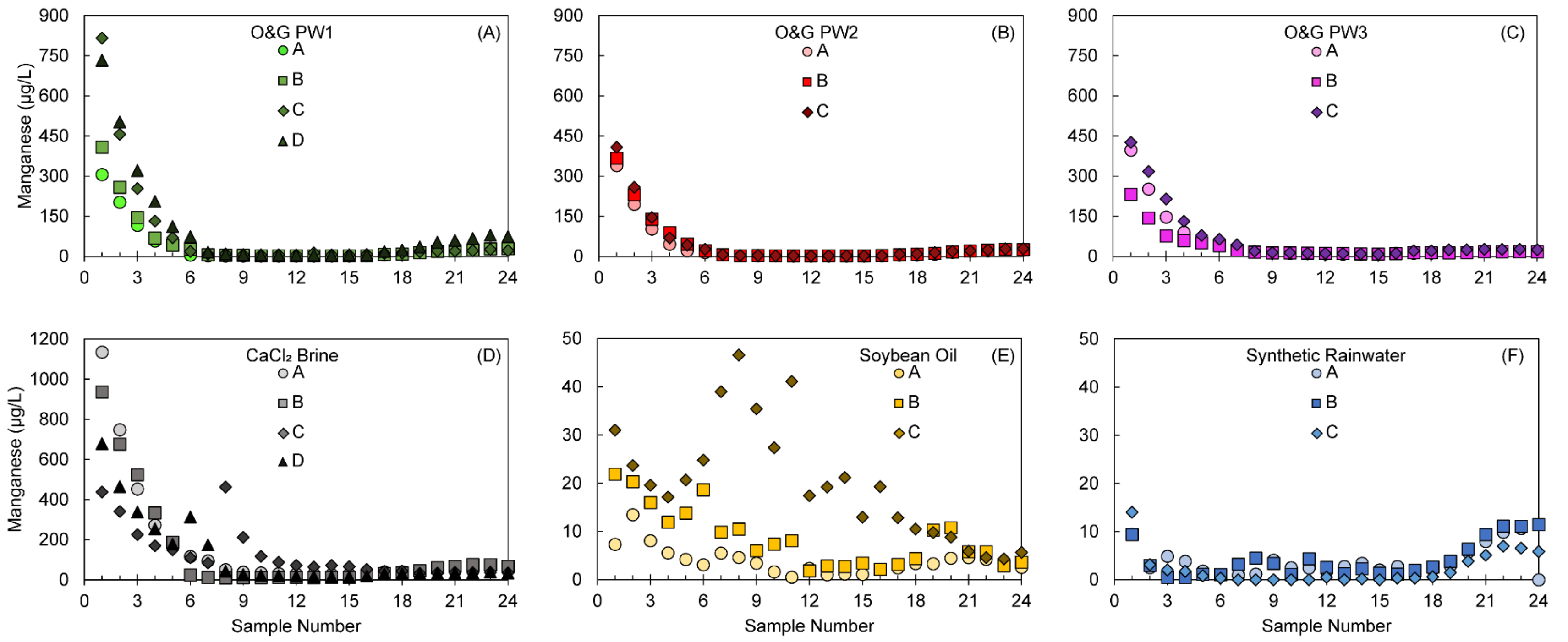

Figure A.10 Comparisons of dissolved manganese (Mn) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The EPA secondary drinking water standard for manganese is 0.05 mg/L total Mn and the Pennsylvania water quality criteria for manganese is proposed to be lowered to 0.3 mg/L total Mn.

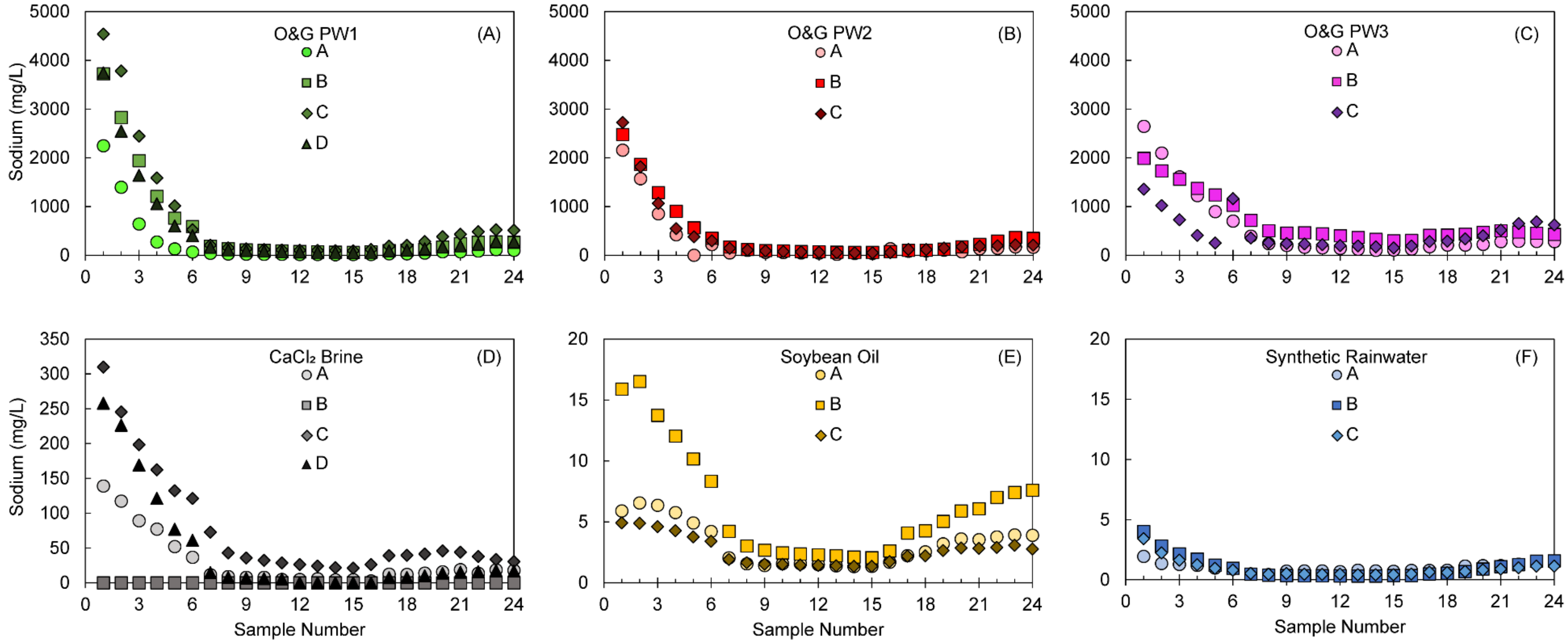

Figure A.11 Comparisons of dissolved sodium (Na) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. A Regulatory Threshold is 920 mg/L Na from USDA Irrigation Water Quality Guidelines.

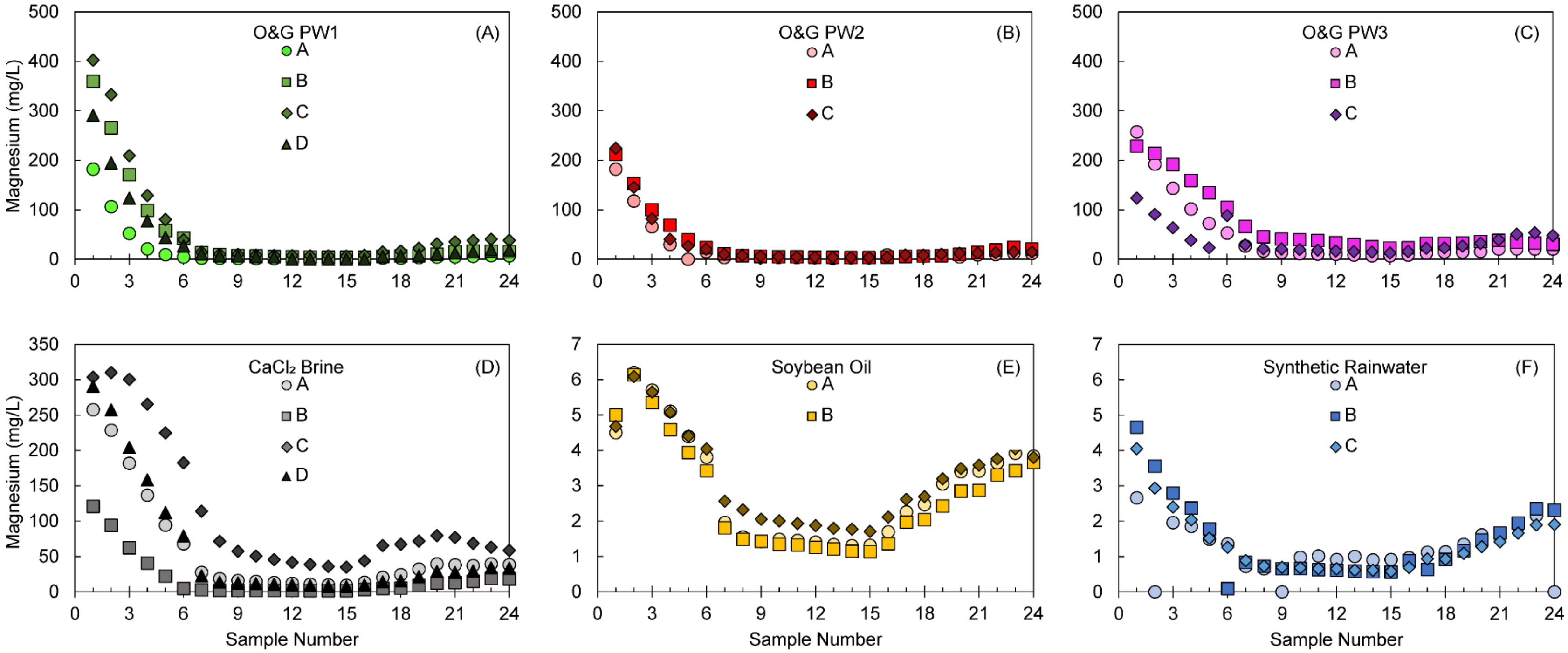

Figure A.12 Comparisons of dissolved magnesium (Mg) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. A Regulatory Threshold is 61 mg/L Mg from USDA Irrigation Water Quality Guidelines.

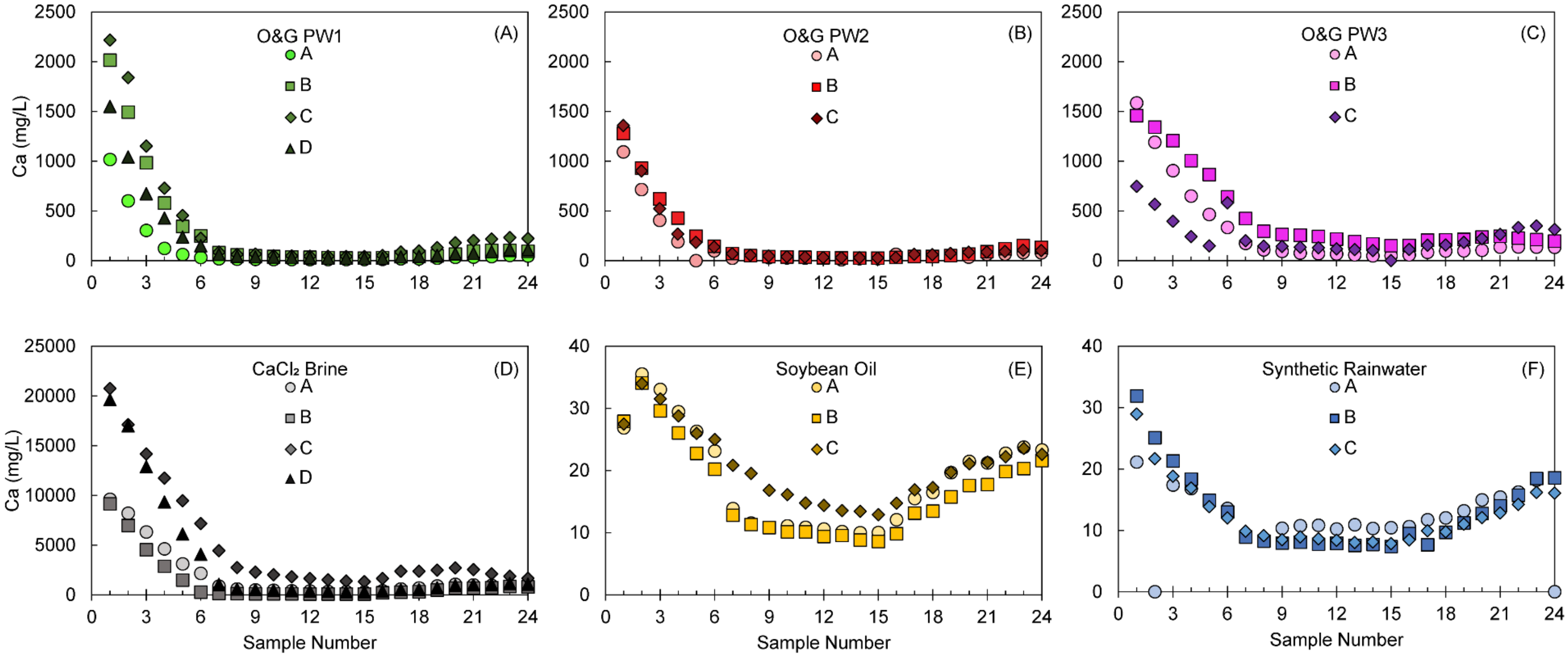

Figure A.13 Comparisons of dissolved calcium (Ca) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. A Regulatory Threshold is 401 mg/L Ca from USDA Irrigation Water Quality Guidelines.

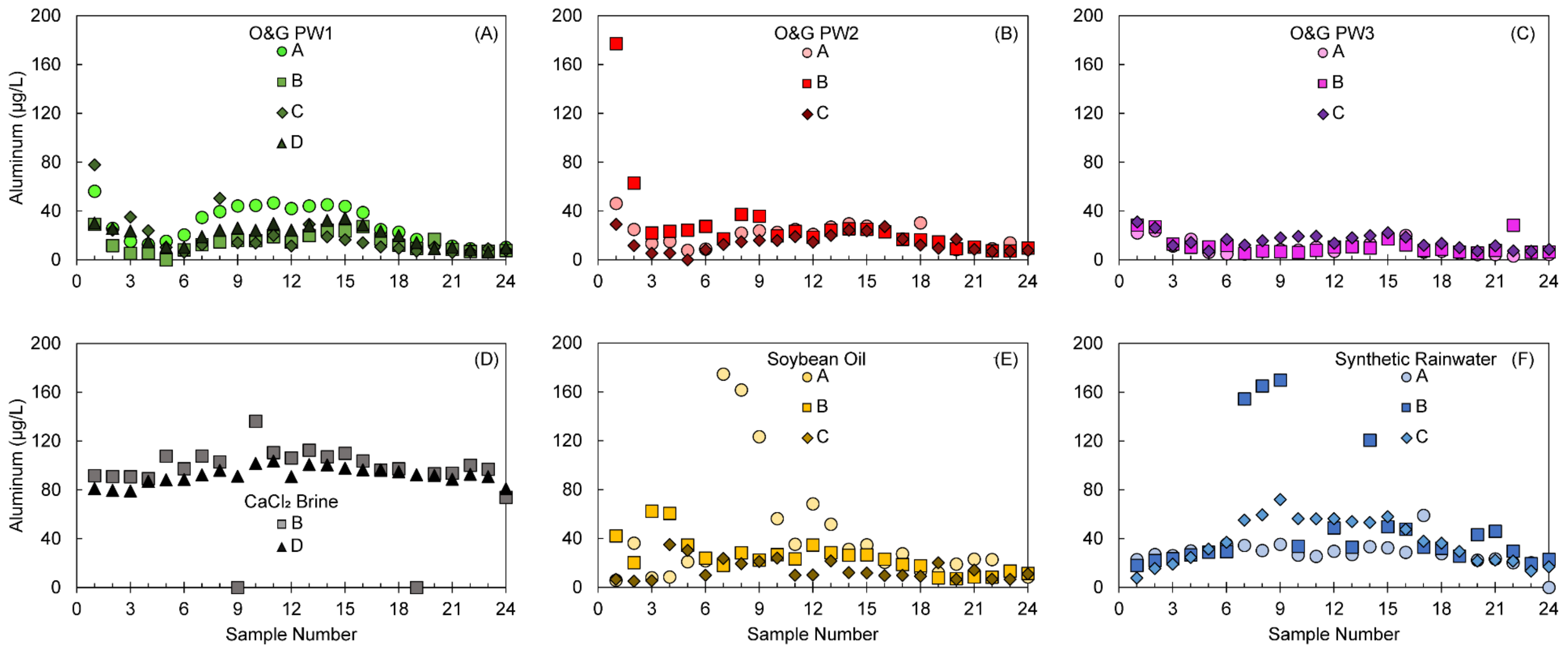

Figure A.14 Comparisons of dissolved aluminum (Al) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. The EPA secondary drinking water standard for aluminum ranges from 0.05 to 0.2 mg/L total Al.

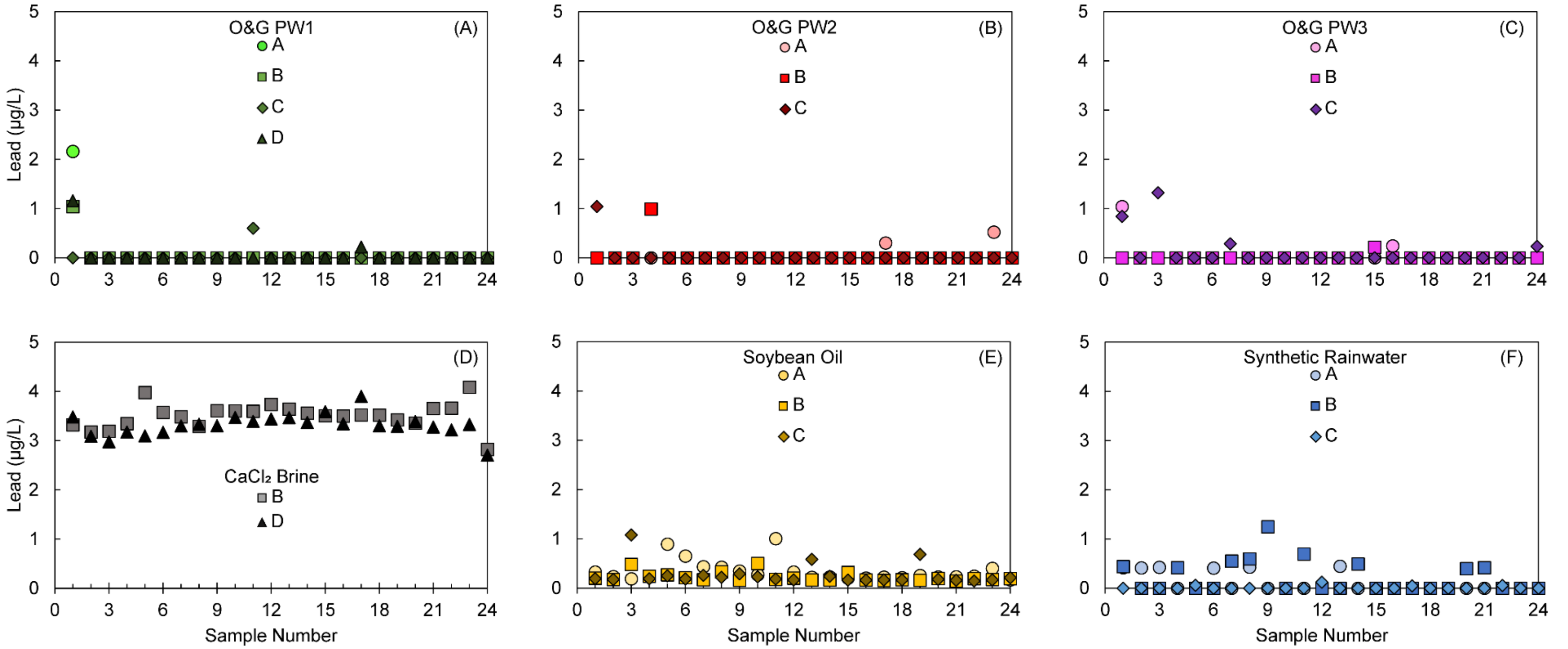

Figure A.15 Comparisons of dissolved lead (Pb) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. The EPA primary drinking water action level for lead is 0.015 mg/L total Pb (= 15 µg/L).

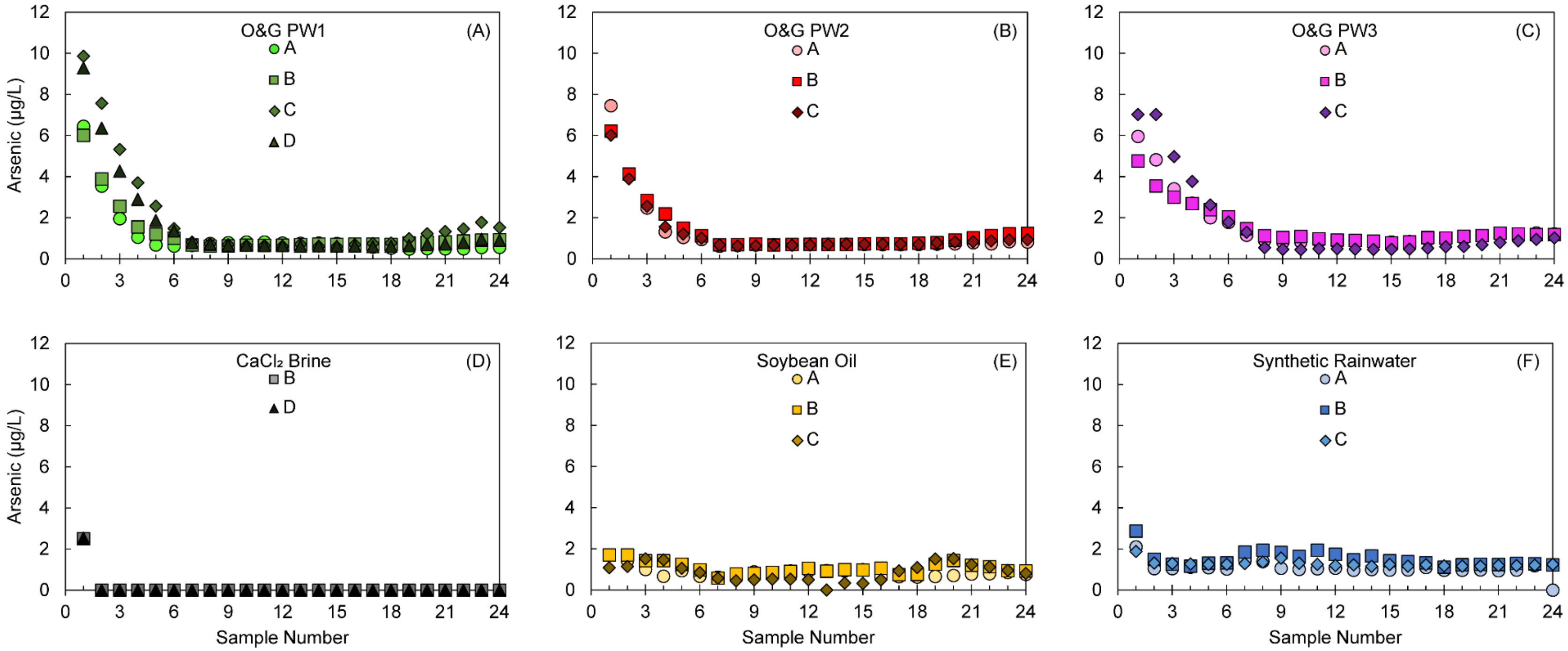

Figure A.16 Comparisons of dissolved arsenic (As) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. The EPA primary drinking water standard for arsenic is 0.01 mg/L total As (= 10 µg/L).

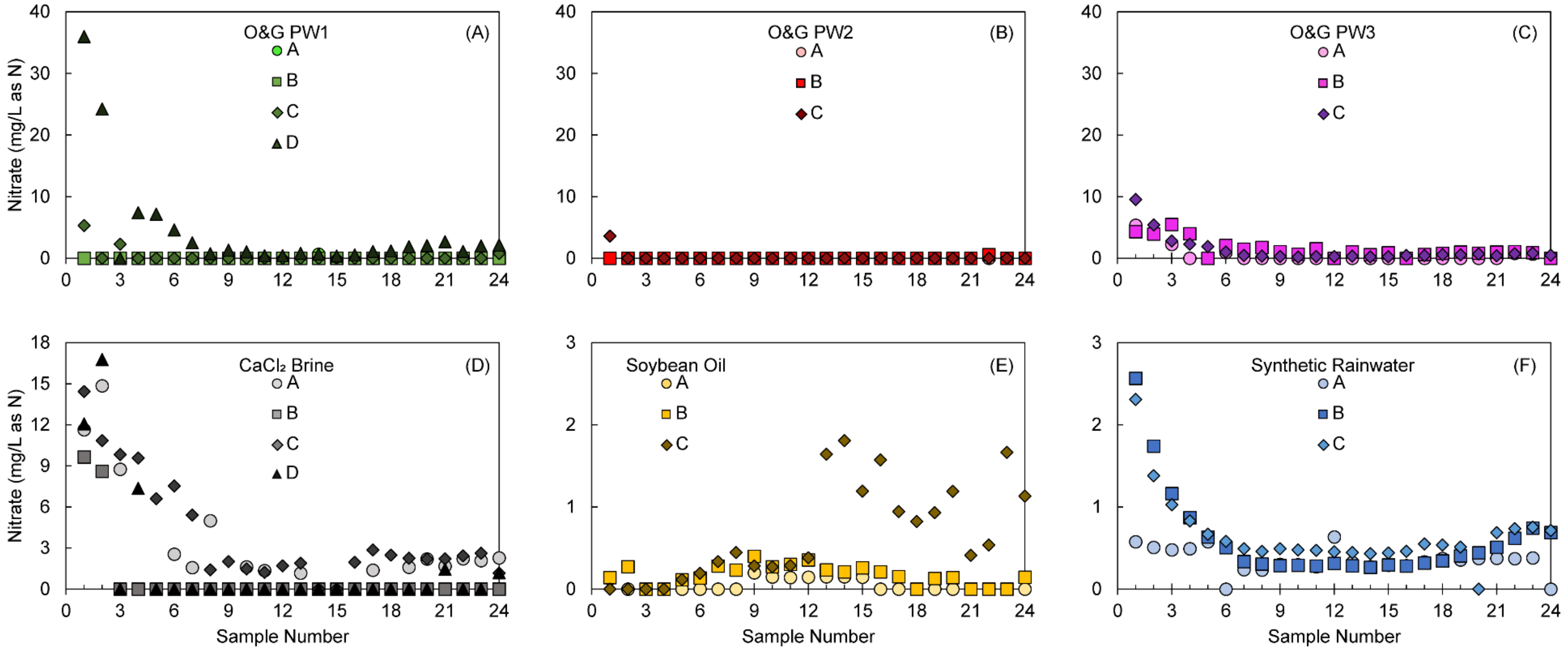

Figure A.17 Comparisons of dissolved nitrate (NO_3^-) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The EPA secondary drinking water standard for nitrate is 10 mg/L N.

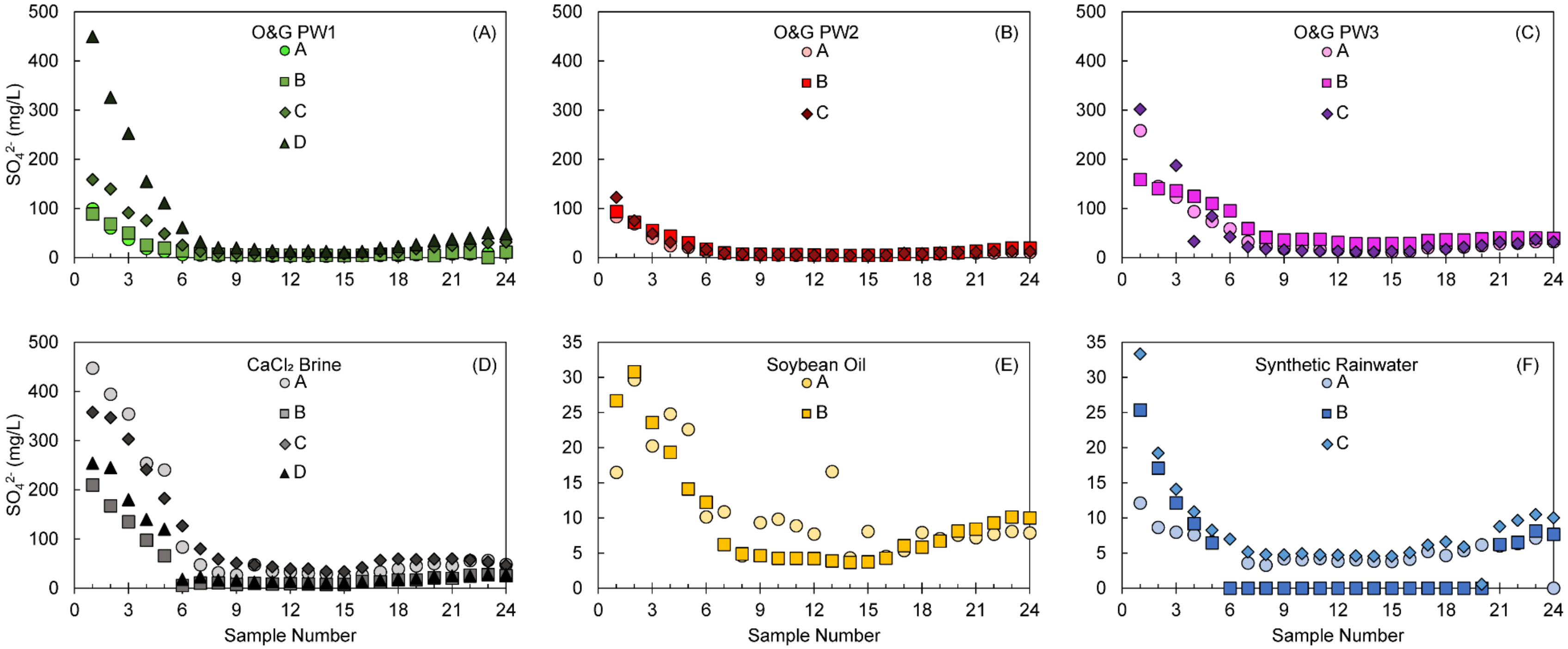

Figure A.18 Comparisons of dissolved sulfate (SO_4^{2-}) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The EPA secondary drinking water standard for sulfate is 250 mg/L SO_4.

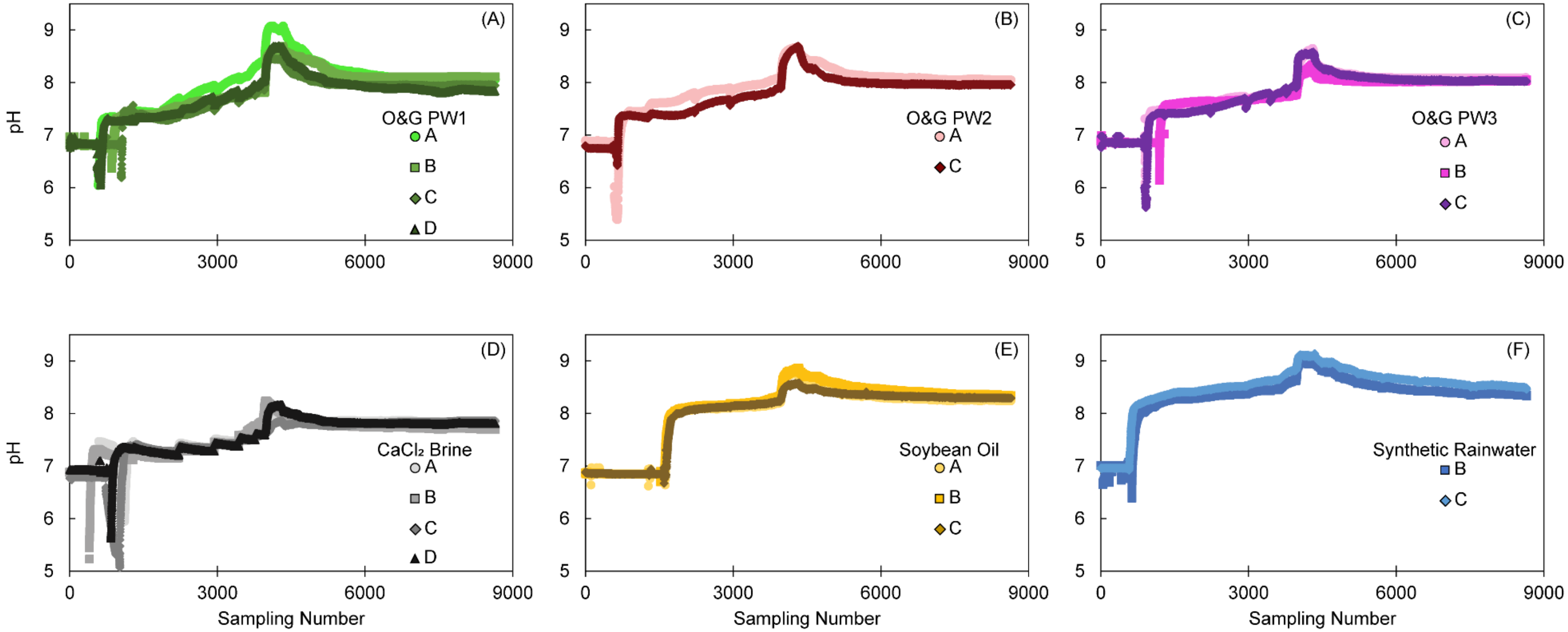

Figure A.19 Comparisons of pH measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected every 10-seconds of the 24-hour storm. A normal range for pH in surface waters is 6.5 to 8.5 and up to 9.5 in limestone systems. The EPA secondary drinking water standard for pH is 6.5 to 8.5.

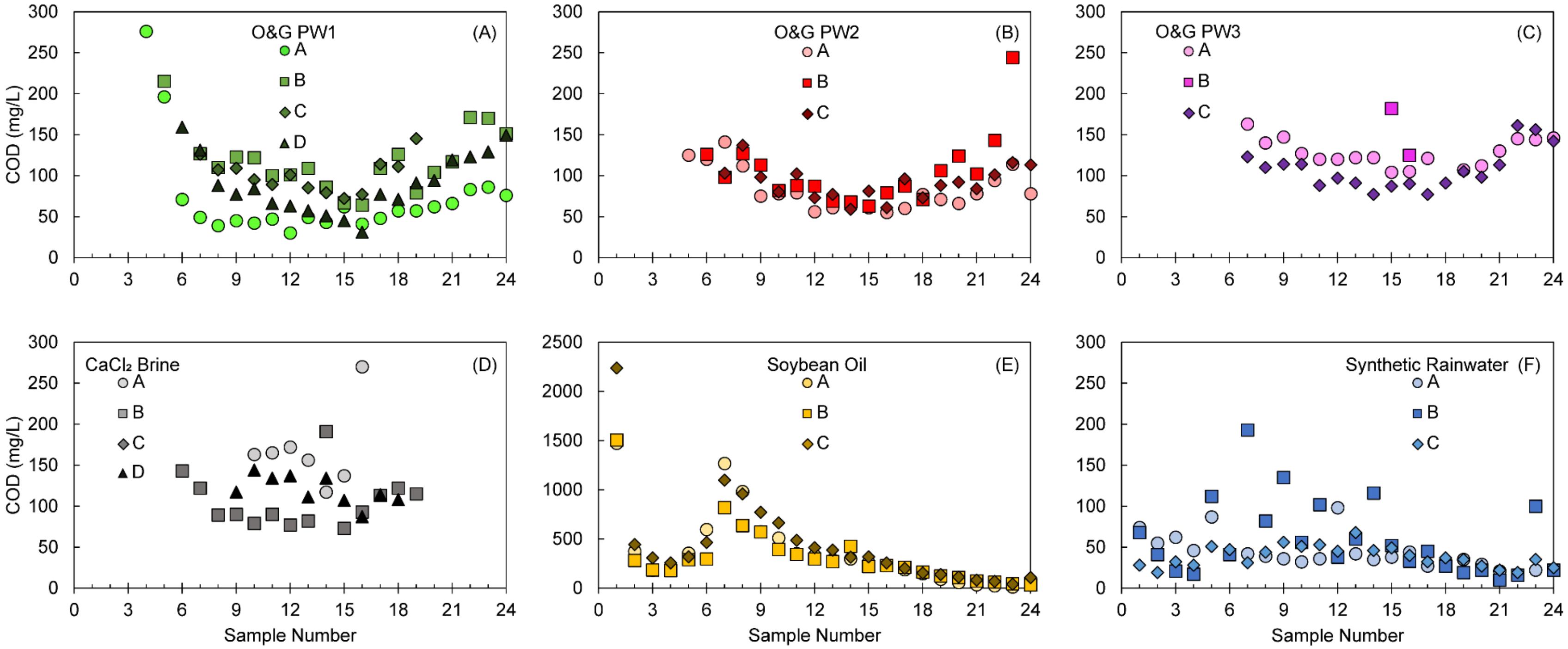

Figure A.20 Comparisons of chemical oxygen demand (COD) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. There are no EPA standards for COD.

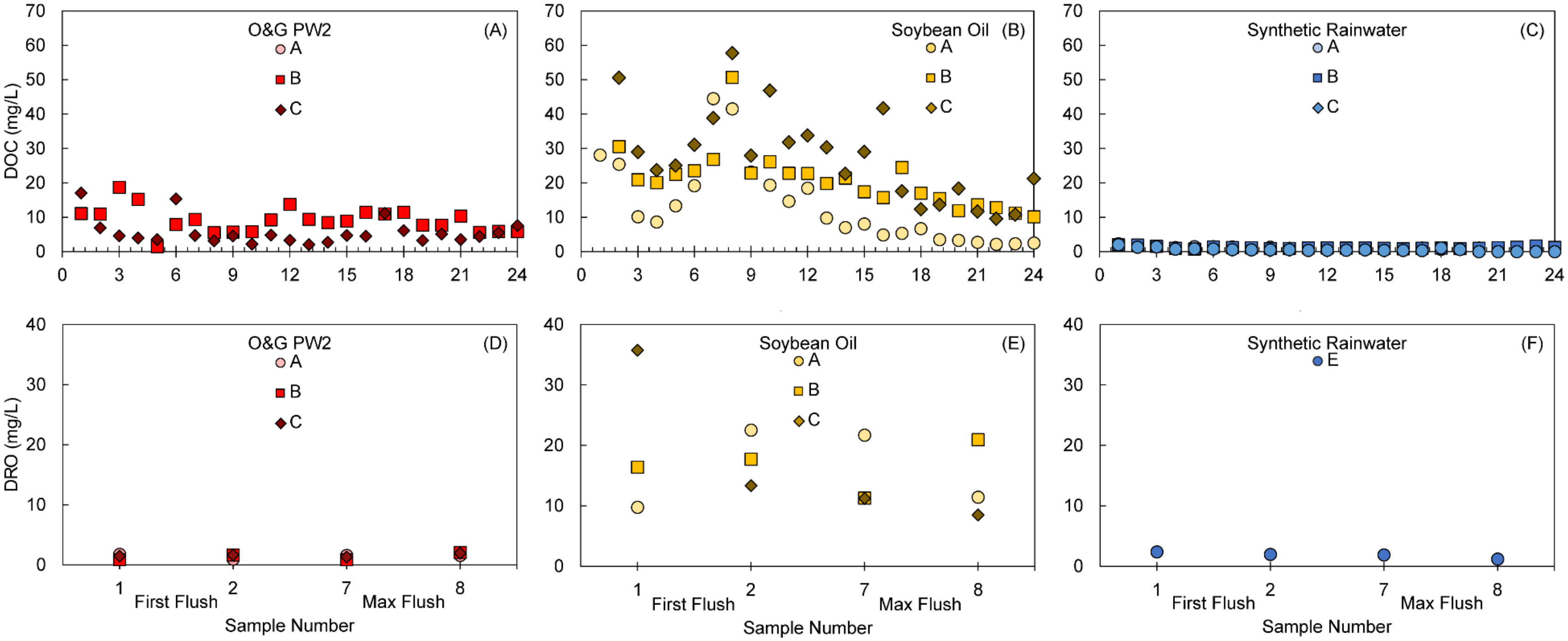

Figure A.21 Comparisons of concentrations of dissolved organic carbon (DOC – panels A – C) and diesel range organics (DRO – panels D – F) measured in runoff from gravel roadbeds treated with three of the dust suppressants used in this study – A) and D) Oil & Gas Produced Water 2; B) and E) Soybean Oil; and C) and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples for DOC measurements were analyzed for every 1/24th of the storm volume. Samples for DRO measurements were analyzed for the first flush samples (1,2) and maximum flush samples (7,8).

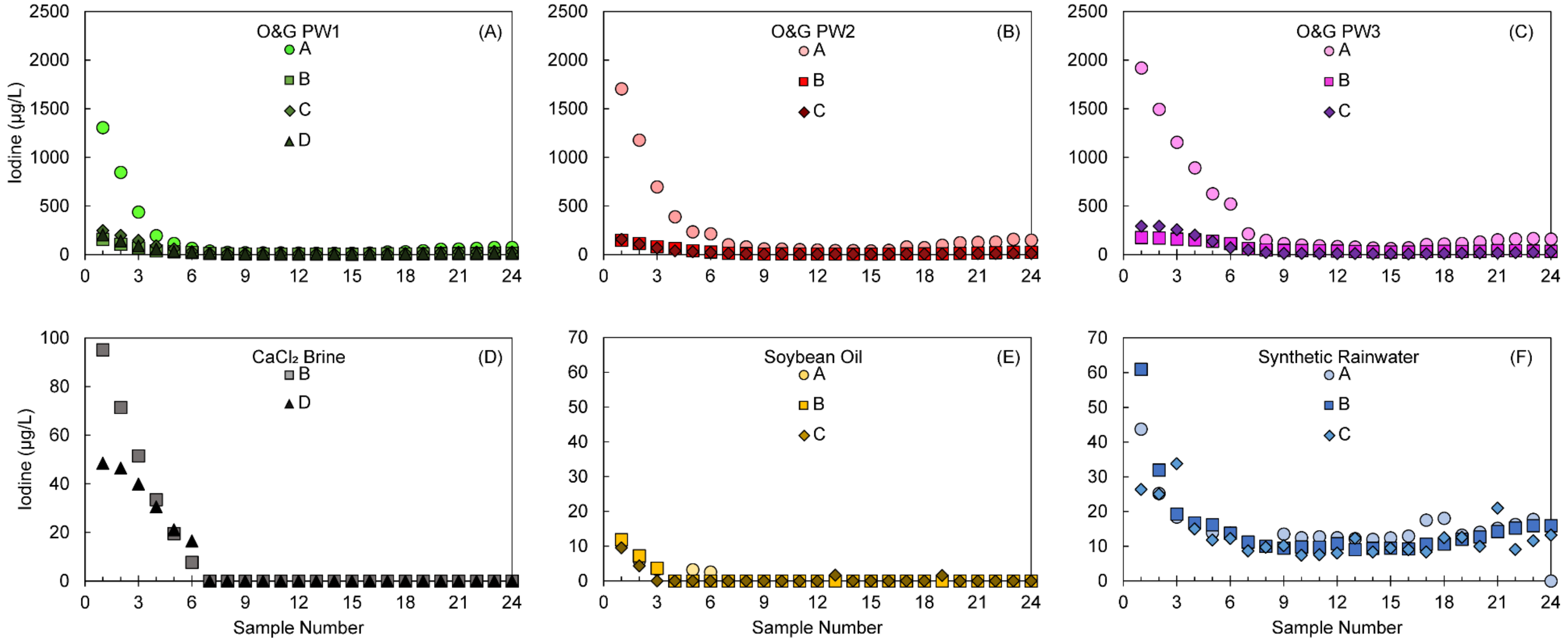

Figure A.22 Comparisons of dissolved iodine concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. There are no EPA standards for iodine.

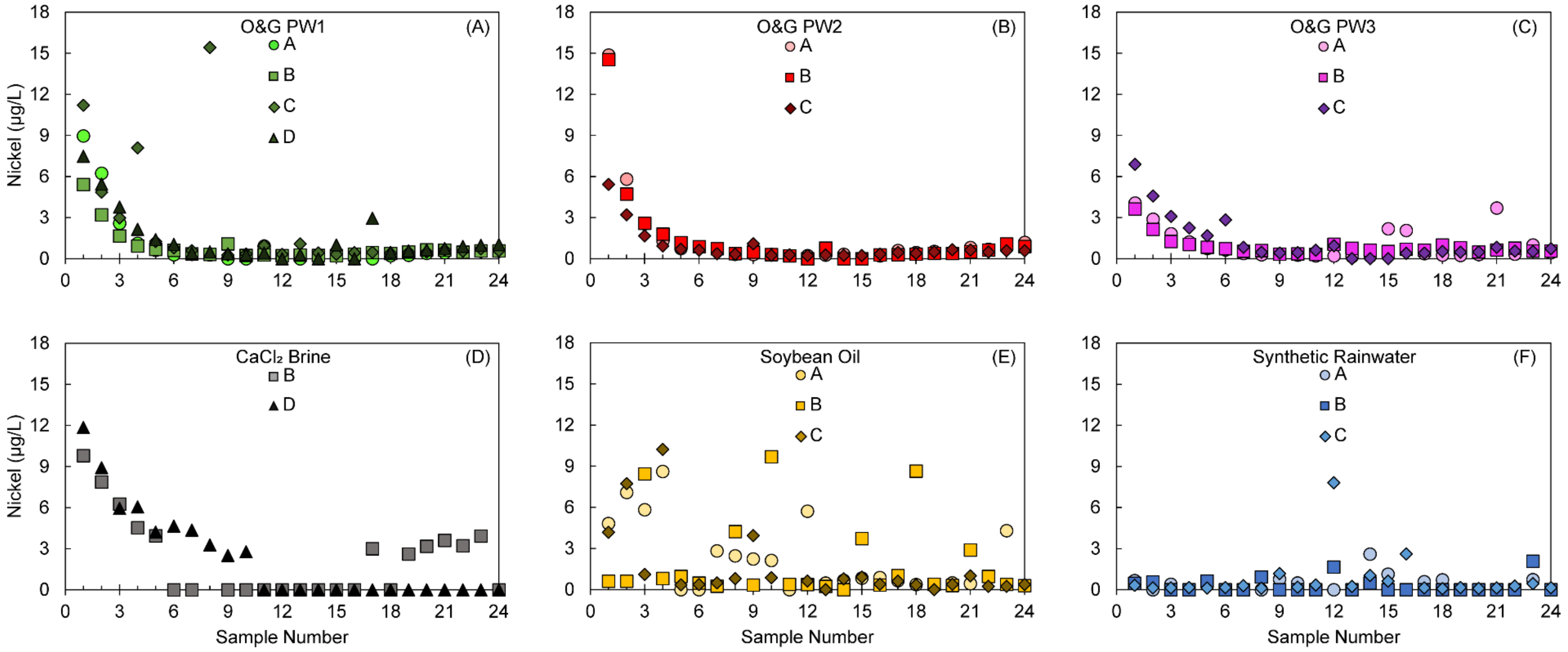

Figure A.23 Comparisons of dissolved nickel (Ni) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. The EPA aquatic life criteria for nickel is 0.052 mg/L total Ni (= 52 µg/L).

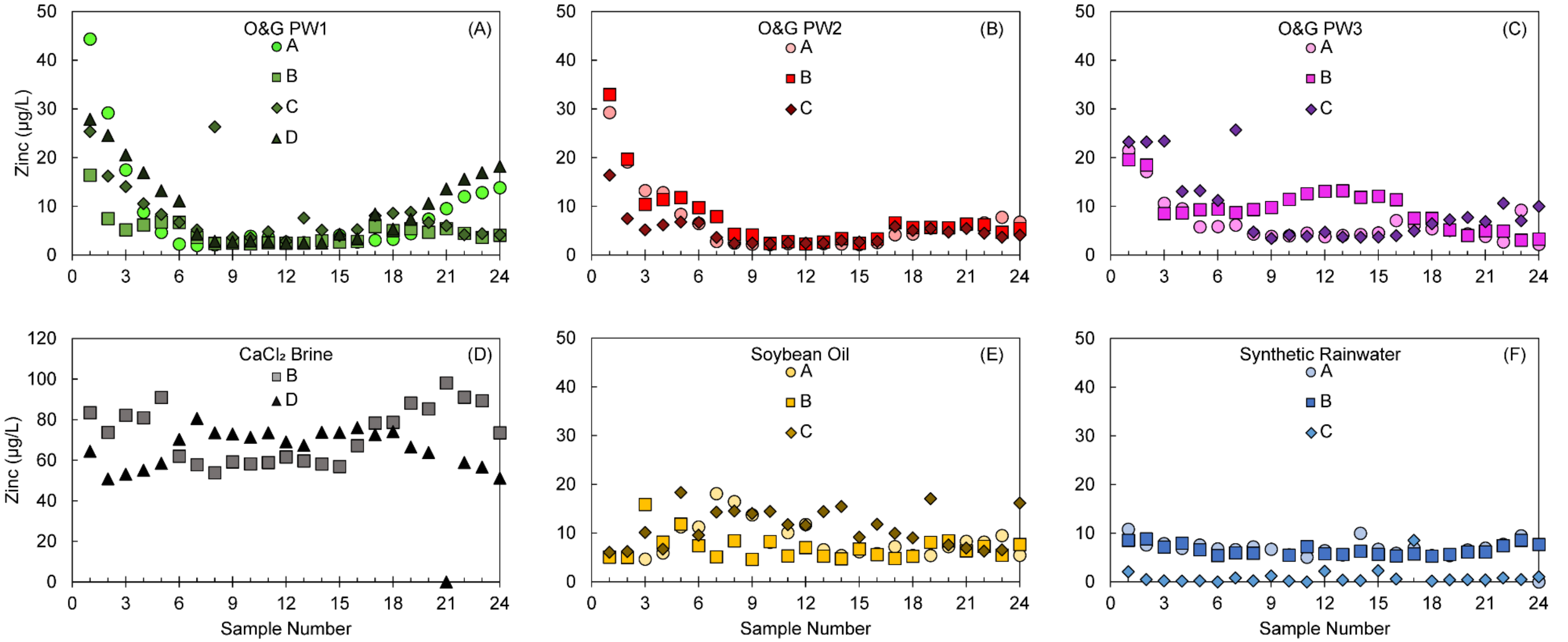

Figure A.24 Comparisons of dissolved zinc (Zn) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scale used panel D. The EPA secondary drinking water standard for zinc is 5.0 mg/L total Zn and the EPA aquatic life criteria for zinc is 0.12 mg/L total Zn (= 120 µg/L).

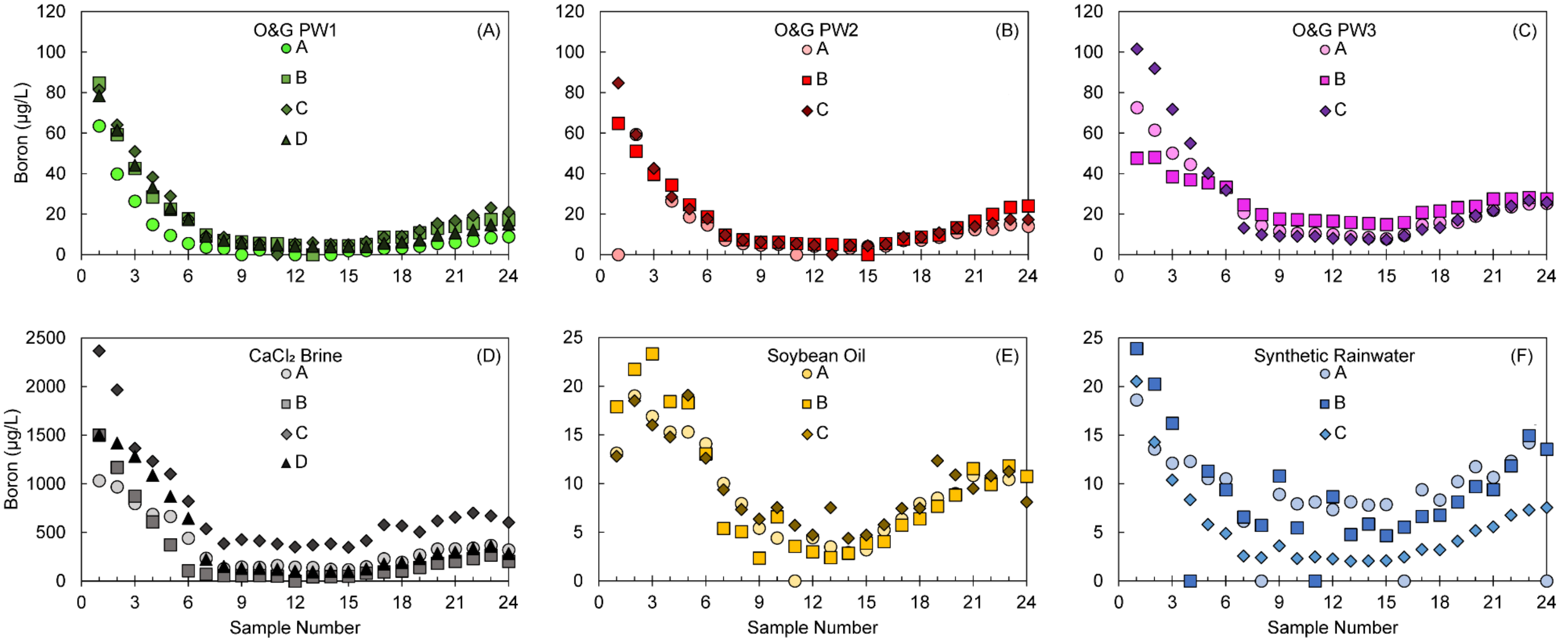

Figure A.25 Comparisons of dissolved boron (B) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scales used in each panel. The WHO drinking water quality guideline for boron is 2.4 mg/L total B.

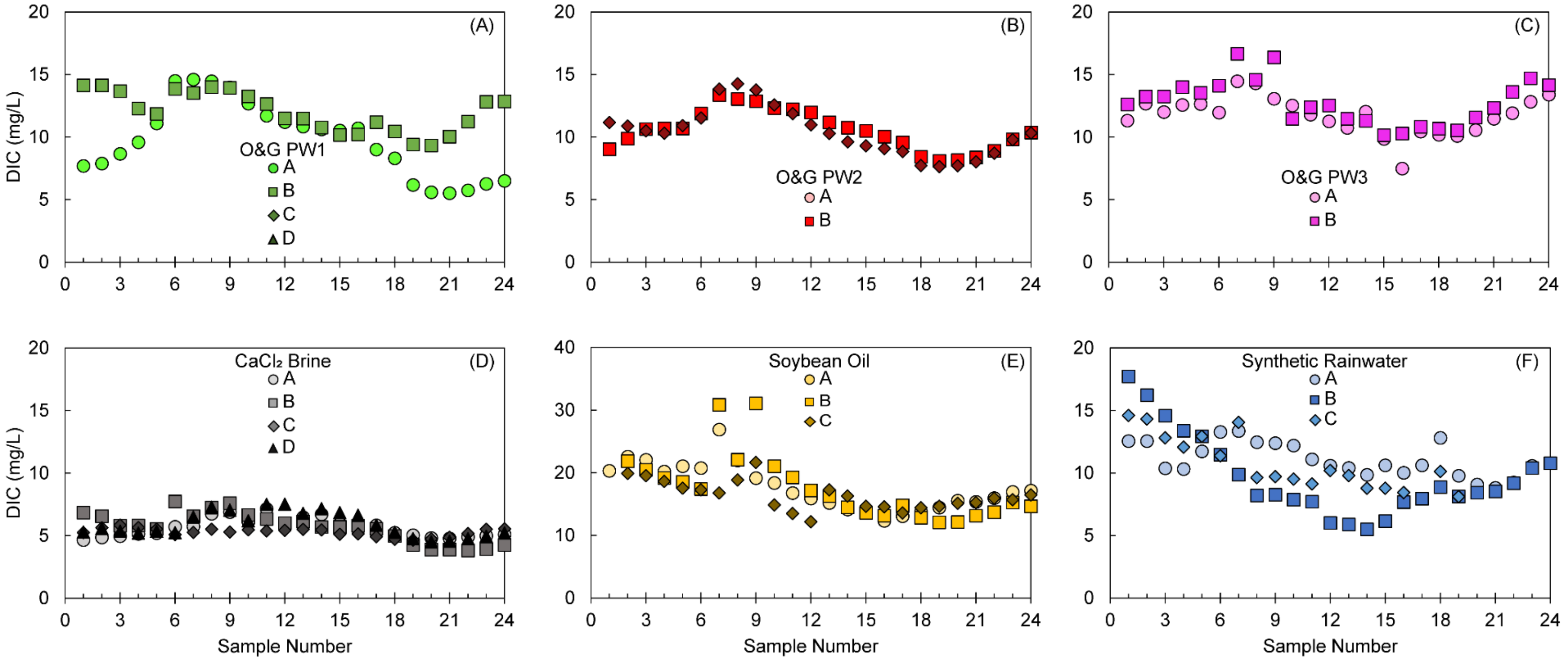

Figure A.26 Comparisons of dissolved inorganic carbon (DIC) concentrations measured in runoff from gravel roadbeds treated with the six dust suppressants used in this study. A) Oil & Gas Produced Water 1, B) Oil & Gas Produced Water 2, C) Oil & Gas Produced Water 3, D) Calcium Chloride Brine, E) Soybean Oil, and F) Synthetic Rainwater. Different letters refer to replicate tests. Samples collected after every 1/24th of the storm volume. Note different y-axis scale in panel E. There are no EPA standards for DIC.