

Introduction

I would like to thank members of the House Environmental Resources and Energy Committee for the invitation to present at the June 10, 2024, hearing on the spreading of brine from oil and gas (O&G) wells on roads in Pennsylvania. I would particularly like to thank the Chair of the committee, Representative Greg Vitali, Pennsylvania Senator Katie Muth and Pennsylvania Senator Carolyn Commita for asking me to participate in a previous hearing on April 17, 2024.

I am a Professor of Environmental Engineering at The Pennsylvania State University where I have worked since 1995. I earned a BS in Mechanical Engineering, a MS in Environmental Engineering, and a PhD in Environmental Engineering, all from Virginia Tech. I am a member of the Academy of Distinguished Alumni for the Charles E. Via, Jr. Department of Civil and Environmental Engineering at Virginia Tech. I am a member of the American Chemical Society, having served as the Geochemistry Division Chair, a member of the American Society of Civil Engineers, and a member of the Association of Environmental Engineering and Science Professors.

I have conducted research on the environmental impacts of disposal practices associated with oil and gas development in Pennsylvania since 2015. I have co-authored a dozen papers on various aspects of these practices in well-regarded peer-reviewed scientific journals. The most relevant papers will be referenced herein and have been included as appendices to this document.

I would like my testimony to be as understandable as possible to the public and try not to overwhelm people with scientific details. I grew up in Yardley, Pennsylvania in Bucks County. In talking with my friends from southeast Pennsylvania, I found that not everyone is aware of the amount of gravel roads in the State and not familiar with the amount of maintenance needed to keep gravel roads (and driveways) functional. Additionally, many Pennsylvania residents may be unaware that significant amounts of water are co-produced from oil and gas wells, and that this industrial wastewater, referred to as produced water (PW), has been allowed to be spread on our roads. Therefore, I chose to organize and present written testimony on the following topics:

1. Background on gravel road maintenance
2. Background on the US Environmental Protection Agency's and the Pennsylvania Department of Environmental Protection's criteria for the beneficial use of industrial waste
3. Background on oil and gas produced water
4. Summary of research that we have conducted at Penn State in this area

1. Background on gravel road maintenance

Chemical treatments are applied to roads during winter and summer maintenance operations to create a more stable driving surface and improve driver safety. Winter road maintenance typically uses rock salt (sodium chloride) for deicing and liquid brine solutions for anti-icing. In summer, unpaved dirt and gravel roads are commonly treated with chemical dust suppressants such as calcium chloride-based and magnesium chloride-based salts. Pennsylvania contains nearly 25,000 miles of gravel roads that equates to roughly 20% of the total road miles in the State. Gravel roads require maintenance in both warm and cold months. In warm weather, roads can dry out and cars traveling fast enough on dry roads can generate a lot of dust.

Sodium chloride (NaCl), calcium chloride (CaCl₂), and magnesium chloride (MgCl₂) are common brines used for road maintenance. Certain brines can help the roadbed retain moisture and physically stabilize the road aggregate, making it more difficult for vehicle traffic to entrain fine particles as dust. Calcium chloride and magnesium chloride work well as dust suppressants because they contain the divalent cations Ca²⁺ and Mg²⁺. Divalent cations help retain moisture and bridge clay particles together, physically stabilizing the roadbed. Clay particles are the finest materials in the roadbed and constitute most of the dust generated from vehicular traffic. Due to their ability to bridge clay particles, calcium chloride and magnesium chloride brines are sometimes marketed as both road stabilizers and dust suppressants.

Sodium chloride does not work as a dust suppressant because it contains the monovalent cation Na⁺. The sodium cation will disperse clay particles and destabilize the roadbed. Because of this, gravel roads treated with sodium chloride can produce more dust as compared to just wetting the road with rainwater.

Cold weather maintenance includes deicing and anti-icing. Deicing typically involves the application of rock salt (NaCl) to roads covered with snow or ice. Anti-icing typically involves the application of liquid NaCl to the road as a preventive measure before snow or ice has accumulated on the road. All brines will melt snow and ice because high salt concentrations lower the melting point of water.

Sodium chloride is not usually used for deicing a gravel road because it will disperse clay particles and destabilize the roadbed. Additionally, sodium chloride-treated gravel roads hold moisture during freeze thaw cycles and cause rutting, decreasing the performance of the road, and increasing maintenance requirements. Agencies that own a lot of gravel roads, such as the Pennsylvania State Forests or the US Forest Service, do not apply rock salt for winter maintenance. Cinders and sand or fine gravel are used to improve traction in the snow on gravel roads. Rock salt would not be recommended.

This background is presented to stress that all brines are not the same, and that brines with elevated sodium concentrations can harm gravel roads.

2. Background on the US Environmental Protection Agency's and the Pennsylvania Department of Environmental Protection's criteria for the beneficial use of industrial waste

An approach to a more sustainable means to manage industrial waste is to promote the 'beneficial use' of one industry's waste as a feedstock in another industry's production process. Guidance from the United States Environmental Protection Agency (US EPA) recommends that waste products proposed for beneficial use meet two criteria: 1) they perform as well as or better than the material being replaced, and 2) using the waste product does not increase the risk of harm to either the environment or human health.

Examples of industrial beneficial use include coal fly ash used as a replacement for portland cement in concrete, flue gas desulfurization gypsum as a substitute for mined gypsum in wallboard, and spent foundry sands used in soil-related applications, such as manufactured soil

and road subbase ([Frequent Questions About the Methodology for Evaluating the Beneficial Use of Industrial Non-Hazardous Secondary Materials and the Beneficial Use Compendium | US EPA](#)).

In Pennsylvania, it is unclear whether the use of oil and gas brine as a dust suppressant for gravel roads was ever evaluated with respect to these two criteria. Within the Pennsylvania Department of Environmental Protection (PADEP), it is unclear whether such an evaluation should be made by the Office of Oil and Gas Management or the Bureau of Waste Management. Currently, there is a moratorium on spreading brine from oil and gas wells on roads in Pennsylvania. However, the practice continues as some oil and gas operators claim an exemption because this practice represents the 'beneficial reuse' of industrial waste and/or their brine should be regarded as an acceptable industrial 'co-product' allowable for use as a road palliative.

To reduce the costs associated with dust suppression and winter road maintenance, certain states allow oil & gas produced water (O&G PW) to be spread on roads. O&G PW is often offered as a free alternative to commercial products and is typically hypersaline. Because of its high salinity, O&G PW retains moisture in the roadbed or lowers the freezing point of water in the same manner as commercial chloride products. However, O&G PW often has elevated concentrations of radioactivity, heavy metals, and organic compounds that pose additional risks to human and environmental health.

3. Background on oil and gas produced water

Oil & gas wells produce a significant amount of wastewater along with the recovered petroleum products. For example, in northwestern Pennsylvania the water-to-oil ratio is often around 8 barrels of water per one barrel of oil. This water has been referred to as oil & gas drilling waste, flowback water, produced water, oil & gas wastewater, brine, and other terms. It can be further classified as conventional O&G PW or unconventional O&G PW depending on the type of well it came from. Unconventional wells use directional drilling and hydraulic fracturing to release petroleum products from 'tight' formations (e.g., Marcellus Shale and Utica Shale formations). Conventional wells use vertical drilling to access petroleum products. Unconventional O&G PW is not allowed to be disposed of via road spreading in Pennsylvania. In 2018, a moratorium was issued by PADEP to halt road spreading of conventional O&G PW.

The chemical characteristics of conventional and unconventional O&G PWs from Pennsylvania overlap considerably with respect to major constituents (e.g., Na, Ca, Mg, Cl) and radium activity (Tasker et al., 2020, Geochemical and isotope analysis of produced water from the Utica/Point Pleasant Shale, Appalachian Basin, *Environmental Science: Processes & Impacts*, 2020, 22, 1224; included as Appendix 1). For example, the combined radium activity ($^{226}\text{Ra} + ^{228}\text{Ra}$) was 2,034 pCi/L (n=25) in conventional O&G PW, was 1,794 pCi/L (n=40) in unconventional Marcellus Shale O&G PW, and was 3,105 pCi/L (n=24) in unconventional Utica Shale O&G PW. Chloride concentrations in conventional, Marcellus Shale, and Utica Shale O&G PWs were 153,000 (n=1123), 102,000 (n=127), and 145,000 (n=24), respectively. Sodium concentrations in conventional, Marcellus Shale, and Utica Shale O&G PWs were 55,300 (n=1072), 39,500 (n=126), and 53,000 (n=24), respectively. Calcium concentrations in conventional, Marcellus Shale, and Utica Shale O&G PWs were 26,600 (n=1099), 14,700 (n=126), and 21,300 (n=24), respectively.

From a practical and statistical standpoint, it is challenging to chemically distinguish between conventional and unconventional O&G PW in Pennsylvania. These industrial wastewaters are quite similar. In fact, highly sophisticated isotope geochemistry analytical techniques are required to definitively distinguish between conventional and unconventional O&G PW (and even then, differences may not be statistically significant because of geologic/geographic variabilities and/or sample size).

4. Summary of research that we have conducted at Penn State in this area

I will present an abbreviated summary of our work to answer key questions about the risks associated with road spreading conventional O&G PW.

Q1 – What are the contaminants of concern in conventional oil & gas produced water spread on roads in Pennsylvania?

Our first study on the chemical composition of conventional O&G PWs spread on roads in Pennsylvania was published in 2018 (Tasker et al., 2018, Environmental and Human Health Impacts of Spreading Oil and Gas Wastewater on Roads, *Environmental Science & Technology*. 2018, 52, 7081–7091; included as Appendix 2). We contacted road masters in 14 townships in northwestern Pennsylvania who allowed us to collect samples from their brine tanks. These tanks were typically filled by local O&G operators and used to fill township tanker trucks that spread the fluid on local gravel roads. We measured concentrations of a range of chemical constituents and found that these fluids contained elevated concentrations of total dissolved solids (TDS), chloride, bromide, radium, barium, and in some cases, petroleum hydrocarbons, along with other contaminants of concern. The median TDS concentration of the 14 O&G PWs was 294,000 mg/L, as compared to typical seawater that has a TDS concentration of 35,000 mg/L. The median chloride concentration was 183,000 mg/L, as compared to the drinking water standard of 250 mg/L. The median radium activity was 1,230 pCi/L, as compared to the drinking water standard of 5 pCi/L. We also tested the toxicity of these fluids to *Daphnia magna* (common aquatic indicator organism) and human reporter-gene-based assays. The high salinity of these fluids was toxic to *Daphnia magna* while petroleum hydrocarbons in these fluids could promote cancer in humans.

The release of radium, a known human carcinogen, via road spreading O&G PWs is another concern. For example, in Pennsylvania from 2008 to 2014, spreading O&G PW on roads released over 4 times more radium to the environment than O&G wastewater treatment facilities, and 200 times more radium than spill events. In 2016, we found that 11 million gallons of O&G PW were reported to be spread on roads in Pennsylvania. This amount represented approximately 6% of the total wastewater volume reported from conventional O&G wells in Pennsylvania that year.

Q2 – What are the contaminants of concern in other products spread on roads in Pennsylvania?

A more recent study completed similar measurements on commercially available products used for dust suppression or deicing and on other O&G PWs that might be considered for dust suppression (Farnan et al., 2023, Toxicity and chemical composition of commercial road palliatives versus oil and gas produced waters, *Environmental Pollution*. 2023, 334, 122184; included as

Appendix 3). A total of 17 road palliatives were studied that represented the major product categories used in the US, including calcium chloride brines, magnesium chloride brines, sodium chloride brines, petroleum extracts, soybean oil, and O&G PWs from Pennsylvania. We found that O&G PWs contained chloride from 47,900 to 182,000 mg/L, and radium from 84 to 2,500 pCi/L. We found that calcium chloride brines contained up to 702 pCi/L, magnesium chloride brines contained up to 66 pCi/L, and sodium chloride brines contained up to 69 pCi/L. We found that organic compounds in the petroleum extract UltraBond were toxic based on human reporter gene-based assays, raising concerns with this product.

Elevated contaminant concentrations in road palliatives pose risks to road maintenance workers and residents who live on roads that are frequently treated with these products. While it was known that radium is elevated in O&G PWs, finding elevated radium in calcium chloride-based road products was a bit surprising. Therefore, the PADEP or PennDOT may want to request radium measurements for currently approved calcium chloride-based products, and prior to approving new calcium chloride-based products. Requesting additional chemical characterizations of magnesium chloride-based products may not be warranted.

Q3 – Can we predict if a conventional oil & gas produced water or brine will be an effective dust suppressant?

While O&G PWs and some commercially available products contain contaminants of concern, we also wanted to confirm that these products work as intended. Therefore, we designed a bench-scale method to measure the amount of dust generated from road aggregate discs that were treated with various dust suppressants and then subject to mechanical abrasion (Stallworth et al., 2018, Laboratory Method to Assess Efficacy of Dust Suppressants for Dirt and Gravel Roads, *Transportation Research Record*. 2020, 267, 188-199; included as Appendix 4). This bench-scale method was field-validated using the same dust measurement equipment mounted behind a car driven on gravel roads that had different roadbed moisture contents.

Before discussing these results, I would like to describe how we can suppress dust on dirt and gravel roads. First, increasing the moisture content of the roadbed by spreading water (or by rainfall) will keep fine particles from getting mobilized by vehicular traffic. As the roadbed moisture content decreases, dust generation increases (however, roadbeds can be deformed by traffic if the moisture content is too high). Brines with high TDS can increase the roadbed's ability to retain moisture from the air because the applied salts increase the hygroscopicity of the roadbed.

The chemical composition of the brine, however, impacts the physical stability of the roadbed. Because of their small size, clay minerals comprise a substantial fraction of dust mobilized from gravel roads. Because of surface charge characteristics, clay minerals are stabilized by divalent cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) and better retained in the roadbed. In contrast, clay minerals are destabilized by monovalent cations such as sodium (Na^+) and more readily released from the roadbed as dust or eroded from the roadbed with runoff. The sodium adsorption ratio (SAR – the relative ratio of sodium to calcium and magnesium concentrations) of a brine can be calculated based on measured concentrations of calcium, magnesium, and sodium,

and used to predict the efficacy of that brine's ability to function as a dust suppressant. In general, brines with a high TDS and a low SAR are highly effective dust suppressants.

While conventional O&G PWs from Pennsylvania are high-TDS brines, they also contain high concentrations of sodium that yield high SAR values. High concentrations of sodium substantially decrease dust suppression efficacy of the brine and decrease the stability of the roadbed. Sodium chloride is also less hygroscopic than calcium chloride or magnesium chloride, so it is worse at scavenging ambient moisture.

Q4 – Do conventional oil & gas produced waters from Pennsylvania meet the US EPA guidelines for beneficial use of industrial waste?

Our most recent study directly addressed this question (Farnan et al., 2024, Oil and gas produced waters fail to meet beneficial use recommendations for use as dust suppressants, *Science of the Total Environment*. 2024, 919, 170807; included as Appendix 5). Guidance from the United States Environmental Protection Agency recommends that waste products proposed for beneficial use meet two criteria: 1) they perform as well as or better than the material being replaced, and 2) using the waste product does not increase the risk of harm to either the environment or human health.

To address criteria 1, we compared dust generation from road aggregate discs individually treated with five calcium chloride-based brines, five organic-based products, and ten O&G PWs from Pennsylvania. We found that commercial brines and most commercial organic products consistently outperformed O&G PWs as dust suppressants. Under low humidity test conditions, O&G PWs did not significantly reduce dust compared to rainwater controls, and in some cases, increased dust generation. Based on dust generation, O&G PW did not perform as well as the CaCl₂ brine it is intended to replace.

To address criteria 2, we conducted large-scale laboratory rainfall-runoff experiments using model roadbeds treated with various dust suppressants then subjected the roadbed to a simulated storm event. We compared roads treated with a calcium chloride brine, soybean oil, three O&G PWs from Pennsylvania, and a rainwater control. Runoff from the roadbeds was collected over the course of the storm and analyzed for contaminants of concern. We found that measured contaminant concentrations in the runoff generally reflected the concentrations in the dust suppressant originally applied to the road (i.e., most constituents were washed off the road). All radium added to the roadbed during O&G PW application was mobilized during the storm event. This release of radium would increase the risk of harm to the environment and human health.

Spreading O&G PW on roads can decrease roadbed stability because the high sodium concentrations present in O&G PW cause clay dispersion (also observed in dust generation experiments). Roadbeds treated with O&G PW did not reduce total solids lost from the roadbed compared to roadbeds treated with rainwater. In contrast, CaCl₂ brine significantly reduced solids lost during the storm event compared to the rainwater controls. Based on this second performance metric, O&G PW did not perform as well as the CaCl₂ brine it is intended to replace.

O&G PWs from Pennsylvania do not perform as well as commercial products and pose unique risks to environmental health. Thus, O&G PWs do not meet either of the two recommended criteria for

beneficial use as a dust suppressant. Spreading O&G PW on roads can harm aquatic life and pose health risks to humans, while not effectively suppressing road dust.

To summarize our findings:

- 1) Conventional O&G PWs from Pennsylvania contain contaminants of concern such as radium that are toxic to aquatic organisms and human health (Tasker et al., 2018; Farnan et al., 2023).
- 2) In Pennsylvania, the chemical characteristics of conventional and unconventional O&G PWs are quite similar and analytically challenging to differentiate (Tasker et al., 2020).
- 3) Most contaminants of concern, including radium, are flushed from the roadbed during a heavy storm (Farnan et al., 2024) and pose risks to adjacent surface water and ground water resources.
- 4) Conventional O&G PWs from Pennsylvania are less effective at dust suppression than the commercial products they are intended to replace and often no better than rainwater (Stallworth et al., 2020; Farnan et al., 2024).
- 5) Some calcium chloride-based dust suppressants contain contaminants of concern such as radium (Farnan et al., 2023).

Q5 – What might this all mean for the environmental and transportation agencies in Pennsylvania?

Road palliatives are required for safety and maintenance purposes. The potential harm to environmental and human health caused by any road product is hopefully offset by improved safety and/or operational performance. For example, the use of sodium chloride to control snow and ice on roads can lead to the salinization of freshwater streams. Yet salting roads in the winter is estimated to have reduced wintertime car crashes up to 87%.

Road dust poses similar traffic safety concerns (e.g., when too dusty to see the road ahead). Road dust also poses environmental and human health concerns (e.g., coating roadside vegetation and respiratory problems from dust inhalation). Dust suppressants, like de-icing and anti-icing products, are needed to improve safety and reduce maintenance costs (e.g., dust blowing off the road and solids being washed off by stormwater amount to loss of road aggregate). However, O&G PWs are generally ineffective dust suppressants. There is no public benefit to road spreading O&G PWs. Therefore, there is nothing to offset the known environmental impacts of this practice. It is all risk, no reward. The only beneficiaries are the O&G operators who choose this disposal option.

A complete ban on road spreading of O&G PW in Pennsylvania will affect only a small portion of the conventional O&G industry. As noted above (Tasker et al., 2018), before the 2016 moratorium, the fraction of O&G wastewater reported to be disposed of via road spreading rarely exceeded 5% of the total wastewater volume. Pennsylvania should ban road spreading of O&G PW.

With respect to calcium chloride-based dust suppressants, PADEP or PennDOT should request that manufacturers provide radium measurements for their products.

Appendix 1 - Tasker et al., 2020

key finding: Produced water from conventional and unconventional oil & gas formations in Pennsylvania generate produced waters have very similar compositions.



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Geochemical and isotope analysis of produced water from the Utica/Point Pleasant Shale, Appalachian Basin†

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While development of the Utica/Point Pleasant Shale (UPP) is extensive in Ohio (U.S.) and increasing in Pennsylvania and West Virginia, few studies report the chemistry of produced waters from UPP wells. These data have important implications for developing best management practices for handling and waste disposal, or identifying the fluid in the event of accidental spill events. Here, we evaluated the elemental and isotope chemistry of UPP produced waters from 26 wells throughout Ohio, Pennsylvania, and West Virginia to determine any unique fluid chemistries that could be used for forensic studies. Compared to the Marcellus, UPP produced waters contain higher activities of total radium ($^{226}\text{Ra} + ^{228}\text{Ra}$) and higher $^{228}\text{Ra}/^{226}\text{Ra}$ ratios. As with the Marcellus Shale, elemental ratios (Sr/Ca) and isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) can distinguish UPP produced waters from many conventional oil and gas formations. Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can fingerprint small fractions ($\sim 0.1\%$) of UPP produced water in freshwater. However, because Marcellus and UPP produced waters display similar major elemental chemistry (*i.e.*, Na, Ca, and Cl) and overlapping ratios of Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$, $^{228}\text{Ra}/^{226}\text{Ra}$ ratios may be the best tracer to distinguish these waters.

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Environmental significance

It is important to understand the chemistry of Oil and Gas produced water to help (1) identify spatial variability in formation waters, (2) evaluate treatment strategies, and (3) identify accidental releases and track contamination through the environment. Multiple studies have discussed geochemical signatures of unconventional oil and gas wastewater, but many focused solely on water from the Marcellus Formation. Now, with the production of hydrocarbons from the Utica/Point Pleasant Formations (UPP) rapidly increasing along with the volume of produced water, it is vital to evaluate the chemistry of water produced from these formations. In this study, the chemistry of produced water from the UPP is documented along with elemental and isotopic tracers that could be used to identify freshwaters contaminated by UPP wastewaters.

Introduction

Oil and gas (O&G) production from low-permeability, unconventional shale formations continues to rise in the Appalachian Basin, U.S., generating over 45% of the domestic natural gas in 2018.¹ From 2007 to 2018 annual U.S. natural gas production from shale plays rose from 36 billion cubic meters (bcm) [1293 billion cubic feet (bcf)] to 617 bcm [22 054 (bcf)]. During that same timeframe the percentage produced from the Appalachian Basin in the states of West Virginia, Ohio, and Pennsylvania rose from less than 1% to over 45%, largely due to the continued development of two unconventional shale formations, the Marcellus and Utica/Point Pleasant (UPP).¹ O&G development

was historically limited to permeable reservoirs known as conventional formations but has expanded into low permeability unconventional O&G formations over the last 20 years because of technical improvements in horizontal drilling and hydraulic fracturing. During hydraulic fracturing, large volumes of water (30 million liters per well for Marcellus and 38 million liters per well for UPP) mixed with other additives are pumped into the formation at high pressure causing the rock to fracture and stimulate hydrocarbon release.² After this process, millions of liters of a salty and radium-bearing fluid (*i.e.*, flow back and produced waters) returns to the surface where it is typically disposed in underground injection control (UIC) wells, reused to stimulate other wells, or treated for reuse at wastewater treatment plants.³ Flowback waters are generally defined as fluids comprising mixtures of *in situ* formation waters and hydraulic fracturing fluids that flow from a well shortly after the stimulation pressure is released. Produced waters often refer to waters that return after the wells have been in production for some time and are thought to better represent the *in situ*

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formation waters or salts from the formation that could have been mobilized by hydraulic fracturing fluids rather than the chemistry of the hydraulic fracturing fluids that were injected.

The two largest unconventional shale reservoirs in the Appalachian Basin are the Marcellus and UPP Formations, which are estimated to contain over 2.4 trillion cubic meters (*i.e.*, 84.8 trillion cubic feet) and 1.1 trillion cubic meters (*i.e.*, 38.8 trillion cubic feet) of recoverable natural gas, respectively.^{4,5} The Marcellus is the oldest organic rich shale in the Middle Devonian sequence and overlies the Onondoga Limestone. Currently, there are over 10 000 active Marcellus wells in Pennsylvania.⁶ The UPP Shale is several hundred meters below the Marcellus Shale and has been called the “natural gas giant below the Marcellus”.^{7,8} The UPP Formation is present throughout Ohio, Pennsylvania, West Virginia, New York, Ontario, and Quebec ranging in depth from 2300 meters in northwest Pennsylvania to 4000 meters in West Virginia and southern Pennsylvania.⁷ Throughout the Appalachian Basin, the Utica Shale directly overlies the Point Pleasant Shale with both formations having variable concentrations of carbonate (20–60%), clay (30–60%), and total organic content (~1–5%) that is likely related to their geographic location and varying depositional environments.⁷ Collectively, the UPP is thickest (120 to 150 m) throughout southwest and northeast Pennsylvania and gets thinner in eastern Ohio (60–90 m).⁷ Unconventional O&G development in the Appalachian Basin began in the Marcellus around 2007 but has expanded into the UPP since 2011.⁶

Most UPP development has occurred in Ohio but has recently increased in both Pennsylvania and West Virginia. As of January 2020, there were over 2700 UPP wells in Ohio and over 160 in Pennsylvania.^{6,9} One of the largest environmental concerns with the increased unconventional O&G production throughout the Appalachian Basin is the possibility of ground water or surface water contamination by hydraulic fracturing fluids or produced waters. In areas dominated by Marcellus development, there are numerous incidents where spills (1181 spill events in Pennsylvania from 2005–2014),^{10,11} surface water disposal,^{12,13} improper management at wastewater disposal facilities,^{14,15} and potentially faulty well casings¹⁶ caused Marcellus produced waters to migrate to water resources. No similar incidents have been reported from the more recent growth in UPP O&G development; however, this could be because there is only one study that the authors are aware of that has tested freshwater for UPP produced water contamination.¹⁷

Despite the environmental concerns and wastewater management challenges associated with unconventional O&G development, UPP produced water chemistry has been published for only two wells.^{18,19} Total dissolved solid (TDS) concentrations in produced waters are highly variable from unconventional shale formations because of variable amounts of dilution with injection waters.^{20–22} Therefore, any comparisons of elemental concentrations among produced waters from different formations should be limited to water of similar TDS, preferably the most saline waters that represent original formation waters.^{20–22} Comparisons among these high-salinity waters for different formations in the Appalachian Basin indicate that they can have significantly different concentrations of

Ca, Sr, Ba, Ra, and B, among other elements. For instance, the Marcellus has unusually high concentrations of Ba, Sr, and ²²⁶Ra relative to other formations in the Appalachian Basin. Formations throughout the Basin also have unique elemental or isotope ratios (*i.e.*, Sr/Ca, ²²⁸Ra/²²⁶Ra, ⁸⁷Sr/⁸⁶Sr, ¹¹B/¹⁰B, and ⁷Li/⁶Li) that can identify small quantities (often <0.1%) of produced water mixed with groundwater, surface water, or stream sediments.^{12,22–27} In almost every case study investigating potential O&G contamination events, unique isotope or elemental ratios were used as a forensic tool to determine the source of pollution (*i.e.*, unconventional brine *vs.* conventional brine *vs.* road salt *vs.* acid mine drainage). As development expands in the UPP, similar data could be important in fingerprinting UPP produced waters in the environment, understanding heterogeneities in the formation, and developing strategies for managing UPP produced water from various parts of the play. The existing data for UPP produced water chemistry is not adequate to conduct this fingerprinting because it is from only two wells and is limited to a few analytes (SO₄, Cl, Na, Ca, Mg, and K).^{18,19}

The management of UPP produced waters in Pennsylvania, Ohio, and West Virginia fall under the same regulatory statutes and disposal practices as Marcellus fluids, which includes disposal through injection disposal wells, reuse without any treatment to fracture other wells, or treatment at zero liquid discharge treatment plants that remove some of the suspended solids and precipitate out barium-sulfate minerals before reuse for hydraulic fracturing.²⁸ Current and future concerns with handling the wastes from UPP development will likely be related to the proper disposal of radioactive sludge generated from facilities treating the fluids, faulty casings on gas-producing wells that may allow fluid migration, or potential spills at the surface. From 2010 to 2013, approximately 5% of the Marcellus Shale wells in Pennsylvania received violations for well cementing issues.²⁹ The greatest threat to water quality is likely from surface spill events which occur at approximately 10% of the unconventional wells each year.³⁰ Therefore, it is essential to develop forensic tools for identifying potential contamination from UPP development after the spill is diluted with freshwater.

The objectives of this work were to (1) document the chemistry of liquid wastes from UPP wells, and (2) determine unique isotope or elemental ratios for tracing UPP releases in the environment. To address these objectives, liquid wastes from the UPP were collected from producing wells and analyzed for inorganic chemistry (Cl, Br, SO₄, Na, Ca, Mg, Sr, K, Li, B, Ba, Fe, Pb, Cu, As, and U), radioactivity (²²⁶Ra and ²²⁸Ra), and isotope ratios (⁸⁷Sr/⁸⁶Sr). Unique signatures for tracing environmental contamination from UPP development were identified by comparing our results to analyses from other O&G formations in the Appalachian Basin.

Methods

Produced water collection

UPP produced waters were collected from 26 wells throughout Ohio, Pennsylvania, and West Virginia (Fig. 1). Based on well

production reports and communication with collaborators from industry, all wells were in production for over 120 days, reducing chemical variabilities commonly observed in produced waters collected early after a well goes into production.^{20,31} Produced water samples were collected from O&G water separators at well heads, stored in 10 liter high-density polyethylene (HDPE containers), and preserved to pH < 2 with nitric acid for cation analyses or unpreserved for anion analyses. Thereafter, 100 mL of each sample for cation analysis was digested with 6 mL of aqua regia for 4 hours at 70 °C. There were no suspended solids in any of the samples after digestion. Acid dissolution of suspended particulates could increase the possibility of excess dissolved Fe (and potentially other metals). However, because metal precipitation can occur rapidly after produced waters flow from a gas well,²¹ all samples were digested prior to filtering to analyze total metals in solution. The true vertical depth of the sampled UPP wells varied from ~2300 m in northwest Pennsylvania, ~3500 m in northeast Pennsylvania, to ~3700 to 4000 m in West Virginia and southern Pennsylvania (Fig. 1).

Produced water characterizations

Major and minor trace element analyses were performed on a Thermo Scientific iCAP 6000 inductively coupled plasma optical emission spectrometer (ICP-OES; Na, Ca, Mg, Sr, K), Thermo X-Series 2 mass spectrometer (ICP-MS; Li, B, Ba, Fe, Pb, Cd, Cu, As, U) located at Penn State University's Energy and Environmental Sustainability Laboratories (EESL), and Dionex ICS-1100 ion chromatography (IC; Cl, Br, SO₄). Before elemental analyses, samples were filtered (0.45 µm cellulose acetate) and

diluted in 2% nitric acid or ≥18 MΩ ultrapure water (Cl, Br, SO₄) to reach dilution factors of 2000 for Na, Ca, Mg, Sr, and K, 100 for Cl, Br, and SO₄, or 50 for all other metals. Mass interferences and matrix complications of analyzing high salinity samples by ICP-MS or ICP-OES were accounted for by using internal spikes (Sc, In, Re, Y) and high salinity, matrix-matched standards.³² Calibration curves for all analyses were verified by confirming <5% differences between measured and known elemental concentrations in check standards (USGS M – 220, USGS T-227, and SRM1640a).

Isotope analyses were performed using a ThermoFisher Neptune Plus high resolution multicollector (MC-ICP-MS; ⁸⁷Sr/⁸⁶Sr) located at Penn State University EESL and a small anode germanium detector gamma spectrometer from Canberra Instruments at the Tracing Salinity with Isotopes Lab (SALTs) also located at Penn State University (²²⁸Ra/²²⁶Ra). Radioactivity (²²⁶Ra, ²²⁸Ra) was measured in acid digested produced waters at geometries (20 mL and 3 L geometries) consistent with well characterized internal standards from an inter-laboratory comparison that reported most probable radium activities in three Appalachian Basin O&G produced waters.³² After a 21 day equilibration, ²²⁶Ra was calculated directly at 186.2 keV and then confirmed from the average activity of ²¹⁴Bi (609.3 keV) and ²¹⁴Pb (295.2 & 351.9 keV). Direct measurement of ²²⁸Ra were performed using its ²²⁸Ac daughter at 911.1 keV. Prior to ⁸⁷Sr/⁸⁶Sr analysis, strontium was separated from wastewaters with recoveries of 99% ± 3.7 using Sr Spec EICHRON resin and nitric acid (2 N) to yield 0.25 to 1 µg of strontium. Strontium isotope accuracy was determined by comparisons to NIST SRM 987. The average ⁸⁷Sr/⁸⁶Sr ratio of the

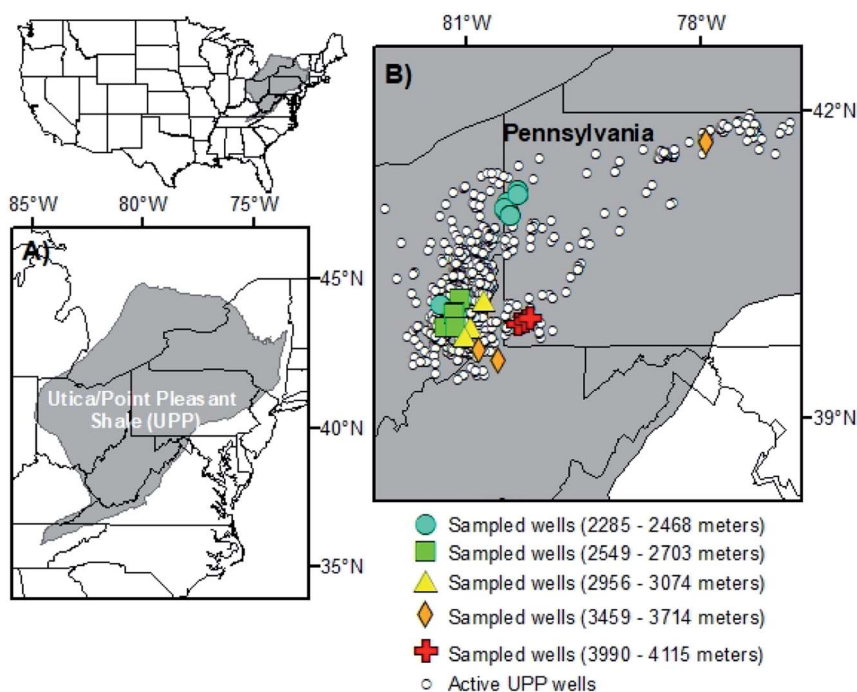


Fig. 1 Sampled oil and gas wells from the Utica/Point Pleasant (UPP) formation in the northern Appalachian Basin, U.S. (A) The UPP play is shaded gray. (B) Active O&G wells producing from the UPP formation are represented with white circles. Produced waters from 26 of the active wells were sampled throughout the Basin with well depths indicated by symbols.

SRM over 41 analyses was 0.710240 with a standard deviation of 0.000002 (actual value = 0.710240).

Additional data sources

Produced water chemistry from the UPP were compared to existing produced water chemistry from O&G formations in the Appalachian Basin. Produced water chemistry data from conventional and unconventional formations were compiled from the US Geological Survey (USGS) Produced Water Database version 2.3n.³³ Produced water chemistry from hydraulically fractured oil and gas wells is known to vary with time after a well goes into production. While all of the UPP wells sampled in this study were over 120 days of production and were believed to have a fluid chemistry reflective of the formation mineralogy or *in situ* formation fluids, an operational chloride threshold was used to reduce potential unknown sources of error in the UPP produced water chemistry and to allow for comparisons of produced water chemistry from different formations. The operational chloride threshold was defined as only including data from wells where chloride concentrations were $\geq 76\,800\text{ mg L}^{-1}$ chloride (*i.e.*, the 5th percentile chloride concentration from the 26 UPP samples collected for this study). This was a reasonable threshold in limiting potential sources of error (*e.g.*, mixing with hydraulic fracturing fluids) in the UPP produced water chemistry. One of the collected UPP samples (UPP 24 in Table S1†) that was excluded from statistical analyses by this threshold was later found to be compromised by a local hydraulic fracturing job. The sample (UPP 24) had lower TDS (*e.g.*, $\sim 71\,000\text{ mg L}^{-1}$) than was expected for a well with over 120 days of production. After contacting the oil and gas company about this sample, the company stated that the produced water chemistry in sample UPP 24 was likely influenced by fracturing fluids that migrated along a fault line from the local hydraulic fracturing job.

In order to compare the UPP produced water chemistry to produced waters from other formations in the Appalachian Basin, all produced water data collected from the US Geological Survey (USGS) Produced Water Database was also filtered to only include samples with $\geq 76\,800\text{ mg L}^{-1}$ chloride (*i.e.*, the 5th percentile chloride concentration from the 26 UPP samples collected for this study). While the authors acknowledge that this data inclusion method could cause potential sources of bias, the method would likely bias results so formations would appear to have more similar fluid chemistries; therefore, any observed differences in fluid chemistries are likely real. The total conventional produced water data set from the US Geological Survey (USGS) Produced Water Database included 2434 analyses from 84 formations. Conventional wastewater results were reduced to 1122 entries by only including data from wells where chloride concentration was $\geq 76\,800\text{ mg L}^{-1}$ chloride. Similarly, data for the Marcellus Shale were reduced from 448 entries to 128 by only including wells with $\geq 76\,800\text{ mg L}^{-1}$ chloride.

Elemental and isotope ratios for the formations were also compared to ground and surface water resources in Appalachian Basin using the Water Quality Portal from the National Water Quality Monitoring Council.³⁴ Water quality data for streams, rivers, and ground water wells were collected from

2000–2005 ($n = 9006$). Of the 9006 entries, 5589 included Cl, 460 included Br, 24 included B, 3504 included Na, 5542 included Ca, 348 included Mg, 101 included Ba, 113 included Sr, 25 included ²²⁶Ra, and 25 included ²²⁸Ra. The ⁸⁷Sr/⁸⁶Sr ratios in freshwaters were also referenced from additional sources.³⁵

Statistical analyses

All statistical analyses were performed in RStudio.³⁶ Shapiro Wilk tests for normality (Table S7†) confirmed that most of the data was not normal. Therefore, Kruskal–Wallis and Wilcoxon rank sum tests with Bonferroni corrections were used to determine if there were any statistical differences between the produced water chemistry from UPP, Marcellus, and conventional formations. Statistical differences between the compared formations were interpreted as being significant if *p* values were less than 0.05. Elements with concentrations below detection limits were not included in these analyses.

Results and discussion

Chemistry of produced waters from the Utica and Point Pleasant Shale

Consistent with produced waters from other O&G formations in the Appalachian Basin, UPP produced waters are dominated by

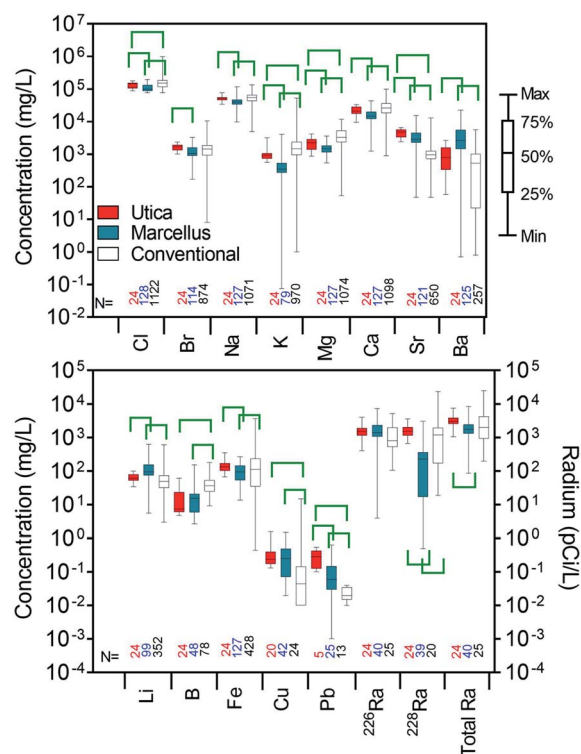


Fig. 2 Produced water chemistry from the UPP (red) analyzed in this study compared to other formations in the Appalachian Basin. Produced water analyses from the Marcellus (blue) and conventional O&G formations (white) were previously reported in the USGS Produced Water Database.³³ Numbers above the x-axis represent the number of analyses for each formation. Green brackets indicate comparisons between two formations that have significantly different produced water chemistry ($p < 0.05$).

sodium, calcium, and magnesium (accounting for >90% of the total cation charge equivalents) and are nearly 100% charge balanced by chloride (Fig. 2). Based on the data inclusion method used in this study (*i.e.*, wells with over 76 800 mg L⁻¹ chloride), the UPP and conventional gas formations have produced waters with higher chloride, calcium, and sodium concentrations than produced waters from Marcellus wells. Median bromide concentrations in UPP produced waters were also 1.6 times higher than produced water from the Marcellus. These differences in bromide concentrations were greater than reported levels of analytical inaccuracy (*i.e.*, typically $\pm 20\%$ accuracy for O&G wastewater³²).

Like the Marcellus, UPP produced waters are characterized by high concentrations of barium (ranging from 57 to 2700 mg L⁻¹) and strontium (2000 mg L⁻¹ to 6500 mg L⁻¹) (Table S1 and S3†). No sulfate was detected in any of the UPP produced waters (*i.e.*, all samples < 100 mg L⁻¹ SO₄), indicating strong reducing conditions in the formation. Low sulfate concentrations allow high concentrations of dissolved alkaline earth metals that would otherwise precipitate in low solubility sulfate minerals (*e.g.*, *K_{sp}* of barite $\sim 10^{-10}$).²⁰ Both the Marcellus and UPP produced waters have median barium and strontium concentrations that are greater than the concentrations measured in produced waters from conventional gas wells (Fig. 2). High concentrations of these alkaline earth metals in produced waters are variously attributed to evaporated seawater brines reacting with local rock formations over geologic time^{26,37} or reductive weathering of shales during hydraulic fracturing.^{38,39}

UPP produced waters have high radioactivity. While the median ²²⁶Ra activities in UPP produced water are similar to Marcellus produced waters (*e.g.*, 1522 pCi L⁻¹ in UPP and 1417 pCi L⁻¹ in Marcellus produced waters), the UPP has higher

²²⁸Ra activities (*e.g.*, 1566 pCi L⁻¹ in UPP and 228 pCi L⁻¹ in Marcellus Shale produced waters). These differences in ²²⁶Ra and ²²⁸Ra radioactivity result in ²²⁸Ra/²²⁶Ra activity ratios in UPP produced waters (*i.e.*, 1.0 to 1.2 based on the 25th to 75th percentiles; Table S5†) that are greater than the values reported for Marcellus produced waters (*i.e.*, 0.01 to 0.4 based on the 25th to 75th percentiles). Differences in ²²⁸Ra/²²⁶Ra activity arise from different ratios of their respective radioactive parents (²³²Th for ²²⁸Ra and ²³⁸U for ²²⁶Ra) in the host reservoir rocks. Typically, the Th/U mass ratios for most silicate rocks fall in the range of 1.5 to 6.0 and generate ²²⁸Ra/²²⁶Ra activity ratios of 0.5 to 2.0 for both the rocks and for equilibrated formation waters.^{40–42} To generate the median ²²⁸Ra/²²⁶Ra activity ratio in UPP waters (1.08, Table S5†), the UPP reservoir rocks would have to contain a ²³²Th/²³⁸U activity ratio of 1.0 and a Th/U mass ratio of 3.0 that is typical of clay-bearing silicate rocks.^{40,41}

Elemental and isotopic ratios for identifying UPP produced water

Several elemental and isotopic ratios could be used to identify contamination from UPP (Fig. 3). Median Na/Cl, Cl/Br, (Ca + Mg)/Cl, (Ba + Sr)/Mg, and Sr/Ca molar ratios for all O&G produced waters from the Appalachian Basin are statistically different from freshwaters (Fig. 3 and Table S6†). However, the only ratios that are unique to the UPP produced waters are ratios that incorporate strontium or radium. For instance, (Ba + Sr)/Mg and Sr/Ca ratios for UPP and Marcellus produced waters are not statistically different from each other but are different from conventional O&G produced waters and freshwater (Fig. 3). ⁸⁷Sr/⁸⁶Sr ratios for UPP produced waters are also in a relatively narrow range (*e.g.*, ⁸⁷Sr/⁸⁶Sr = 0.71088 to 0.71143 based on the 25th to 75th percentiles; Table S5†) that could be

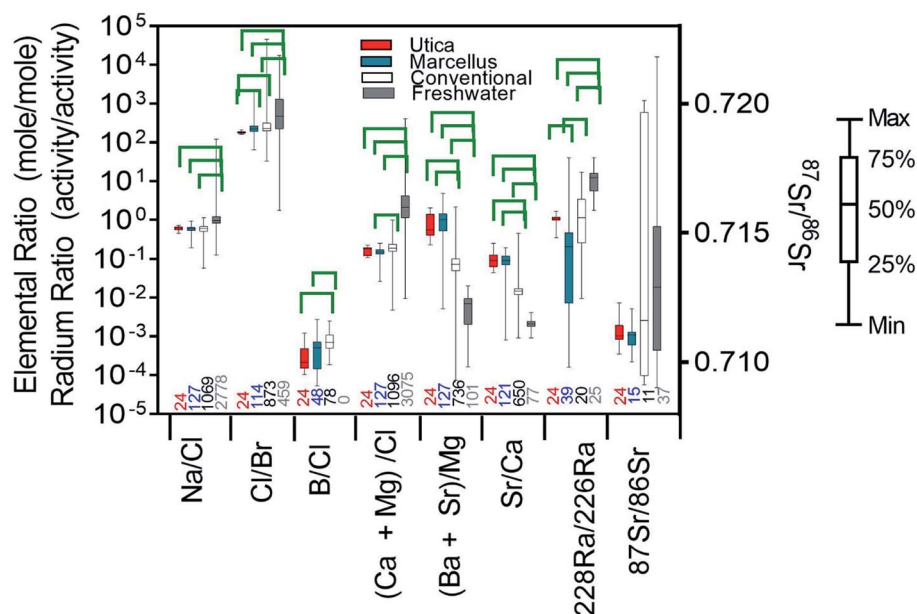


Fig. 3 Comparison between elemental and isotopic ratios in O&G produced waters and freshwaters throughout the Appalachian Basin. Green brackets indicate comparisons between two fluids that have significantly different ratios ($p < 0.05$).

useful in forensic applications. Additionally, the UPP has higher $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios than Marcellus produced waters but lower activity ratios than freshwaters. A framework is illustrated below that outlines how these different ratios could be used to identify freshwater contamination by the various O&G formations in the Appalachian Basin.

Conservative mixing models between freshwater and O&G produced waters were created in PHREEQC⁴³ to test the sensitivity of various elemental and isotopic ratios for identifying freshwater resources impacted by UPP produced water (Fig. 4). All produced water with $\geq 76\ 800\ \text{mg L}^{-1}$ chloride (*i.e.*, the 5th percentile chloride concentration from the 26 UPP samples collected for this study) and all freshwater samples from the USGS Water Quality Portal ($n = 9006$ from 2000–2005) are included in Fig. 4 to show the potential endmembers that could be used in mixing models. For the purposes of identifying ratios

that could be used to detect UPP produced waters in freshwaters, mixing models were performed with the 5th and 95th percentile concentrations for each of the endmembers.

Freshwaters throughout the Appalachian Basin have highly variable Cl/Br mass ratios, ranging from 12 to 1700 (5th to 95th percentile, respectively). Cl/Br ratios in produced waters are also highly variable but are generally lower than freshwaters (*e.g.*, 5th to 95th percentile mass ratios of 52 to 250). Mixing trends between O&G produced water and freshwater show that the large variability in Cl and Br concentrations in freshwaters could make it difficult to utilize Cl/Br ratios in determining uncontaminated *versus* contaminated freshwater (Fig. S1[†]). However, this method could provide an initial indication of potential O&G contamination if the chloride concentrations measured in freshwater are greater than $100\ \text{mg L}^{-1}$ and have Cl/Br mass ratios less than ~ 130 (*i.e.*, the 75th percentile Cl/Br mass ratio for Appalachian Basin O&G produced waters). While Cl/Br ratios could be used as an initial indicator of potential O&G contamination, they do not provide any specificity as to the source of contamination (*i.e.* produced waters from UPP, Marcellus Shale, or conventional O&G formations).

Many of the same elemental tracers that work for identifying Marcellus produced waters in the environment also work for identifying UPP produced waters. For example, UPP and Marcellus produced waters have higher Sr/Ca mass ratios (*e.g.*, 0.10 to 0.53 based on the 5th to 95th percentiles; Fig. 4A) than waters from conventional O&G formations, which have ratios of 0.01 to 0.07 (5th to 95th percentiles; Fig. 4A). Therefore, if sampled waters have Sr/Ca mass ratios greater than 0.07, this could indicate that the solution contains greater than 0.5% UPP or Marcellus water by volume. Smaller additions (*i.e.*, less than 0.5%) result in Sr/Ca ratios that overlap with conventional formations, making it difficult to distinguish if the contamination is from unconventional shale reservoirs or conventional O&G produced waters. The purple shaded area in Fig. 4A represents the Sr/Ca mass ratios and corresponding strontium concentrations that could definitively indicate contamination from UPP or Marcellus produced waters. The upper bounds for this shaded area are the 95th percentile mixing trends for UPP and the lower bounds are the 95th percentile mixing trends for conventional produced waters. Therefore, if sampled fluids have Sr/Ca and strontium concentrations that are within the purple shaded area, it is likely that fluids originate from or are contaminated by Marcellus Shale or UPP produced waters. The use of this tracer for detecting freshwater contamination by UPP produced waters is most applicable in eastern Ohio, where the current unconventional development is focused on the UPP. In areas where there is both UPP Shale and Marcellus development (*e.g.*, West Virginia and Pennsylvania), this tracer is also sensitive in identifying potential contamination events from these unconventional shale gas reservoirs; however, the overlap in Sr/Ca ratios between UPP and Marcellus produced waters reduces the effectiveness of this tracer in differentiating potential contamination from one of these two sources.

We further evaluated the sensitivity of isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ and $^{226}\text{Ra}/^{228}\text{Ra}$) as tracers for identifying UPP produced waters in the environment. These isotope ratios have

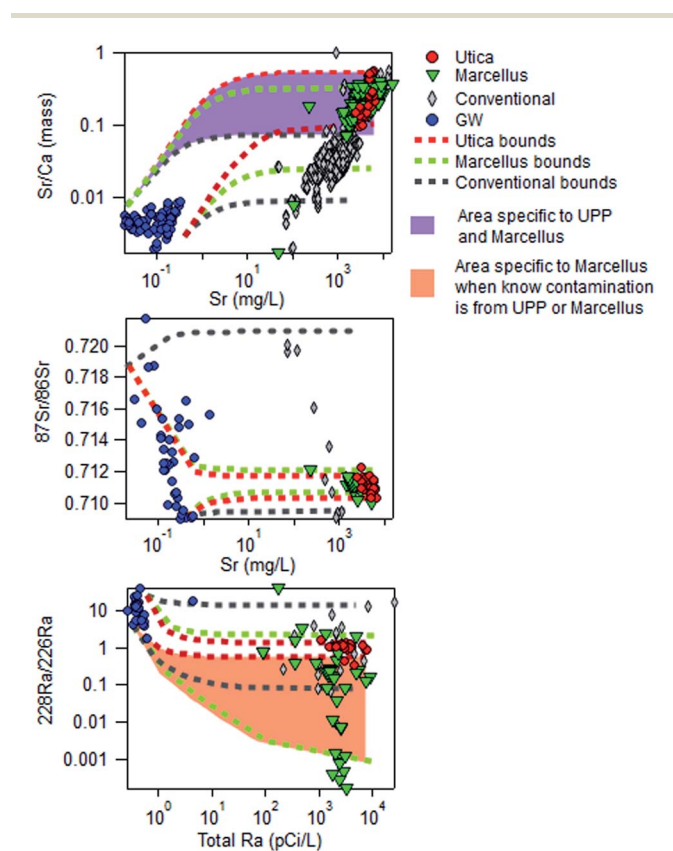


Fig. 4 Conservative mixing trends between freshwaters (blue) and produced waters from UPP (red), Marcellus (green), and conventional (gray) O&G formations. Dashed lines represent mixing trends between 5th and 95th percentile concentrations (or activities for radium) in O&G produced water and freshwater. (A) The purple shaded area shows Sr/Ca mass ratios and Sr concentrations that could definitively indicate contamination from with UPP or Marcellus produced water. (B) Panel B shows $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and conservative mixing trends between freshwaters and produced waters from various formations. (C) If a sampled fluid has a Sr/Ca ratio and Sr concentration within the purple shaded area, the fluid could be analyzed for $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios to determine if the fluid is contaminated with UPP or Marcellus produced water. If the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio and total radium activity is within the orange shaded area, the fluid is likely contaminated by Marcellus produced water instead of UPP produced water.

advantages over the elemental ratios described previously as they are not subject to fractionation from ion exchange equilibria, mineral solubility, or changes in temperature and salinity.^{12,44} Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) combined with Sr/Ca molar ratios are highly sensitive indicators for tracing Marcellus produced waters, detecting as low as 0.01% produced water additions to freshwater.^{24,44} Similarly, this same isotope tracer works to identify contamination from UPP produced waters. Both the UPP and Marcellus have similar strontium isotope ratios (e.g., $^{87}\text{Sr}/^{86}\text{Sr} = 0.71088$ to 0.71143 in UPP produced waters and $^{87}\text{Sr}/^{86}\text{Sr} = 0.71071$ to 0.71117 in Marcellus produced waters based on the 25th to 75th percentiles; Table S5[†]) that are traceable in freshwater and are distinguishable from some conventional produced waters that have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as high as 0.7200 (Fig. 4B). However, similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in conventional, UPP, and Marcellus produced waters (p value = 1; see Table S3[†]) make them difficult to distinguish from each other if there is suspected contamination. Therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ are not always an appropriate forensic tool for determining the source of produced water in the Appalachian Basin (Fig. 4B).

When it is essential to determine if the suspected contamination is from Marcellus Shale or UPP, radium isotopes are likely the best tracer (Fig. 4C). UPP produced waters have $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (i.e., 1.0 to 1.2 based on the 25th to 75th percentiles) that are greater than the values reported for Marcellus produced waters (i.e., 0.01 to 0.4 based on the 25th to 75th percentiles). Therefore, to determine if a contamination event is from UPP or Marcellus Shale produced water, we recommend to analyze Sr/Ca ratios first to confirm if the fluid contains produced water from an unconventional shale formation (i.e., UPP and Marcellus Shale produced water). Thereafter, if $^{228}\text{Ra}/^{226}\text{Ra}$ activities are less than 1.0 (i.e., 25th percentile activity ratio for UPP produced waters) and total radium activities are greater than 4.4 pCi L^{-1} (i.e., the highest radium activity for freshwater reported on the USGS water quality portal), then this could indicate that the water contains greater than 1% Marcellus produced water (Fig. 4C orange shaded area). In summary, if the Sr/Ca ratio and Sr concentration confirm that the fluid contains produced water from an unconventional shale formation and additional analyses show that the fluid has a $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio and total radium activity within the orange shaded region of Fig. 4C, it is likely that the fluid contains Marcellus produced water instead of UPP produced water.

Conclusions

Many of the same tracers that distinguish Marcellus produced waters from freshwater or other conventional O&G produced waters also work for UPP produced waters. In western Ohio where there is very little Marcellus development, Cl/Br, Sr/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can identify potential UPP produced water contamination events. These isotope and elemental ratios in UPP produced waters are different than produced waters from conventional O&G development in Ohio, making them unique fingerprints that could identify potential contamination events

from the UPP development. In regions of the Appalachian Basin with both UPP and Marcellus development, it may be more difficult to distinguish potential contamination between these two sources due to their overlapping Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. However, these two formations have Sr/Ca ratios in their produced waters that are higher than conventional produced waters. Therefore, basic water quality analyses that utilize ICP or IC instrumentation to determine Cl, Br, Ca, and Sr concentrations can provide useful information in trying to determine if samples are contaminated with conventional or unconventional (e.g., UPP or Marcellus) produced waters. These analyses can also be performed at a lower cost (~\$30 to \$60) than other isotopic methods (e.g., gamma spectroscopy, MC-ICP-MS, etc.) which can cost over \$100 per sample. If it is necessary to identify if pollution is from Marcellus or UPP produced water, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio could distinguish UPP produced waters from Marcellus produced waters. The $^{228}\text{Ra}/^{226}\text{Ra}$ in UPP produced waters was the only tracer that was consistently different from the ratio observed in Marcellus produced waters.

There are also limitations with using elemental and isotopic tracers that need to be acknowledged before identifying potential contamination by unconventional or conventional produced waters. If freshwater is contaminated with UPP produced water, the resulting elemental ratios in the fluid mixture will be influenced by the volume of produced water that was mixed with the freshwater and the elemental concentrations of the two solutions. If no chemical or physical reactions occur after mixing, the resulting elemental concentrations could be calculated using a simple mass balance approach (i.e., conservative mixing model). However, if the two solutions were incompatible or mixed together in a complex environment with multiple phases (i.e., air, water, soil, etc.), the elemental concentrations in the combined fluid would not be explained by a conservative mixing model.⁴⁵ For instance, mixing strontium and barium-rich produced waters with sulfate or carbonate-rich fresh waters can result in mineral precipitation reactions that influence conservative mixing trends; similarly, cation-exchange reactions between contaminated freshwater and bedrock could result in the exchange of calcium (or other alkaline earth metals) ions in the contaminated water for sodium ions on clay minerals. While elemental and isotopic ratios are highlighted in this work as conservative tracers, the authors recommend that the type of mixing environment (i.e., water, subsurface environment, soil, etc.) and the compatibility of the fluids being mixed together be considered in case-specific scenarios of suspected freshwater contamination.

Conflicts of interest

There are no conflicts to declare.

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Appendix 2 - Tasker et al., 2018

key findings: Oil & gas brines spread on roads in northwestern Pennsylvania contain elevated concentrations of radium, a known human carcinogen.

The high salinity of O&G brines was shown to be toxic to the freshwater indicator organism *Daphnia magna*.

Organic contaminants in O&G brines were shown to be toxic to humans based on human receptor gene assays.

Environmental and Human Health Impacts of Spreading Oil and Gas Wastewater on Roads

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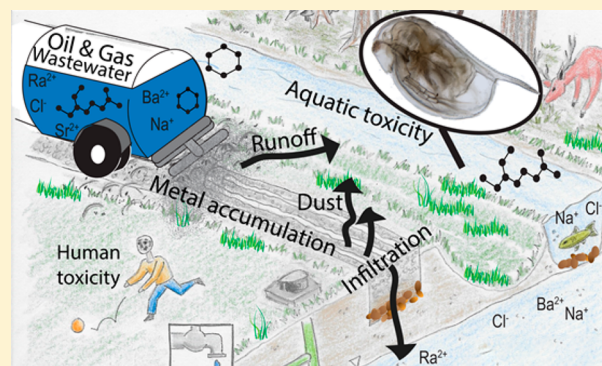
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Supporting Information

ABSTRACT: Thirteen states in the United States allow the spreading of O&G wastewaters on roads for deicing or dust suppression. In this study, the potential environmental and human health impacts of this practice are evaluated. Analyses of O&G wastewaters spread on roads in the northeastern, U.S. show that these wastewaters have salt, radioactivity, and organic contaminant concentrations often many times above drinking water standards. Bioassays also indicated that these wastewaters contain organic micropollutants that affected signaling pathways consistent with xenobiotic metabolism and caused toxicity to aquatic organisms like *Daphnia magna*. The potential toxicity of these wastewaters is a concern as lab experiments demonstrated that nearly all of the metals from these wastewaters leach from roads after rain events, likely reaching ground and surface water. Release of a known carcinogen (e.g., radium) from roads treated with O&G wastewaters has been largely ignored. In Pennsylvania from 2008 to 2014, spreading O&G wastewater on roads released over 4 times more radium to the environment (320 millicuries) than O&G wastewater treatment facilities and 200 times more radium than spill events. Currently, state-by-state regulations do not require radium analyses prior to treating roads with O&G wastewaters. Methods for reducing the potential impacts of spreading O&G wastewaters on roads are discussed.



INTRODUCTION

Fugitive dust emissions from unpaved roads represent a global human and environmental health hazard. Approximately 34% of the 6.6 million kilometers of roads in the United States (U.S.) are unpaved and produce 47% of the annual airborne particulate matter (<10 μm size) emissions.¹ Airborne particulate matter from roads can contribute to chronic respiratory and cardiovascular diseases² as well as vegetative stress in local plant communities.³ Throughout the U.S., road managers work to alleviate these adverse human and environmental health effects by spreading products on roads to suppress dust.

There are over 190 different dust suppressants used to treat unpaved roads in the U.S.⁴ After application, dust suppressants change the physical properties of the road aggregate by forming coatings or causing particles to agglomerate together and retain moisture. It is estimated that nearly 75% of all dust suppressants applied to unpaved roads are chloride salts or salt brine products that average around \$0.25/L.⁴ In regions

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where road managers have low annual budgets for road maintenance, even \$0.25/L may be too costly.

A free alternative in many states is to use wastewater from oil and gas (O&G) wells. The high salt content of the O&G wastewater is effective in retaining road moisture for suppressing dust or lowering freezing points for deicing. Here, road spreading of O&G wastewater in northwestern Pennsylvania and northeastern Ohio was evaluated as a demonstrative case study. Much of the unpaved road materials in this region are from glacial till with fine particulate material that is mobile in air and rain runoff.⁵ The long history of O&G development in this region has provided opportunities for well operators to give O&G wastewater to townships as a free dust suppressant. In 2015, townships in northwestern Pennsylvania spread an average of 280,000 L of O&G wastewater on their roads,⁶ equivalent to saving approximately \$70,000 dollars per township.

There are concerns with spreading O&G wastewaters on roads. Wastewater contaminants may threaten environmental and public health by leaching into surface or groundwater,⁷ accumulating around roads,⁸ modifying adjacent soil chemistry,⁹ or migrating in air and dust. The Pennsylvania Department of Environmental Protection (PA DEP) investigated the potential for radium, a known carcinogen, to accumulate around roads treated with O&G wastewaters. Large variabilities in radium concentrations measured in untreated and treated roads led to inconclusive results. Further studies were recommended to evaluate radionuclide concentrations in O&G wastewaters used on roads and their transport after road treatment.¹⁰

O&G wastewater contaminants not retained in the road or soils will be transported to water resources and require significant dilution to prevent the salinization of freshwater resources. There are two reported cases in Ohio where spreading O&G wastewaters on roads caused groundwater contamination and salinization.^{7,11} Salinization of freshwater resources^{12,13} is not a new issue as several studies document increasing chloride and sodium concentrations in fresh water resources.^{14,15} Wastewater pollutants that migrate to water resources could have toxic effects on fish, macroinvertebrates, amphibians, and other salinity-intolerant species.¹⁶ Therefore, it is important to assess the extent of O&G wastewater spreading in the U.S. and its potential impact on human and environmental health.

The objectives of this research were to 1) identify states that spread O&G wastewater on roads and then review their associated regulations, 2) document the spatial and temporal trends of spreading O&G wastewater on roads in Ohio and Pennsylvania as demonstrative case studies, 3) determine the chemical characteristics of O&G wastewater spread on roads, 4) evaluate the mobility of O&G wastewater contaminants after road application and rainwater leaching, and 5) measure the aquatic and human toxicity potential of O&G wastewaters used on roads.

MATERIALS AND METHODS

Regulatory Review and Data Collection. Road spreading and beneficial reuse regulations for all 50 states were reviewed by using the LexisNexis law database and contacting O&G state regulators throughout the United States. Wastewater volumes applied to roads were determined by reviewing data on the PA DEP O&G reporting Web site⁶ or digitizing monthly spreading reports collected from Ohio and Pennsylva-

nia through public records requests. Certificate of analyses for wastewaters applied to roads in New York and Pennsylvania were also collected from public records requests.

Inorganic Analyses of O&G Wastewaters Spread on Roads in Pennsylvania. O&G wastewaters were collected in 10 L high density polypropylene containers from storage tanks in 14 townships throughout northwestern, PA that were to be spread on roads in the summer 2017. Elemental analyses of wastewaters were performed on a Thermo Scientific iCAP 6000 inductively coupled plasma optical emission spectrophotometer (ICP-OES) for Na, Ca, Mg, Sr, and K, a Thermo X-Series 2 mass spectrophotometer (ICP-MS) for Ba, Fe, Pb, Cd, Cr, Cu, and As, and a Dionex ICS-1100 ion chromatograph (IC) with an AS18 column for Cl and Br at the Pennsylvania State University. Before elemental analyses, samples were filtered (0.45 μm) and diluted in 2% nitric acid or 18M Ω ultrapure water (Thermo Scientific Barnstead Nanopure) to reach a dilution factor of 2000 for Na, Ca, Mg, Sr, and K, 100 for Cl, Br, and SO₄, or 50 for all other metals. Dilutions were made on a mass basis but were converted to volume using the specific gravity of the O&G wastewaters. Mass interferences and matrix complications of analyzing high salinity samples by ICP-MS or ICP-OES were accounted for using internal spikes (Sc, In, Re, Y) and high salinity, matrix matched standards synthesized from High Purity Standards Inc. Calibration curves for all analyses were verified with check standards (USGS M-220, USGS T-227, and SRM1640a). Radioactivity was measured on a small anode germanium detector (Canberra Instruments) at geometries consistent with internal standards. After a 21-day equilibration, ²²⁶Ra was measured using Bi-214 (609 keV) and Pb-214 (295,351 keV) decay products. Direct measurement of ²²⁸Ra was performed using its ²²⁸Ac daughter at 911.16 keV.

Organic Analysis of O&G Wastewaters Used on Roads. Organic compounds were extracted from 100 mL of O&G wastewater sample using 3, 50 mL aliquots of dichloromethane (DCM) per pH adjustment to pH < 2 with H₂SO₄ and pH > 10 with NaOH (EPA method 3510C: Separatory Funnel Liquid-Liquid extraction). Extracts were concentrated to 1 mL using a Kuderna-Danish apparatus and nitrogen gas blow down. Extracts were analyzed for diesel and gas range organics using comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (LECO Pegasus 4D GCxGC-TOFMS). The separation was performed using a 100 m \times 0.25 μm ID \times 0.5 μm df RTX-DHA-100 column in the first dimension followed by a 1.7 m \times 0.25 μm ID \times 0.25 μm df Rxi-17SilMS column in the second dimension using He as carrier gas at 2.0 mL/min. The GC oven was held at 50 $^{\circ}\text{C}$ for 0.2 min followed by a 5 $^{\circ}\text{C}/\text{min}$ ramp to 315 $^{\circ}\text{C}$. The secondary GC oven was offset by 5 $^{\circ}\text{C}$, while the modulator was offset by 15 $^{\circ}\text{C}$ from the primary GC oven. A modulation time of 3.0 s was used. The TOFMS was operated from 50 to 550 amu at -70 eV at an acquisition frequency of 200 Hz. Diesel and gas range organics were determined using an Alaska UST Standard (Restek, Bellefonte, PA) and TN/MS DRO mix (Restek, Bellefonte, PA), with naphthalene-d8 (Restek, Bellefonte, PA) used as an internal standard.

Evaluating Contaminant Leachability after Spreading O&G Wastewaters on Roads. Laboratory experiments were conducted to determine the mobility of contaminants in O&G wastewaters applied to road materials. In the field, roads are recommended to be treated with 1.6 L of O&G wastewaters per m² which does not easily translate to a volume per mass of road aggregate.¹⁷ We assumed that the volume of dust

suppressant in contact with a road aggregate would be influenced by the water retention capacity of the aggregate itself. For lab experiments, O&G wastewater was applied to road aggregate collected from Erie County, PA based on the amount of water that the aggregate could retain. The water retention capacity was determined to be 0.2 mL/g by mixing 100 g of aggregate (sieve < 1.18 mm) with 100 mL of water and then measuring the amount of water that could be recovered after filtering through a glass fiber filter. Three O&G wastewaters (PA01, PA02, and PA07; Table S5) were applied to 100 g of the sieved road aggregate at the water retention capacity (0.2 mL/g), dried (50 °C), and leached with 2000 mL of synthetic rainwater (pH = 4.2) for 18 h according to the EPA synthetic precipitation leaching procedure (SW-846 Test Method 1312). Experiments were run in duplicate for the three wastewaters, and leachates were tested for Cl, Br, Na, Mg, Ca, Sr, Fe, and Pb according to the analytical methods above. A mass balance was performed to determine the percent of the contaminant mass that leached from the road aggregate.

A modified leaching method was used to test the mobility of radium and organics after treating road aggregate with O&G wastewaters. With the previous method, only 0.2 pCi/g of radium would be applied to road aggregate from the O&G wastewaters, making it difficult to measure the fate of radium in the solid material. Therefore, three O&G wastewaters (PA01, PA02, and PA03) were applied to aggregate (30 g) at higher application volumes (0.9 mL/g) to increase the measurable radium and organic concentrations in solid and liquid phases. After drying at 50 °C for 4 days, the treated aggregate was leached with 25 mL of synthetic rainwater for 18 h. The leachate was collected, and then the solid was leached 2 more times with 25 mL of synthetic rainwater to ensure that all leachable contaminants were removed from the solid material prior to analysis—similar to leaching procedures reported elsewhere.^{18–20} Leached roads samples were dried at 50 °C and analyzed for radium using gamma spectroscopy. A mass balance was performed to determine the amount of radium that could be retained in roads treated with O&G wastewaters. These same experiments were repeated to determine the fate of organic compounds after road spreading. After completing the leaching experiment, road aggregate and leached road aggregate were sequentially extracted 3 times for 10 min with 100 mL of a 50:50 acetone:DCM mixture using ultrasonic disruption (Omni Sonic Ruptor 400 Ultrasonic Homogenizer) in accordance with EPA Method 3550C. Extracts were analyzed on the LECO Pegasus 4D GCxGC-TOFMS, and organic concentration differences between O&G wastewaters, untreated road aggregates, and leached road aggregates were used for mass balance calculations.

Multiple road spreading and runoff events were simulated in lab experiments to better understand the fate of radium. Road aggregate was treated with O&G wastewater (PA03), dried, leached (same methods as previous paragraph), and measured for ²²⁶Ra retained in the road material. This was repeated four times to determine how much radium could accumulate in roads treated multiple times with O&G wastewater. Radium in O&G wastewaters that leach from the road after rain events could also attenuate in roadside ditches or soils below the road surface. Rain events were simulated by mixing road subgrade and ditch material from Erie County, PA (30 g) with a 200 mL solution of O&G wastewater diluted (5, 25, and 50 times dilution) in synthetic rainwater. After 24 h of mixing, samples were then centrifuged (3,000 rcf; 5 min), decanted, and rinsed

three times with 25 mL of ultrapure water (18 MΩ). Dried samples were analyzed for ²²⁶Ra by gamma spectroscopy.

Evaluating the Potential Human Toxicity of O&G Wastewaters Spread on Roads. Potential human toxicity of O&G wastewaters spread on roads was evaluated using five commercial bioassays. The particular suite of bioassays was selected to cover the major toxicity pathways commonly observed in water samples,²¹ including pathways for induction to xenobiotic metabolism, specific modes of toxic action, and induction of adaptive stress responses.²¹ Bioassays with the human aryl hydrocarbon receptor (AhR) and pregnane-X receptor (PXR) tested for induction to xenobiotic metabolism, while the human estrogen receptor alpha (ERα) tested for ability to interfere with hormone action. Bioassays with the nuclear factor erythroid 2–related factor 2 (Nrf2) and nuclear factor kappa-light-chain-enhancer of activated B cells (NFκB) tested for oxidative signaling and inflammatory stress. All bioassays were purchased from INDIGO Biosciences (State College, PA) and were used according to the manufacturer's protocols (Table S1). Each kit contains a luciferase reporter gene that is specific for the human form of the signaling proteins mentioned above. An increase in luciferase expression is indicative of the signaling pathway.

Prior to bioassay testing, three O&G wastewater samples and 18MΩ ultrapure water (PA01, PA02, PA03, and Blank; all 1 L) were extracted and concentrated in DCM as described above. Extracts were evaporated with nitrogen gas and then redissolved in dimethyl sulfoxide (DMSO). Extracted samples and a reference compound (e.g., 1-methyl-6-bromoindirubin-3'-oxime—MeBIO for AhR) prepared in DMSO were then serially diluted in triplicate across a 96 well plate using the manufacturer's compound screening media (CSM). The reference compound (included in each kit) was used as a positive control, while a solution of 0.1% DMSO diluted in CSM was used as a negative control. All samples were diluted in triplicate. Dilution factors for the O&G samples were converted to the relative enrichment factor (REF) which is calculated as REF = DCM extraction enrichment factor/dilution factor in bioassay.²² Diluted samples were transferred to another 96 well plate containing cells grown from the manufacturer's cell recovery media and incubated for 24 h at 37 °C with 5% CO₂. Following incubation, the manufacturer's luciferase detection reagent (LDR) was added to each well, and the luminescence was quantified using a Molecular Devices microplate reader (SpectraMax i3).

Luminescence results were normalized according to previous studies.^{23,24} Response data for reference compounds were fitted to a four parameter sigmoid log–logistic equation where the minimum response (Min_{control}) was fixed from the negative control results. The remaining parameters such as the maximum (Max_{ref}) luminescence response, the reference compound concentration causing 50% of the maximum response, and the slope of the curve were calculated using GraphPad Prism version 7.03 (see the [Supporting Information](#) for more details). Thereafter, the responses of the DMSO extraction control (Blank) and DMSO with O&G wastewaters extractants were normalized to the response of the reference compound as follows: % effect = (response – Max_{ref})/(Max_{ref} – Min_{control}). The limit of quantification (LOQ) for each bioassay plate was calculated as 10× the standard deviation of the % effect observed in the negative control according to previous methods.²² Bioanalytical equivalent concentrations (BEQs), which normalize the effect observed in unknown

samples to the effect of a reference compound (1-methyl-6-bromoindirubin-3'-oxime—MeBIO for AhR), were calculated for samples inducing responses above the LOQ. BEQs were calculated using the linear-concentration effect method.²⁴ Normalized data from 0 to 30% effect were fit to a line (y intercept = 0), and the slope was compared to the reference compound to calculate the BEQ as follows: $BEQ = \text{slope}_{\text{unknownsample}} / \text{slope}_{\text{reference compound}}$. Concentration units are the same as the reference compound. Additional descriptions of these bioassays are provided in the [Supporting Information](#).

Evaluating the Potential Aquatic Toxicity of O&G Wastewaters Spread on Roads. Toxicity studies on *Daphnia magna* were used to assess the potential aquatic toxicity of O&G wastewaters spread on roads. O&G wastewaters (PA01, PA02, and PA03), saltwater (SW)-matched controls, and organics extracted from the O&G wastewaters into DCM (Organics-only controls) were serially diluted with dechlorinated Edmonton, Canada city water to reach REFs ranging from 10^{-4} to 10^{-1} . Organic extracts in DCM were blown down with nitrogen and suspended in DMSO prior to dilution with the water. The SW-matched controls (Table S3) were designed to have an ionic composition similar to the three O&G wastewaters but with no organic compounds. Five neonate *D. magna* (<24 h old) were transferred from a parental culture into 50 mL glass beakers with the appropriate dilution of O&G wastewater or SW-matched control and were maintained at 22 °C. Each series was run in triplicate, and mortality was recorded at the end of the 48 h exposure according to the Organisation for Economic Co-operation and Development (OECD) guidelines.²⁵ *Daphnia* immobility was also assessed for O&G wastewaters and Organics-only controls according to OECD protocols. Immobility was determined on a binary scale and was scored as immobile if the animal did not locomote within 15 s after gentle agitation.²⁶ The Toxicity Relationship Analysis Program (TRAP) version 1.30a (EPA, Washington, DC, USA) was used to calculate the lethal REF that would kill 50% of the *Daphnia* (LC_{50}), the effective REF that would cause 50% of the *Daphnia* to be immobile (EC_{50}), and the associated 95% confidence intervals (C.I.) for each treatment.

RESULTS AND DISCUSSION

Oil and Gas Wastewater Spreading on Roads in the United States. At least 13 U.S. states allow the “beneficial use” of O&G wastes (e.g., wastewaters, sludges, oils) for road maintenance, dust suppression, or deicing (Figure 1). To

O&G wastewater use on roads in the U.S.

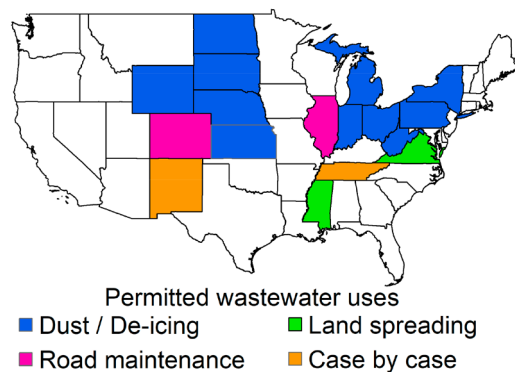


Figure 1. U.S. states with regulations for spreading oil and gas (O&G) wastewaters on roads.

document O&G beneficial use practices, we reviewed regulations on a state-by-state basis, documenting these practices for 22 states (Figure 1; Table S4). States not included in our review either had no O&G development or regulators could not confirm their state’s beneficial use practices. Most states attempt to incentivize O&G developers to recycle O&G wastewater or inject it into subsurface formations;²⁷ however, the beneficial use of O&G wastes on roads is permitted in 13 states (Figure 1). An additional 4 states may also allow road spreading under state laws that permit land spreading or beneficial uses on a case-by-case basis (Figure 1).

A closer review of Pennsylvania and Ohio road spreading data reveals that there is significant spreading activity in these states where millions of liters of O&G wastewater are spread annually (Figure 2). The PA DEP and the Ohio Department of

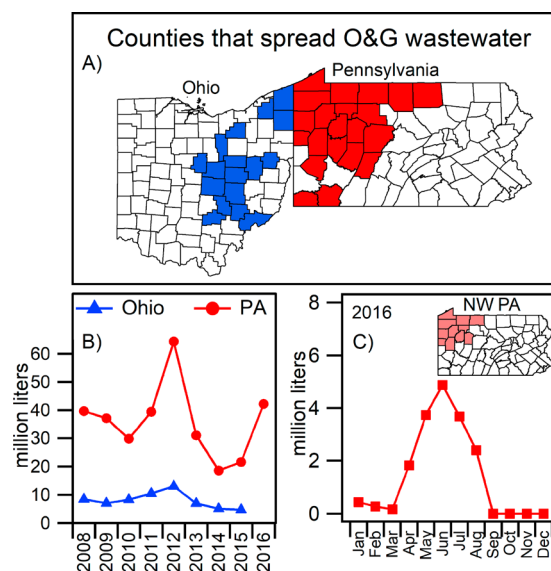


Figure 2. A) Counties in Pennsylvania and Ohio that spread O&G wastewaters on roads since 2008.⁶ B) Volumes of O&G wastewater spread on roads in PA and Ohio. C) Monthly volumes of O&G wastewater spread in NW PA.

Natural Resources (OH DNR) track road spreading by requiring spreaders to complete monthly reports that document O&G wastewater volumes spread on roads. More O&G wastewater is spread on roads in Pennsylvania than Ohio. Since 2008, an average of 35 million L/year of O&G wastewater were spread on roads in 21 counties in Pennsylvania, whereas 5 million L/year were spread in Ohio. The majority of road spreading in Pennsylvania occurs in the northwestern part of the state during April to August (Figure 2C). In 2016, there were 42 million L spread in Pennsylvania, with 96% of this spread on roads in northwest Pennsylvania (Figure 2). This represents approximately 6% of the total wastewater volume (633 million L) generated from conventional O&G wells in Pennsylvania.⁶

The O&G wastewaters spread on Pennsylvania roads are primarily from conventionally drilled wells. Before the increase in high volume hydraulic fracturing (HVHF) in 2008, Pennsylvania’s O&G industry historically drilled vertical wells into permeable sandstone reservoirs, referred to as conventional O&G formations. In comparison, low permeability unconventional O&G formations are developed using directional drilling and HVHF. Current regulations for Colorado, New York,

Table 1. Contaminants of Concern in O&G Wastewaters Spread on Roads^a

pollutant	data source	% reported	% BDL	MCL	median	max	median DF	max DF
TDS	analyzed	100	0	500 ⁽⁺⁾	293,000	356,000	590	710
	digitized	68	0		318,000	481,000	640	960
Cl	analyzed	100	0	250 ⁽⁺⁾	183,000	211,000	730	840
	digitized	87	0		185,000	389,000	740	1600
Br	analyzed	100	0		1,950	2,970		
	digitized	NR	NR		NR	NR		
Ba	analyzed	100	0	2 ^(*)	4.12	22	2.06	11
	digitized	30	0		2.03	490	1.01	245
Sr	analyzed	100	0	10 ⁽⁻⁾	1,270	4,310	130	430
	digitized	NR	NR		NR	NR		
Ra	analyzed	100	0	5 ^(*)	1,230	2,270	250	450
	digitized	NR	NR		NR	NR		
Cr	analyzed	100	93	0.1 ^(*)	0.097	0.097	0.97	0.97
	digitized	19	60		0.019	0.021	0.19	0.21
Cd	analyzed	100	100	0.005 ^(*)	BDL	BDL		
	digitized	19	60		0.009	0.20	1.8	40
As	analyzed	100	72	0.01 ^(*)	0.147	0.161	16	20
	digitized	17	22		0.087	0.7	8.7	70
Pb	analyzed	100	57	0.015 ^(*)	0.099	0.432	6.6	29
	digitized	32	76		0.086	0.31	5.7	21
Cu	analyzed	100	71	1.3 ^(*)	0.963	3.27	0.74	2.5
	digitized	13	57		0.094	0.16	0.07	0.12
benzene	analyzed	NR	NR	0.005 ^(*)	NR	NR		
	digitized	36	53		0.023	0.053	4.6	11
DRO	analyzed	86	0		3.41	685		
	digitized	NR	NR		NR	NR		
GRO	analyzed	86	0		7.89	25.9		
	digitized	NR	NR		NR	NR		

^aResults are from 14 O&G wastewaters collected and analyzed from northwest PA and 53 digitized certificate of analyses from NY and PA. The percent of the wastewater pollutants reported in digitized certificate of analyses are shown along with regulated primary^(*), secondary⁽⁺⁾, or industrial effluent⁽⁻⁾ concentrations for drinking water and/or surface water. Of the values reported, the % of the results below detectable concentrations (BDLs) are calculated. Dilution factors (DF) represent the amount of O&G wastewater dilution needed to reach the maximum contaminant levels (MCLs) recommended for a receiving stream. DRO = diesel range organics; GRO = gas range organics; NR = not reported. All values are in mg/L except radium (pCi/L).

Ohio, Pennsylvania, and West Virginia state that no produced waters from formations developed with HVHF can be spread on roads (Table S4). Conventional and unconventional O&G wastewaters have organic and inorganic constituents that are similar.²⁸ However, wastewaters from unconventional O&G development may also include chemicals from the HVHF process that could be potentially more toxic than the formation specific constituents.²⁹

Chemical Characteristics of Oil and Gas Wastewater Spread on Roads. O&G wastewaters spread on roads in the northeast, U.S. (NY and PA) are chloride-rich fluids with sodium, calcium, magnesium, and strontium comprising greater than 90% of the total cation charge equivalents (Table 1; Table S5). Notably both the TDS and total radium concentrations are elevated compared to the 500 mg/L TDS and 5 pCi/L radium standards for drinking water, with median values over 293,000 mg/L and 1,230 pCi/L, respectively. Previous disposal of these wastewaters through treatment facilities into streams raised concerns of metal accumulation in stream sediments,^{8,30–32} salinity-driven toxicity impacts in receiving waterways,³³ and increased potential for disinfection byproduct formation in drinking water.³⁴ These same concerns also extend to roads treated with O&G wastewaters.^{7,8,11}

Chemical characterizations of the 14 O&G wastewaters collected for this study are consistent with formation brine from

conventional O&G formations. The Sr/Ca molar ratios and ⁸⁷Sr/⁸⁶Sr ratios (Table S5; Figure S1) for these 14 O&G wastewaters indicate that they were likely sourced from Lower Silurian or Upper Devonian age conventional O&G formations which generally have Sr/Ca < 0.05 and ⁸⁷Sr/⁸⁶Sr between 0.710 and 0.715.²⁸ Therefore, the wastewaters currently spread on roads in northwest PA appear to be in compliance with state regulations that only permit road spreading with O&G wastewaters from conventional gas formations.

Considering the chloride concentrations in the 14 O&G wastewaters and 53 certificate of analyses (Table 1), these fluids require 730 to 1,600 times dilution to prevent drinking water quality degradation around road spreading locations. Comparisons to primary and secondary standards show that TDS, chloride, strontium, and radium are the pollutants in O&G wastewaters that require the most dilution to reach maximum contaminant level (MCL) concentrations for drinking water (Table 1). Based on the data collected from the 14 O&G wastewaters spread on roads in northwest PA, radium requires more dilution (250–450 times dilution) than every contaminant in the wastewater except chloride and TDS. At least six of the 13 states with regulations for road spreading require a certificate of analysis before O&G waste is permitted for use on roads. However, there are no universal standards that limit the contaminant concentrations in O&G wastewaters applied to

roads (Table S4). Chloride concentrations are reported in nearly 87% of the certificates of analysis for O&G wastewaters spread on roads in NY and PA, while radium concentrations were never reported (Table 1).

Mobility of Oil and Gas Wastewater Contaminants after Road Application. Exposure to pollutants in O&G wastewaters spread on roads relates to their potential to be transported from the road. Laboratory experiments were conducted to determine the mobility of contaminants in O&G wastewaters applied to road materials (Figure 3). Most

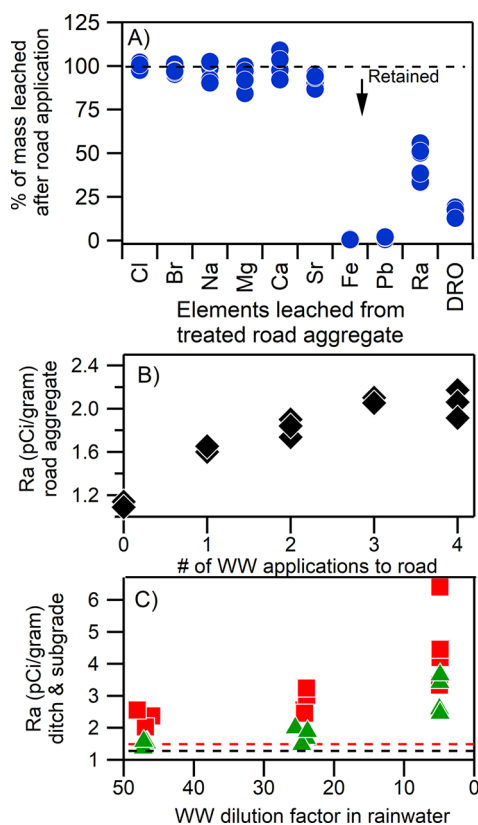


Figure 3. A) Lab experiments showing the percent of contaminant mass that was leached from road aggregate after O&G wastewater application, drying, and leaching with synthetic rainwater. Values below 100% indicate mass retention in the road aggregate. B) Radium in road aggregate after multiple O&G wastewater applications and rainwater leachings. C) Radium in ditch ■ (red) and subgrade ▲ (green) materials after reacting with O&G wastewater diluted with synthetic rainwater. The red and black dotted lines represent background radium activity in the ditch and subgrade materials, respectively.

contaminants in O&G wastewater applied to roads were leached with synthetic rainwater (chloride, bromide, sodium, magnesium, calcium, and strontium). In contrast, a few contaminants were retained in the road aggregate at greater than 99% (iron and lead) after rainwater leaching. Both radium and diesel range organics (DRO) displayed intermediate behavior. The majority of DRO (>75%) applied to roads was retained after rainwater leaching, while 50% of the radium was retained.

Both sorption and mineral precipitation reactions could be controlling the fate of iron and lead in the road aggregate. When O&G wastewaters are applied to roads, iron likely precipitates as iron oxides that are retained in the road material.

During leaching experiments, the pH of the synthetic rainwater (4.2) increased to approximately 7 after interacting with the treated road aggregate. This increase in pH would promote precipitation of iron hydroxides. The formation of iron oxides, which have a high sorption capacity for trace metals,³⁵ could also influence lead and radium retention in road aggregates. Studies modeling the reactive transport of trace metals in O&G wastewaters after spill events show that sorption and exchange processes are important in controlling the mobility of trace metals.³⁶ These modeling studies also highlight that precipitation reactions with hydroxide and carbonate minerals are the primary factors controlling the fate of trace metals such as lead.³⁶ Lead is known to cause physiological, biochemical, and behavioral dysfunctions in humans.³⁷ Therefore, further studies should explore how lead attenuates in road aggregate and if it is accumulating in dust or fine particulates around roads treated with O&G wastewaters.

O&G wastewaters used on roads also contain C₆–C₃₀ diesel range organics (DRO) that are largely retained in road aggregates even after multiple rainwater leaching events. Previous research showed that petroleum hydrocarbons in O&G wastewaters can migrate to drinking water aquifers following accidental spill events.³⁸ However, the majority of DRO in O&G wastewaters applied to roads are retained (>75%) in road aggregate after rainwater leaching (Figure 3A), potentially limiting migration to water resources. The high affinity of DRO for road aggregate can be attributed to the low water solubility of these C₆–C₃₀ hydrocarbons.³⁹ Dust originating from roads treated with O&G wastewaters could contain adsorbed hydrocarbons, representing another exposure pathway.

Radium in O&G wastewaters will accumulate in roads following spreading events but likely at concentrations below regulatory standards. Two previous studies analyzed radium accumulation around roads spread with O&G wastewaters, but findings were difficult to interpret because the O&G wastewater composition was unknown and radium concentrations in the road aggregate were not measured immediately before and after spreading.^{8,10} Leaching experiments with three O&G wastewaters (PA01, PA02, and PA03; Table S2) showed that approximately 45% of the radium applied to a road aggregate leached out after one application (Figure 3A). To test radium accumulation in the road aggregate after multiple applications, one O&G wastewater (PA03) was repeatedly applied to road aggregate, dried, and leached with synthetic rainwater. Radium concentrations in the road aggregate increased following multiple applications but approached a maximum concentration of 2 pCi/g after four treatments (Figure 3B).

Radium Release from Spreading O&G Wastewater on Roads. Radium not retained in the road aggregate will run off into ditches or underlying soils. To determine the potential radium concentrations in soils around roads following spreading and rain events, O&G wastewater was diluted with synthetic rainwater and reacted with ditch and road subgrade material (Figure 3C). At low dilution with rainwater (4 times dilution), radium in the O&G wastewaters accumulated up to 3–4 pCi/g in the ditch and subgrade materials. As the wastewater was diluted with more rainwater (>50 times dilution), less radium accumulated. In all cases, radium concentrations were below the regulatory standard of 5 pCi/g above background for remediating land surfaces impacted by radioactive waste materials (40 Code Federal Regulations §

192.12) or limiting materials that can be sent to landfills [(Ohio Revised Code § 3734.02 (P)(2)].

Where all the radium goes after spreading O&G wastewaters on roads is still an unanswered question. There are numerous processes that influence the mobility of radium in the environment, including salinity, pH, coprecipitation with minerals (e.g., with barite), and sorption onto clays, oxides, or pyrite.⁴⁰ While this study suggests that radium may not accumulate to concentrations above regulatory standards in areas where roads have been treated with O&G wastewaters, further work is needed to investigate if the radium will migrate to groundwater or accumulate in areas where mineral precipitation or sorption processes are favorable. For instance, radium sorption decreases as salinity increases.⁴⁰ After rain events, radium from O&G wastewaters spread on roads could migrate away from roads, becoming more diluted, and potentially sorb to clay minerals in a more favorable low salinity environment.

Spreading conventional O&G wastewaters on roads could release more radium to the environment than any other O&G wastewater disposal option. In Pennsylvania, more O&G wastewater is disposed of by wastewater treatment plants (180 million L in 2016) than road spreading (40 million L in 2016) (Figure 4). However, treated effluents from these facilities contain median radium concentrations of 14.5 pCi/L,⁴¹ levels that are close to the national primary drinking water

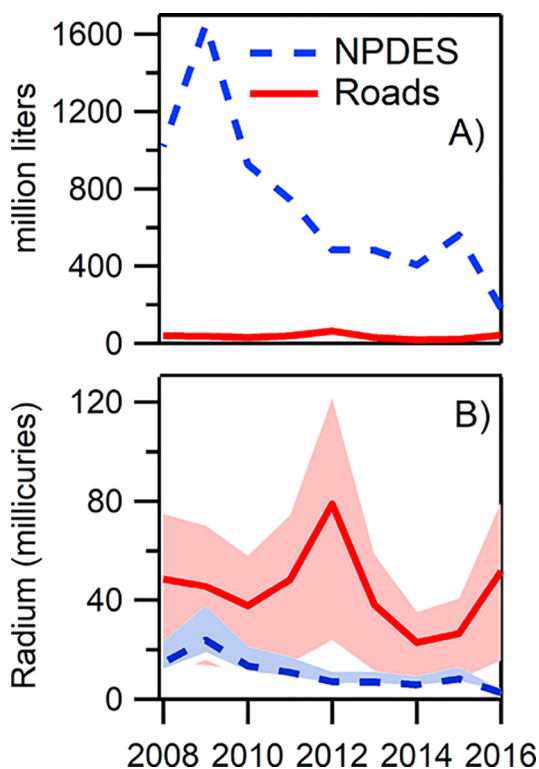


Figure 4. A) Volumes of O&G wastewater spread on roads or discharged through wastewater treatment plants with NPDES permits in Pennsylvania.⁶ B) Annual radium loads to the environment based on radium effluent concentrations reported for O&G wastewater treatment facilities⁴¹ and radium concentrations in 14 O&G wastewaters spread on Pennsylvania roads in 2017 (this study). Blue and red shaded regions represent loads based on the 25th–75th percentile radium concentrations. Solid and dotted lines represent median loads.

MCL of 5 pCi/L radium. In contrast, the O&G wastewaters spread on roads in northwest Pennsylvania had a median radium concentration of 1,230 pCi/L (Table 1; Table S5). For estimating radium loads to the environment, the known volumes of O&G wastewater disposed by these different disposal options were multiplied by the 25th percentile, median, and 75th percentile radium concentrations in treated wastewaters⁴¹ or wastewaters spread on roads (this study). In 2016, based on median radium concentrations, approximately 52 millicuries (mCi) of radium were spread on roads (Figure 4), whereas 2.6 mCi of radium were discharged through O&G wastewater treatment facilities. Although less O&G wastewaters is spread on roads, the release of radium could be much higher than the release of radium from wastewater treatment facilities.

Road spreading may also release more radium to the environment than spill events. While there is uncertainty in the number of O&G wastewater spills and their associated volumes,⁴² we used previously published data from 2008 to 2014 to estimate the total O&G wastewater spilled from unconventional O&G development in Pennsylvania. Only saltwater spill volumes from flowback, recycled, or produced water were included to reduce the contributions from other nonformation derived wastes such as hydraulic oils, fracturing chemicals, etc. From 2008 to 2014, O&G wastewater saltwater spill volumes were reported for 91 of the 256 incidents, with median spill volumes of 794 L.⁴² Assuming that unconventional O&G wastewaters contain a median radium concentration of 1550 pCi/L,²⁸ these incidents (from 2008 to 2014) released approximately 0.3 mCi of radium to the environment (median spill volume × 256 spills × radium concentration). Allowing for various assumptions for spill size, radium released from incidents in 2008–2014 ranged from 0.06 to 1.5 mCi (Table S6). In comparison, approximately 83 mCi of radium were discharged to rivers from O&G wastewater treatment facilities, while 320 mCi were spread on roads during that same seven year span. Although there has been considerable focus on spill events and discharges of O&G wastewaters from wastewater treatment plants into surface waters throughout the U.S.,³¹ our results demonstrate that from 2008 to 2014 road spreading may have released over 4 times more radium to the environment than O&G wastewater treatment facilities and potentially over 200 times more radium than spill events. In 2016, road spreading may have released 20 times more radium than O&G wastewater treatment facilities.

Aquatic and Human Toxicity Potential of O&G Wastewaters Used on Roads. While radium is a known carcinogen, organic compounds in O&G wastewaters also exhibit potential toxicity. Organics extracted from O&G wastewaters (PA01, PA02, and PA03) covering a range of DRO and GRO concentrations were tested for their potential to cause human toxicity. Mechanism and human cell-based assays detected that organic micropollutants in these samples could induce xenobiotic metabolism associated with the aryl hydrocarbon receptor (AhR) (Figure 5; Figure S2). PXR activation, which is also involved in regulating xenobiotic metabolism, was detected in two of the three O&G wastewaters tested (Figure S3). However, a minor response in the blank led to uncertainty in these PXR results. Several AhR and PXR agonists are associated with altering drug and xenobiotic metabolism in humans and causing hepatotoxicity and liver tumors in laboratory animals.^{43,44} There were no significant increases in activity of bioreceptor assays targeting endocrine disruption (ER α), oxidative stress (Nrf2), and inflammation

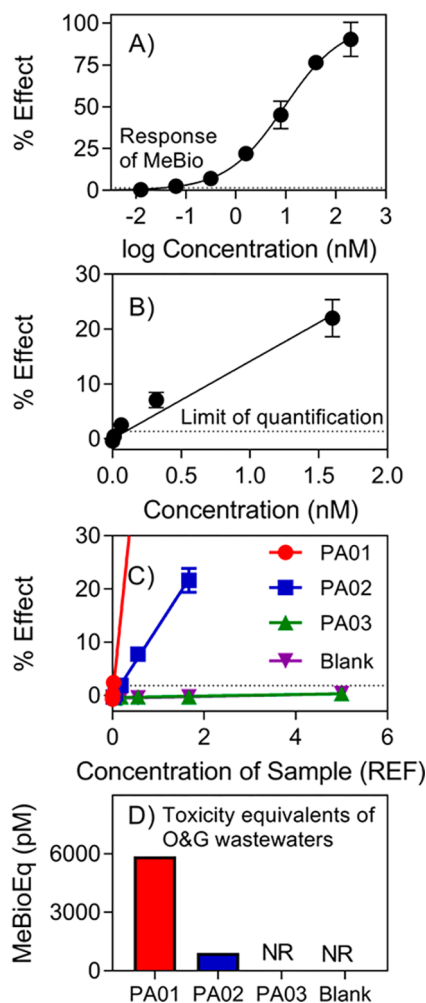


Figure 5. Induction to AhR human receptor by O&G wastewaters (PA01, PA02, and PA03). The response curve for the 1-methyl-6-bromoindirubin-3'-oxime (MeBio) reference compound is shown in parts A) and B). The % effect curves for the O&G wastewater samples are normalized to the minimum and maximum responses observed from the reference compound. Linear response data from 0 to 30% effect were used for calculating BEQs. PA01 induced the greatest response, while PA03 generated no response (NR).

(NFkB) (Table S7; Figures S4–S6). The absence of induction in these other bioassays could have been the result of REFs not high enough to generate responses or the lack of bioactive micropollutants in the O&G wastewaters.

Induction to AhR was influenced by the DRO and GRO concentrations in the O&G wastewaters. BEQs for the bioactive compounds in the samples were calculated in terms of a reference compound known to interact strongly with the receptor (MeBio for AhR) (Figure 5). Steeper linear response curves (Figure 5C) from 0 to 30% effect responses reflect higher BEQs within samples.²⁴ Organic compounds extracted from PA01 had the highest BEQ value for AhR (6000 pM MeBio). PA02 was also active toward AhR, while PA03 generated no AhR response. The BEQ values for all three samples corresponded to their concentrations of DRO and GRO. PA01 had the highest DRO and GRO concentrations (684 mg/L DRO; 23.5 mg/L GRO) and induced the greatest AhR response among the three wastewaters, while PA03 had the lowest DRO and GRO (0.60 mg/L DRO; 8.11 mg/L GRO) and generated no response to AhR. These data suggest

that induction to this potential human toxicity pathway could be reduced by setting DRO and GRO concentration limits to less than 10 mg/L for O&G wastewaters that can be applied to roads.

The O&G wastewater samples (not extracted into DCM solvent) were also shown to be toxic to *Daphnia magna* (Figure 6). *Daphnia magna*, the water flea, is an important aquatic

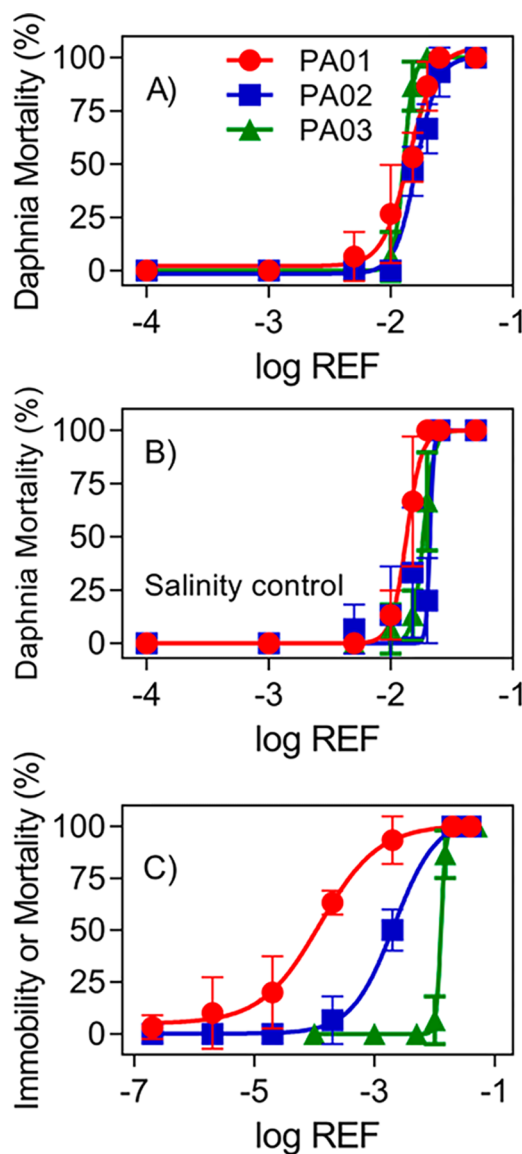


Figure 6. Acute lethal toxicity (Figure 6A) in *Daphnia magna* neonates after 48 hour exposure to oil and gas wastewater samples. *Daphnia* toxicity was also tested after exposure to control samples containing salinities that matched the O&G wastewaters (Figure 6B). The % immobile or dead *D. magna* were also measured after exposure to the O&G wastewaters.

organism in freshwater ecosystems⁴⁵ and a common ecotoxicological model organism for risk assessment and regulatory guidelines.²⁵ In the current study, all three O&G wastewaters yielded statistically similar toxicity to *Daphnia magna*, with LC₅₀ values ranging between REFs of 10^{-1.89} (PA01) and 10^{-1.77} (PA02) (Figure 6A; Table S7). Lower REFs reflect more toxic samples. For PA01 and PA02, there was no difference in toxicity between the O&G samples and their SW-matched

controls. However, for PA03 the SW-matched control was slightly less toxic (causing 50% mortality at a dilution factor of $10^{-1.75}$, relative to $10^{-1.89}$ for the O&G wastewater). We tried to determine if this difference in toxicity could be attributed to organic compounds in the O&G wastewaters that were not in the SW-matched controls. However, organic compounds extracted and concentrated by DCM from the three O&G wastewaters (Organics-only control) had no lethal toxicity responses to *Daphnia magna* over 48 h experiments, even in undiluted samples (Table S7). While these results suggest that the additional toxicity observed in PA03 versus its SW-matched control was not from the organic compounds present in PA03, liquid–liquid extractions into DCM may not have extracted polar organic compounds or concentrations of organic pollutants may have been too low to induce a toxic response. Overall, these data suggest that the high salt concentrations of the O&G wastewaters (Table 1) are the most significant factor for *Daphnia magna* toxicity, consistent with recent work examining the toxicity of hydraulic fracturing wastewaters.⁴⁶

During these experiments it was observed that *Daphnia* were physically immobile at the water surface in incubations with O&G wastewater. As the traditional toxicity end point of lethality does not account for physically immobile animals that are still alive, additional experiments were performed by measuring the effective concentrations causing immobility or toxicity. These new effect concentrations (EC_{50}) values were significantly higher than the LC_{50} values for the same samples. For example, the highest EC_{50} occurred in PA01 at an REF of $10^{-2.79}$, a value much greater than the LC_{50} ($10^{-1.95}$). The physical immobility observed was likely caused by organic compounds present in the O&G wastewater. Physical immobility was not observed in SW-controls but was observed in Organics-only controls (Table S7). No experiments were performed to identify the specific organic components responsible for the cessation of movement. However, these results demonstrate that using lethality as an end point for *Daphnia* toxicity studies may not capture the potential toxicity implications of *Daphnia* becoming immobile after interacting with organic compounds in O&G wastewater. Depending on how the mode of action is defined, normal laboratory assessments may underestimate the risk associated with physical immobility from oil and gas wastewaters. Physical immobilization will likely be a significant mechanism for potential toxicity to freshwater zooplankton.⁴⁷

Implications for Spreading O&G Wastewaters on Roads. Spreading O&G wastewater on roads can harm aquatic life and pose health risks to humans. Experiments simulating the application of O&G wastewater to road materials followed by leaching with synthetic rainwater demonstrated that the majority of contaminants are not retained in the road. Despite the presence of biologically active organic micropollutants that could promote cancer, the high salt concentrations in O&G wastewaters transported from the road to surface water after rain events are likely the major potential threat to aquatic toxicity. These wastewaters could require up to 1600 times dilution to reach drinking water quality standards or approximately 100 times dilution to reduce acute toxicity to aquatic organisms.

Some contaminants such as lead, radium, and organic micropollutants may also accumulate in roads treated with O&G wastewaters. Future work should study roads treated with O&G wastewaters to see how these contaminants partition into various grain sizes in road materials. Accumulation in fine

particulate dust particles could be a potential exposure pathway not discussed in this current study. This study showed that radium was partially retained in the road materials, but its concentration reached a plateau after multiple applications of O&G wastewater. Additional radium applied to radium-saturated road materials could be transported to surface water or groundwater or accumulate in local soils. The release of radium, a known carcinogen, is a potential threat to human health. In Pennsylvania, we found that radioactivity associated with radium released to the environment via road spreading exceeds the radioactivity of radium released by spill events or wastewater treatment plants. The spreading of O&G wastewaters on roads could be a significant contributor of inorganic and organic micropollutants to the environment and has been largely ignored in environmental studies on O&G development.

We propose three means to reduce the environmental impacts associated with spreading O&G wastewaters on roads: 1) Only O&G wastewaters that have been treated at wastewater treatment facilities should be considered for road spreading. The high calcium, sodium, and magnesium concentrations in O&G wastewaters are important for suppressing dust. In addition to the high salt concentrations, these wastewaters contain lead, radium, and organic compounds that could be potentially toxic. Wastewater treatment facilities are not designed to remove the high salt concentrations in O&G wastewaters. However, they can effectively remove radium, oil and grease, and other trace metals. 2) O&G wastewaters approved for road spreading should contain <60 pCi/L radium and <10 mg/L of total DRO and GRO, similar to other industrial wastewater effluent standards. No induction to human cell receptors was observed at DRO and GRO concentrations below 10 mg/L. In most cases, the chemical composition of O&G wastewater intended for road spreading must be submitted and approved before use. However, requirements for these chemical characterizations are relatively modest, vary widely between states, and currently do not include radium. Having chemical standards for O&G wastewaters that can be spread on roads could help reduce the potential toxicity concerns associated with this practice. 3) Affordable nontoxic dust suppressants should be developed and used. Many of the townships in Pennsylvania that spread O&G wastewaters on roads have low annual budgets for road maintenance. Based on the cost of many commercial dust suppressants, the annual township budgets would not be enough to maintain roads and suppress dust using these products. Solutions to this road maintenance issue could be to use alternative products or pave roads, but this would require substantial amounts of money that many townships do not possess. O&G wastewaters may be a viable and cheap option for suppressing dust, but as discussed in this study, there could be potential human and environmental health consequences of this practice. Some of these concerns could be mitigated by new regulatory standards as described above or by developing alternative low-cost products so townships can maintain their roads without the need to use O&G wastewaters.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00716.

Detailed method descriptions for performing bioassay testing; chemistry of saltwater matched controls for

Daphnia magna testing; results from human bioassays and aquatic toxicity tests (PDF)

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Notes

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Appendix 3 - Farnan et al., 2023

key findings: Both oil and gas brines and commercially calcium chloride brines were hypersaline and contained elevated concentrations of radium.

Organic contaminants in O&G brines were shown to be toxic to humans based on human receptor gene assays.



Toxicity and chemical composition of commercial road palliatives versus oil and gas produced waters[☆]

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ABSTRACT

Across the United States, road palliatives are applied to roads for maintenance operations that improve road safety. In the winter, solid rock salts and brine solutions are used to reduce the accumulation of snow and ice, while in the summer, dust suppressants are used to minimize fugitive dust emissions. Many of these products are chloride-based salts that have been linked to freshwater salinization, toxicity to aquatic organisms, and damage to infrastructure. To minimize these impacts, organic products have been gaining attention, though their widespread adoption has been limited due to their higher cost. In some states, using produced water from conventionally drilled oil and gas wells (OGPWs) on roads is permitted as a cost-effective alternative to commercial products, despite its typically elevated concentrations of heavy metals, radioactivity, and organic micropollutants. In this study, 17 road palliatives used for winter and summer road maintenance were collected and their chemical composition and potential human toxicity were characterized. Results from this study demonstrated that liquid brine solutions had elevated levels of trace metals (Zn, Cu, Sr, Li) that could pose risks to human and environmental health. The radium activity of liquid calcium chloride products was comparable to the activity of OGPWs and could be a significant source of radium to the environment. The organic fractions of evaluated OGPWs and chloride-based products posed little risk to human health. However, organic-based dust suppressants regulated toxicity pathways related to xenobiotic metabolism, lipid metabolism, endocrine disruption, and oxidative stress, indicating their use could lead to environmental harm and health risks to operators handling these products and residents living near treated roads.

1. Introduction

There are over 4.1 million miles (6.6 million kilometers) of paved and unpaved roads in the United States that are critical for the movement of goods and people throughout the country (Bureau of Transportation Statistics, 2020). Large volumes of chemical treatments are applied to roads during winter and summer maintenance operations to create a more stable driving surface and improve driver safety.

In colder climates, rock salt is applied to roads to remove the buildup of snow and ice on the driving surface. The use of rock salt is estimated to reduce traffic accidents between 42% and 87% (Kuemmel and Hanbali, 1992; Abohassan et al., 2021), drastically improving the safety of winter travel (Usman et al., 2010). Because of its effectiveness, the amount of rock salt used for winter road maintenance (WRM) has doubled since its widespread adoption in the 1950's (Kelly et al., 2019), and in recent years, between 15 and 32 million metric tons of rock salt

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are applied to roads in the US during the winter months (Kelly and Matos, 2017). Solid sodium chloride has been the most common salt used for WRM because of its availability and relatively low cost (Clear Roads Snow and Ice, 2021). Magnesium and calcium chlorides are more effective than sodium chloride because of their lower eutectic points and exothermic dissolution reactions. However, they are less commonly used for WRM because of more difficult handling procedures and increased cost (\$140/ton and \$111/ton for CaCl_2 and MgCl_2 , respectively) relative to NaCl (\$42/ton) (Kelting, 2010; Fay and Shi, 2012).

Recently, WRM has transitioned from deicing operations, which focuses on snow and ice removal as they accumulate, to anti-icing, which proactively applies a liquid brine solution to the road surface before the onset of precipitation. Anti-icing practices melt snow and ice immediately as it lands on the road and weakens attractive forces between any accumulation and the pavement surface, making it easier to remove by plow (Shi et al., 2012). Incorporation of anti-icing strategies in WRM has many advantages, including improved road safety and, because liquid brine solutions are less concentrated than solid rock salt, less material is required and total costs are reduced (Claros et al., 2021).

In the summer, unpaved roads are treated with chemical dust suppressants. Unpaved roads, which comprise over one-third of the road system in the United States (Bureau of Transportation Statistics, 2020), are a major source of inhalable ($<10 \mu\text{m}$, PM_{10}) particulate matter (Bureau of Transportation Statistics, 2002). Long-term exposure to PM_{10} has been linked to aggravated respiratory conditions like asthma (Bhuiyan et al., 2021; Keet et al., 2018) as well as severe health impacts such as heart attacks and death in at-risk populations (Khosravipour et al., 2022; Fang et al., 2013). When released to the environment, fugitive dust emissions can harm roadside vegetation and increase the turbidity of surface water which can impact aquatic biota (Trombulak and Frissell, 2000). As in winter maintenance, chloride-based salts like calcium and magnesium chloride are common materials for dust suppression (Piechota et al., 2002). These compounds increase the moisture content of the roadbed and bridge clay particles together, making it more difficult for wind and vehicle traffic to entrain fine particles (Piechota et al., 2002; Payne, 2018). While the exact amount of salt applied to unpaved roads for dust suppression is unknown (Kunz et al., 2022), more than 70% of surveyed road managers reported using some sort of chemical treatment (Kociolek, 2013). Therefore, it is likely that large volumes of chemical dust suppressants are spread on unpaved roads throughout the United States each year.

The widespread application of chloride salts to roads during summer and winter maintenance operations has been linked to the deterioration of infrastructure and the salinization of freshwater ecosystems across the United States (Dugan et al., 2020; Dugan et al., 2017; Houska). As the salts dissolve in snowmelt or precipitation, runoff is generated with elevated chloride concentrations. Exposure to high-salinity runoff can corrode metal components on vehicles (Li et al., 2013) and steel bridges (Křivý et al., 2019) and induce delamination and spalling of reinforced concrete (Kelting, 2010). Because of their high solubility, salt ions are mobile in the environment and rising salinity has been documented in freshwater resources across North America (Dugan et al., 2017). Most research has focused on salt used for WRM (Fay and Shi, 2012; Hintz and Relyea, 2019; Asensio et al., 2017; Nazari et al., 2015; Arnott et al., 2020), but rising salinity in streams and groundwater near roads treated with chloride-based dust suppressants has also been reported (Goodrich et al., 2009a; Eckstein, 2011; Bair and Digel, 1990). Freshwater salinization impacts drinking water resources (Eckstein, 2011; Pieper et al., 2018) and poses risks to roadside vegetation (Goodrich and Jacobi, 2012; Goodrich et al., 2009b) and aquatic organisms at all trophic levels (Hintz and Relyea, 2019; Arnott et al., 2020; Honarvar Nazari et al., 2021).

To avoid the negative impacts of chloride-based salts on infrastructure and environmental health, more attention has been given to organic-based products such as agriculture byproducts (e.g., beet juice and soybean processing), acetates, glycols, or succinates for WRM (Terry

et al., 2020). Vegetable oils, petroleum emulsions, or electrochemical products are becoming more common for dust suppression, especially in arid climates (Piechota et al., 2002). Despite their demonstrated efficacy, reduced salt loading to the environment, and decreased corrosivity, these products have not been widely incorporated into summer and winter maintenance strategies.

Because organic-based products are often more expensive than traditional chloride salts, it is not economically feasible to use them as a complete replacement for road maintenance. Highway agencies spend more than \$2 billion for winter maintenance annually (FHWA Road Weather Management), amounting to roughly \$750 per road mile for the whole winter season (i.e., multiple salt applications). In comparison, dust suppression can cost \$4000 to \$10,000 per road mile per application (Chase, 2022), amounting to possibly \$40,000 per road mile for the whole 'dust season' (i.e. one application per month from May to August).

To reduce the costs associated with dust suppression and WRM, certain states allow produced water from conventionally drilled oil and gas wells (OGPW) to be spread on roads (Tasker et al., 2018). OGPW is often offered as a free alternative to commercial products and is typically hypersaline (across the whole US, the median concentration of total dissolved solids is 61,600 mg/L) (Blondes et al., 2018). Because of its high salinity, OGPW retains moisture in the roadbed or lowers the freezing point of water in the same manner as commercial chloride products. However, OGPW often has elevated concentrations of heavy metals (Tasker et al., 2020), radioactivity (Lauer et al., 2018), and organic compounds (Tasker et al., 2018) that pose additional risks to environmental health.

The objective of this study was to characterize commercially available road palliatives used for dust suppression and WRM. Seventeen dust suppressants and deicing products were collected, and their inorganic and organic constituents were measured. The potential human toxicity of each product was characterized using cell-based assays. Results of this study allow highway agencies, road maintenance managers, and private landowners to make more informed decisions when selecting chemical road treatments and developing best management practices to better protect human and environmental health.

2. Methods and materials

2.1. Road palliative selection

Seventeen deicers and dust suppressants were collected that represented the major product categories used in the United States (Table 1). For most products, the supplier was contacted directly. Five products were OGPWs, two of which are commercially available (AquaSalina and LS25). The other three OGPW samples were provided under nondisclosure agreements from sources in northwestern Pennsylvania. OGPWs are currently proposed as coproducts for beneficial reuse as a dust suppressant under 25 Pa § 287.8 (Coproduct Determinations). Nine of the surveyed products are chloride brines marketed for dust suppression and deicing operations and were either provided by or purchased from the manufacturer. Three of these products (NaCl rock salt, Nature's Best, and Calcium Chloride Brine) were provided as solid materials. Prior to chemical and toxicological analyses, saturated solutions were prepared by adding excess product to deionized water ($>18.2 \text{ M}\Omega$) until the electrical conductivity (EC) of the solution stabilized. Two products (Soybean Oil and UltraBond) were organic-based dust suppressants.

2.2. Inorganic chemical analysis

The OGPW and brine samples were filtered ($<0.45 \mu\text{m}$, cellulose acetate) and acidified to $\text{pH} < 2$ with 1:1 double-distilled nitric acid for preservation prior to metals analysis. Major metals ($>1 \text{ mg/L}$) were measured on a Thermo iCAP 7400 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and trace metal concentrations ($<1 \text{ mg/L}$) were measured on a Thermo iCAP RQ Inductively Coupled-Mass

Table 1

Product descriptions for road palliatives surveyed in the present study.

Product Name	Supplier	Composition	CAS number
OGPW1	NDA	Conventional OGPW	None provided
OGPW2	NDA	Conventional OGPW	None provided
OGPW3	NDA	Conventional OGPW	None provided
LS25	Seneca Mineral	Conventional OGPW	10043-52-4; 7647-14-5; 7447-40-7; 7786-30-3
AquaSalina	Nature's Own Source, LLC	Conventional OGPW	7647-14-4; 10043-52-4; 7786-30-3; 7447-04-7
Calcium Chloride Brine	Fisher Scientific	Calcium Chloride	10043-52-4
Liquid Calcium Gold Blend	Jet Stream Fuels	Blended Chlorides	7647-14-4; 10043-52-4; 7786-30-3; 7447-04-7
Liquid Snow Shovel	All Season Innovations, LLC	Calcium chloride with polymer stabilizers, anti-spauling and corrosion inhibitors	010043-52-4
UltraCal	Environmental Energy Solutions, LLC	Calcium chloride brine	None provided
UltraMag	Environmental Energy Solutions, LLC	Magnesium chloride brine	None provided
30.7% MgCl ₂	Jet Stream Fuels	Magnesium chloride brine	None provided
Brine Before the Storm	RoadBrine.com	Chloride Brine	None provided
23% NaCl Brine	Penn State University	Sodium chloride brine	None provided
NaCl Rock Salt	Penn State University	Solid sodium chloride	None provided
Nature's Best	Envirotech Services, Inc.	Solid chlorides with proprietary additives	7647-14-5; 7791-18-6; 10043-52-4; 7447-40-7
UltraBond	Environmental Energy Solutions, LLC	Petroleum extracts; heavy naphthenic distillates	64742-11-6
Soybean Oil	Conneautville Soybean Crushing, LLC	Mechanically extracted, degummed soybean oil (>95% total fatty acid)	None provided

Product CAS numbers taken from provided safety data sheets. NDA: information withheld under non-disclosure agreement; OGPW: oil and gas produced water

Spectrometer (ICP-MS) following US Environmental Protection Agency (US EPA) Methods 6010D (U.S. Environmental Protection Agency, 2018a) and 200.8 (U.S. Environmental Protection Agency, 1994), respectively. To reduce instrument interferences from the high salinity matrix of the brines, all samples were diluted up to 100-fold for ICP-OES and up to 1000-fold for ICP-MS. Consistent instrument performance was ensured by using internal standards (Lu, Re, In, and Sc). Certified reference materials (USGS M-220 and SRM 1640A) were used to verify calibration curve accuracy and to validate calibration curve performance throughout the analytical run (<10% difference from expected values).

Because of matrix incompatibility, the organic samples were digested prior to metals analysis in a microwave digester. 0.5 g of Soybean Oil or 5 mL of UltraBond were added to a Teflon digestion vial. Up to 10 mL of double-distilled nitric acid and 3 mL of trace metal grade hydrochloric acid were added to each sample to achieve complete digestion. The temperature of the microwave was raised to 175 °C over a 15 min ramp with a 20 min final hold period. The digested samples were transferred to round-bottom Teflon vials, evaporated to a bead on a hot plate, and resuspended with deionized water to reduce the acid concentration to <5%.

Anions in unpreserved, filtered (<0.45 µm, cellulose acetate) samples were measured on a Dionex 1100 ion chromatograph following a modified US EPA Method 300.1 (U.S. Environmental Protection Agency, 1993). An AG-18 and AS-18 were used as the guard and analytical columns, respectively, and a DRS 600 suppressor and CRD 200 were used to minimize background conductivity and remove carbonate ion interferences. Because of sample incompatibility with the instrument, anions were not analyzed for Soybean Oil and UltraBond.

Radium isotopes (²²⁶Ra and ²²⁸Ra) were analyzed on a Canberra small anode germanium gamma spectrometer. Unfiltered, preserved (pH < 2) liquid samples were transferred directly to a 24 mL plastic vial and solid samples were first crushed in a mortar and pestle then sieved to <1.18 mm. All vials were sealed with paraffin tape and incubated for at least 21 days until secular equilibrium was achieved (Parekh et al., 2003). ²²⁶Ra was measured indirectly by averaging the activities of ²¹⁴Pb (295.2 and 351.0 keV) and ²¹⁴Bi (609.3 keV). ²²⁸Ra was measured using its ²²⁸Ac daughter product (911.1 keV). All samples were analyzed

in the same vial geometries used for the calibration standards, which were uranium ore tailings with known activities obtained through the Canadian Certified Reference Material Project.

2.3. Organic chemical analysis

To characterize organic compounds, aqueous samples were extracted following a modified US EPA Method 3510C (U.S. Environmental Protection Agency, 1996) using dichloromethane (DCM) as the extraction solvent. Because of its miscibility with DCM, the Soybean Oil was extracted according to Wu and Yu (2012) for the determination of polycyclic aromatic hydrocarbons in edible oils. Each sample was spiked with three surrogate standard compounds (*p*-terphenyl-d14, 2-fluorobiphenyl, and 2,4,6-tribromophenol) at a final extract concentration of 1000 pg/µL to calculate extraction recoveries. More extraction details can be found in the supplemental information.

All sample extracts were analyzed using comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (Pegasus 4D GCxGC-ToFMS with an Agilent 7890A gas chromatograph) equipped with a Gerstel Multipurpose Sampler. An Rxi-5Sil MS (60 m × 0.25 mm × 0.25 µm df) coupled to an Rxi-17Sil MS (1 m × 0.25 mm × 0.25 µm df) were used as the column ensemble. For Soybean Oil and the OGPW samples, the column order was switched to obtain better separations. An IP-deactivated guard column (0.6 m × 0.18 mm ID) was used as the transfer line to the ToFMS. MegaMix 8270 (Restek Corporation, Bellefonte, PA) and a mixture of alkanes ranging from C10–C28 were used for calibration. Targeted compounds were quantified using the average response factor (<20% RSD in response factors for calibration standards) (U.S. Environmental Protection Agency, 2018b). Method blanks and continuing calibration verification samples were analyzed to ensure accurate and consistent extraction and instrument performance. Instrument conditions can be found in the supplemental information.

2.4. Human nuclear receptor bioassays

Commercially available, cell-based toxicity assays using human target proteins (INDIGO Biosciences, State College, PA) were used to

determine the potential human toxicity of organic compounds extracted from the surveyed road palliatives. Each sample was separately extracted following a similar protocol used in the analysis of organic compounds. To keep the enrichment factor consistent across all samples and because it was not necessary to avoid high background concentrations, 200 mL of each sample was extracted and cleanup procedures were not used. All final extracts were exchanged into 200 µL of dimethyl sulfoxide (DMSO; 1000-fold enrichment factor). More detailed extraction procedures can be found in the supplemental information.

The bioassays were conducted using a two-tiered approach. Initially, the overt toxicity for each sample extract was determined using the CellTiter Glo 2.0 Cell Viability Assay (Tier 1). Results from first-tier experiments informed the proper sample dilution for second-tier experiments investigating sub-lethal effects using *in vitro* assays provided by INDIGO Biosciences. Induction of five toxicity pathways was investigated in second-tier bioassays: xenobiotic metabolism (XM), endocrine disruption (EDC), oxidative stress (OS), basal metabolism (BM), and lipid and energy metabolism (LEM). For each assay, multiple nuclear receptors were combined into a single cell line based on their involvement in each pathway (Table S1). The selected bioassays were chosen because they represent toxicity pathways commonly analyzed in wastewater and drinking water studies (Escher et al., 2014). Manufacturer’s protocols were used to conduct each assay, and more detail can be found in the supplemental information. Equivalent toxic responses were calculated using a reference compound analyzed on the same 96-well plate. Calibration curves, EC₅₀ values, and sample quantifications were performed in Prism 9.0 (GraphPad Software, Inc., San Diego, CA).

2.5. Statistics

Statistical comparisons made for radium and extract toxicity were performed in Prism 9.0 (GraphPad Software, Inc. San Diego, CA). For radium, unpaired, two-tailed Mann-Whitney tests were used to determine statistical significance at the 90% confidence level. For extract toxicities, a one-way ANOVA was used to compare each sample to a DMSO background control. Dunnett’s test was used to correct for multiple comparisons, and comparisons were made at the 95% confidence interval.

3. Results and discussion

3.1. Inorganic composition of road palliatives

As expected, the OGPWs and commercial brine samples were

hypersaline. Based on electrical conductivity (EC), the commercial brines and OGPWs were not statistically different ($P > 0.05$), though the average EC value for the commercial brines was higher than for the OGPWs (195 versus 159 mS/cm; Table 2). The dominant cations were sodium, calcium, and magnesium which were primarily balanced by chloride and, to a lesser extent, sulfate and bromide (Table 2). On average, the OGPWs (159 mS/cm) and the commercial brines (195 mS/cm) were 2.9- and 3.5-times saltier than seawater (average conductivity of 55 mS/cm (Clean Water Team (CWT), 2004)), respectively. The organic products had much lower salinities (Table 2). Because Soybean Oil is a non-aqueous liquid, the conductivity was not measured for this sample. The conductivity for UltraBond, an aqueous petroleum emulsion, was 0.2 mS/cm which is typical for freshwater that is likely used to manufacture this dust suppressant. The measured concentrations of salt ions agreed with product compositions reported on the manufacturer’s material safety data sheets.

Widespread application of chloride-based palliatives to roads poses risks to environmental health that have mostly been attributed to the hypersaline composition of these products. Salts are highly soluble, and as a result, tend to be mobilized from roads during precipitation events and periods of snowmelt (Bair and Digel, 1990; Galella et al., 2021; Schiff et al., 2016). These impacts tend to be highly localized, as the highest salt concentrations are often observed nearest to roads (Uliasz-Misiak et al., 2022; Bäckström et al., 2004; Monlux and Mitchell, 2007). Elevated salt in runoff water or introduced as a road palliative has been shown to reduce the permeability of roadside soils (Singh et al., 2003), while the accumulation of salt ions has induced foliar burns in roadside vegetation (Goodrich and Jacobi, 2012) and could result in community shifts toward salt-tolerant species (Fekete et al., 2022). Of particular concern are the high chloride concentrations in these products because of its toxic effects to many aquatic species (Dugan et al., 2017; Nazari et al., 2015). Freshwater chloride concentrations are expected to continue to rise in regions where salt is applied to roads and could exceed current regulatory limits designed to protect aquatic health by 2050 (Dugan et al., 2017). However, ecological impacts are likely to be observed beforehand, as chloride concentrations have been shown to induce toxic effects at concentrations much lower than current regulations (Arnott et al., 2020).

While many metals are essential nutrients in trace amounts, they can be toxic to aquatic organisms and human health at elevated concentrations. The concentration of quantifiable trace metals in the surveyed road palliatives is presented in Table 3. Regulatory thresholds from government agencies and guidelines set by Clear Roads and the Pacific Northwest Snowfighters (PNS), two organizations that develop best management practices for winter road management, are also shown. To

Table 2
Salinity and major ion concentrations of road palliatives surveyed in the present study. NA: Not analyzed; n.d.: below quantification limit.

	Analyte	pH	EC	Ca	Mg	Na	K	Cl ⁻	Br ⁻	SO ₄ ²⁻
	Units	std. units	mS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Conventional OGPWs	OGPW1	6.42	121	6760	1360	23,600	117	49,700	922	1480
	OGPW2	6.15	120	6860	1310	23,500	125	47,900	753	1340
	OGPW3	6.50	125	7150	1310	24,300	132	49,000	592	2000
	LS25	5.82	216	37,000	8920	47,700	4690	182,000	1890	n.d.
Commercial Brines	AquaSalina	3.48	215	38,300	7450	51,300	2190	182,000	1710	181
	Calcium Chloride Brine	9.95	197	78,200	n.d.	1460	3120	176,000	3770	7210
	Liquid Calcium Gold Blend	4.28	216	76,200	14,500	20,000	12,300	251,000	3740	n.d.
	Liquid Snow Shovel	9.38	172	108,000	16	2300	6180	273,000	3470	n.d.
	UltraCal	6.32	180	105,000	896	2500	5900	267,000	3430	n.d.
	UltraMag	5.38	143	218	71,000	1790	1980	234,000	3770	1460
	30.7% MgCl ₂	6.35	120	332	80,400	250	918	273,000	n.d.	n.d.
	Brine Before the Storm	6.62	188	1530	112	59,900	144	101,000	n.d.	452
	23% NaCl Brine	6.42	241	578	22	90,300	213	161,000	n.d.	1250
	NaCl Rock Salt	5.70	246	1340	29	102,000	280	183,000	n.d.	3150
	Nature’s Best	5.52	243	1390	1620	154,000	12,700	191,000	n.d.	5140
	Organic Products	Soybean Oil	NA	NA	0	0	n.d.	n.d.	NA	NA
UltraBond		3.99	0	2	0	6	1	NA	NA	NA

Table 3

Trace metal and radium characterizations of road palliatives surveyed in the present study. n.d.: Not detected; NA: Not analyzed; *Radium activities for NaCl Rock Salt and Nature's Best were determined on solid samples, and reported values are in pCi/kg.

Analyte	Fe	Mn	Sr	Ba	Al	Zn	Li	B	Cu	I	Pb	²²⁶ Ra	²²⁸ Ra	Combined Ra
Units	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	pCi/L*	pCi/L*	pCi/L*
<i>Conventional OGPWs</i>														
OGPW1	15	4.1	112	1.6	n.d.	1.8	2.5	0.8	NA	13.8	0.1	212	148	360
OGPW2	1.4	4.8	112	4.4	n.d.	1.9	2.9	1.0	NA	11.2	0.1	52	33	84
OGPW3	44	4.9	453	432	n.d.	2.2	13.3	1.3	NA	14.5	0.1	1800	696	2500
LS25	2.1	0.8	2210	4.6	5.0	1.9	164	119	9.1	23.7	0.1	1780	123	1900
AquaSalina	173	18.6	1250	3.1	10.6	7.0	42.9	18.2	4.5	19.9	0.1	651	392	1040
<i>Commercial Brines</i>														
Calcium Chloride Brine	3.4	0.1	1480	1.6	n.d.	1.8	57.9	22.0	NA	0.2	0.4	159	72	230
Liquid Calcium Gold Blend	4.1	1.6	3070	n.d.	5.2	2.2	91.4	520	8.7	47.5	0.1	615	87	702
Liquid Snow Shovel	6.3	n.d.	27340	1.8	7.0	1.7	114	43.2	8.7	4.9	0.1	258	167	425
UltraCal	6.5	n.d.	2610	3.9	5.5	3.9	111	42.1	9.0	2.5	0.3	255	163	418
UltraMag	0.5	1.9	6.2	0.3	3.8	3.0	0.6	34.5	5.0	n.d.	0.1	34	32	66
30.7% MgCl2	0.7	n.d.	0.4	3.8	3.0	1.0	n.d.	n.d.	4.6	n.d.	0.1	35	24	59
Brine Before the Storm	0.4	0.2	11.6	3.1	2.5	0.9	n.d.	n.d.	5.0	n.d.	0.1	30	31	61
23% NaCl Brine	1.1	0.1	5.1	0.1	2.3	0.8	n.d.	n.d.	4.3	n.d.	0.1	34	36	69
NaCl Rock Salt	4.4	0.1	12.6	0.1	2.4	0.8	n.d.	n.d.	4.5	n.d.	0.4	37	n.d.	37
Nature's Best	0.4	0.2	15.3	0.2	2.5	2.5	1.2	1.4	5.8	n.d.	0.1	29	n.d.	29
<i>Organic Products</i>														
Soybean Oil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	NA	n.d.	n.d.	n.d.	n.d.	n.d.
UltraBond	1.1	0.0	0.0	0.0	0.1	0.1	n.d.	0.0	0.1	1.5	0.0	34	n.d.	34
<i>Regulatory Thresholds</i>	1.0 ^a	0.05 ^b	4 ^c	2 ^b	0.05–0.2 ^b	0.12 ^a	0.01 ^c		1.3 ^b		0.0025 ^a	60 ^d	60 ^a	5 ^b
<i>PNS^e/Clear Roads Limits</i>				100.0		10.00			1.0		1.0			

^a EPA Aquatic Life Criteria.

^b EPA Drinking Water Standard.

^c USGS Human Based Screening Level.

^d Appendix B to 10 CFR Part 20

^e Pacific Northwest Snowfighters.

be listed on the Qualified Products List (QPL) published by PNS and Clear Roads, a product cannot exceed 1.0 mg/L for copper and lead or 100 mg/L for barium (Table 3). Of these elements, only copper exceeded its QPL limit in the OGPW and commercial brine samples. Though the toxicity of copper is dependent on a variety of water quality parameters like hardness and pH, chronic exposure to copper can negatively impact the survival, growth, and physiology of aquatic organisms (U.S. Environmental Protection Agency). Zinc did not exceed its respective QPL limit but did exceed the US EPA's recommended concentration for the protection of aquatic life (Table 3). Notably, the concentration of copper and zinc in the chloride brines in this study are an order of magnitude higher than values published in other studies (Li et al., 2019; Bäckström et al., 2003; Kelly et al., 2018; Titler and Curry, 2011). Otherwise, the compositions of the surveyed brine products in this study are comparable to what was previously reported, though it is important to note that only data for sodium chloride solutions have been published (Li et al., 2019; Bäckström et al., 2003; Kelly et al., 2018; Titler and Curry, 2011). The differences in trace metal concentrations reflect the wide variability in chemical composition of salts mined from different source rocks (Levelton Consultants Limited, 2007).

Of the measured trace metals, Li and Sr exceeded their health-based regulatory thresholds to the greatest degree (Table 3; 16,400- and 768-fold, respectively). The United States Geological Survey sets a Human Based Screening Level for analytes that do not have drinking water standards to provide a human-based context for potential risks to human health (United States Geological Survey). It is important to note that none of these products are intended for human consumption. However, it has been shown that salts applied to roads have contaminated adjacent groundwater (Eckstein, 2011). Therefore, risks to human health are possible in areas where chloride-based road palliatives are applied in high amounts near drinking water wells.

Many of the surveyed road palliatives had elevated radium activities. Radium is a naturally occurring carcinogen present in many natural soils

and waters. The highest concentrations were observed for the OGPW samples (84–2500 pCi/L) and were typical of conventional OGPW produced in the Appalachian Basin (Table 3) (Tasker et al., 2020). These activities were higher than those for magnesium chloride and sodium chloride brines, which ranged from 29 to 69 pCi/L ($P < 0.1$; Table 3). The Ra values for sodium chloride brines in this study are much lower than what was measured in Titler and Curry (2011) after adjusting their measured activity for a 23% solution (what is commonly used for WRM). The radium activities were not significantly different between calcium chloride brines (230–702 pCi/L) and the OGPWs, indicating that when these materials are used for road maintenance, they could contribute substantial amounts of radium to the environment.

The PNS/Clear Roads organizations do not set a limit on the radioactivity for products used in WRM (Clear Roads Snow and Ice, 2021), and often radium is not required to be analyzed for products used for dust suppression. Previous work has shown that Ra can be mobilized from aquifer materials in areas where sodium chloride is used for WRM, increasing the radioactivity of groundwater (Lindsey et al., 2021; McNaboe et al., 1007). However, little attention has been paid to the radium activity of materials initially applied to roads. In the case of the calcium chloride brines and OGPW surveyed in this study, these anthropogenic inputs could be substantial. For example, Tasker et al. (2018) determined that between 2008 and 2014, spreading OGPW on roads in Pennsylvania released 4-times more radium than centralized treatment facilities and potentially 200-times more than accidental spill events (Tasker et al., 2018). Therefore, application of OGPW and calcium chloride products to roads for WRM and dust suppression could be a significant but relatively understudied source of radium to the environment.

3.2. Organic composition of road palliatives

The organic composition of commercial products used for road

Table 4

Targeted semivolatile organic compounds quantified in surveyed road palliatives and known activation of surveyed toxic pathways: xenobiotic metabolism (XM), oxidative stress (OS), endocrine disruption (EDC), lipid and energy metabolism (LEM), and basal metabolism (BM). Activation of these pathways was determined with the CompTox Chemical Dashboard available through the US EPA (<https://comptox.epa.gov/dashboard/>).

Compound ($\mu\text{g/L}$)	Predicted Toxic Pathway	OGPW 1		OGPW 2		OGPW 3		Soybean Oil		
		Average	St.Dev.	Average	St.Dev.	Average	St.Dev.	Average	St.Dev.	
<i>Alkanes</i>	Decane	XM, OS	6	1	0.4	0	3220		0.1	0
	Docosane		8.8	1.8			18400	4310	1.3	1
	Dodecane		11.5	1.7	0.1		16700	12800	0.1	
	Heptacosane		8.4	0.6			8090	11100	1.1	0.8
	Hexacosane		7.2	0.7			14600	7090	3.4	2.9
	Hexadecane	XM, EDC, OS, LEM	9.8	1.1			7480	2570	0.2	0
	Octadecane		10	1.8			3630	784	0.3	0.1
	Tetradecane		11.5	2.1			7560	2360	0.1	0
<i>Aromatic Amines</i>	Carbazole	XM, EDC, LEM					0.6	0.1		
	Diphenylamine	XM, EDC, LEM, BM					8.4	0.6		
<i>PAHs</i>	Acenaphthene	BM, XM, EDC, LEM					4.5	0.6		
	Acenaphthylene	XM, EDC					12.0	6.4		
	Anthracene	XM, EDC, OS					4.8	5.3		
	Benz [a]anthracene	XM, EDC, LEM, OS, BM					1.3			
	Benzo [b]fluoranthene	XM, LEM, EDC, BM					0.9	0.2		
	Chrysene	XM, EDC, OS, BM					8.4	0.5		
	Fluoranthene	XM, LEM, EDC, BM	0.1				10.8	0.1		
	Fluorene	XM, OS, EDC, BM					24.6	29.8		
	Naphthalene	XM, LEM, BM	0.3				87.3	7.4		
	Naphthalene, 1-methyl-	EDC, LEM, BM					173	17.7		
	Naphthalene, 2-chloro-						3140			
Naphthalene, 2-methyl-						229	18.4			
<i>Phenols</i>	Phenanthrene	XM, EDC, LEM, BM, OS	0.8	0.1	0.3	0.1	75.8	2		
	Phenol, 2-methyl-	EDC, OS	6450		2620					
	Phenol, 2,4-dimethyl-	XM, EDC, OS	11.6		0.4	0.3	25.6			

maintenance has not been widely investigated, though many of these products are known to have either natural or added organic compounds to improve performance. OGPWs have been shown to contain petroleum hydrocarbons that originate from the formation being extracted (Tasker et al., 2018; Orem et al., 2007). These compounds include phenols, alkanes, and polycyclic aromatic hydrocarbons, which can induce toxic responses (Table 4). Many commercial brines have proprietary organic additives that aid in performance (e.g., anti-caking) or act as corrosion inhibitors (Shi et al., 2012; Schuler and Relyea, 2018a). Organic-based dust suppressants can be both non-petroleum or petroleum-based (e.g., Soybean Oil and UltraBond, respectively).

Organic compounds present in the surveyed road palliatives were analyzed using two-dimensional gas chromatography-time of flight mass spectrometry (GCxGC-ToFMS) after a liquid-liquid extraction with dichloromethane. This technique allows for resolution of organic compounds in complex matrices and has been successfully employed in analysis of OGPWs (Piotrowski et al., 2018). The solvent extraction demonstrated good recovery, with an average recovery of 66% (range 11–90%). However, surrogates were not recovered for soybean oil samples, which could be explained by removal during the extract cleanup step. No target compounds were detected above the limit of quantification (defined as the lowest calibration level) in any extraction method blank samples. Of the 83 targeted compounds analyzed, 25 were detected in the road palliatives surveyed, but only in the OGPW and Soybean Oil samples (Table 4). Straight-chain alkanes were the most abundant compound class. Surprisingly, the concentration of these compounds was lowest in the Soybean Oil which was expected to have the richest abundance of *n*-alkanes of all the surveyed products (Srbínovska et al., 2020). This is likely due to the Florosil cleanup step performed during the preparation of this sample as nonpolar alkanes would be poorly retained on this adsorbent.

Notably, polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, and aromatic amines were only detected in the OGPWs, albeit in low concentrations. Compound classes targeted in this study have been previously identified in produced water from conventional wells and likely have petrogenic origins (Orem et al., 2007; McLaughlin et al., 2020; Frolov et al., 1989). These compounds were found at highest

concentrations in OGPW 3 and OGPW 1 (Table 4). OGPW 3 was an untreated produced water sample and had a noticeable sheen that was not present on the other samples, explaining the relatively high concentrations of target compounds. OGPW 1 and OGPW 2 were paired samples, where the former was collected from the influent tank to a treatment facility and the latter was collected from the treated effluent. The concentrations of all quantified compounds were less in OGPW 2 relative to OGPW 1, indicating that many of the targeted compounds were removed during treatment. Assuming OGPW-based commercial products are treated before they are sold could explain why no targeted compounds were identified in LS25 and AquaSalina.

3.3. Potential risks of organic compounds in road palliatives to human health

The organic compounds extracted from road palliatives were tested for potential human toxicity using commercially available cell-based bioassays. While radium and salinity arguably pose the largest risks to environmental and human health because of their elevated concentrations in brines (Tables 2 and 3), the organic fraction of OGPWs and organic additives in these products have been shown to elicit toxic effects in human-based and model organism studies (Tasker et al., 2018; Schuler and Relyea, 2018a). Road maintenance workers are potentially exposed to organic compounds present in road palliatives during material handling and application to road surfaces. Additional exposure could occur from the inhalation of contaminated particulate matter released from roads (Honarvar Nazari et al., 2021).

Overt sample extract toxicity was investigated in tier 1 assays. The two organic dust suppressants, UltraBond and Soybean Oil, the three OGPW samples, and NaCl rock salt exhibit toxicities significantly higher than the 0.1% DMSO control ($P < 0.05$; Fig. S1). All other commercial brine samples, even ones with proprietary additives, did not induce significant toxic responses, consistent with the lack of identified organic compounds present in these samples (Table 4).

Sub-lethal toxic effects were investigated using *in vitro* bioassays that contained multiple nuclear receptors associated with a single toxicity pathway (Tier 2). To make direct comparisons between different road

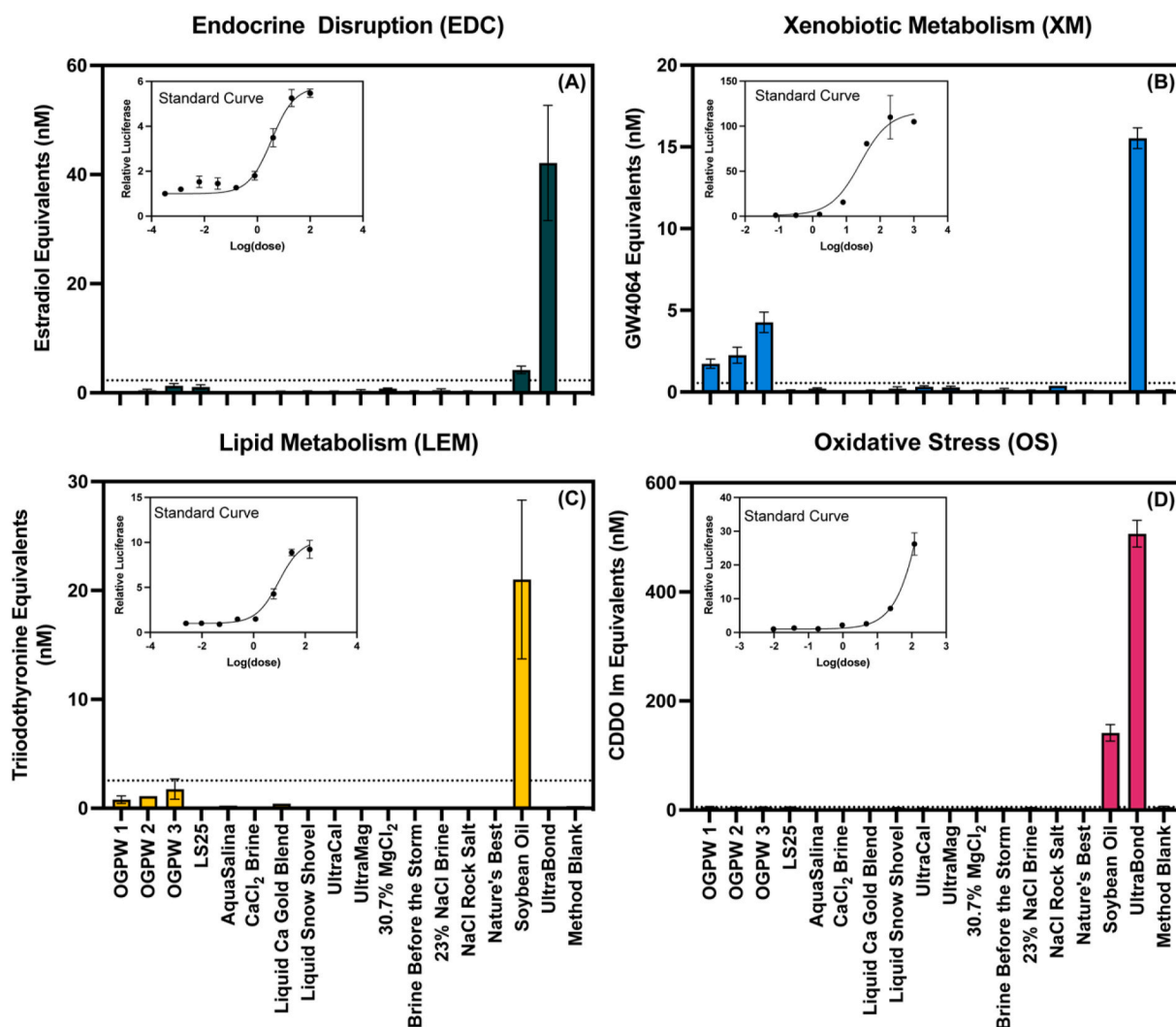


Fig. 1. Sub-lethal toxic responses of extracted organic compounds from road palliatives. The organic dust suppressants, Soybean Oil and UltraBond, contained the most biologically active compounds, while the three OGPWs did activate nuclear receptors related to xenobiotic metabolism. A) Activation of endocrine-disruption pathways; $EC_{50} = 3.48$ nM Estradiol, B) Activation of xenobiotic metabolism, $EC_{50} = 25.56$ nM GW4064, C) Activation of lipid metabolism, $EC_{50} = 9.45$ nM Triiodothyronine, D) Activation of oxidative stress pathways, $EC_{50} = 374.7$ nM CDDO Im. Dashed lines represent the limit of quantification. CAS numbers for reference compounds can be found in [Table S2](#).

palliatives, bioequivalent concentrations were calculated based on reference compounds used for each toxic pathway panel ([Table S2](#)). Results from these assays demonstrate that extracted organic compounds activated pathways associated with xenobiotic metabolism (XM), endocrine disruption (EDC), lipid and energy metabolism (LEM), and oxidative stress (OS) ([Fig. 1](#)). Nuclear receptors associated with basal metabolism (BM) were not strongly activated above the limit of quantification and are not included in [Fig. 1](#).

UltraBond contained extractable organic compounds that elicited the strongest toxic responses in the EDC, OS, and XM panels compared to the other surveyed products ([Fig. 1](#)). The highest response relative to the EC_{50} of the reference compound was observed for the EDC panel, with an estradiol equivalent concentration of 42.1 nM. Nrf2, the nuclear factor used in the OS panel, was also strongly activated by organic compounds present in UltraBond (506 nM CDDO Im; CAS numbers for all reference compounds listed in [Table S2](#)). The response observed in the XM panel (15.5 nM GW4064 equivalent concentration) was driven primarily by activation of the aryl hydrocarbon receptor (AhR, [Fig. S2](#)).

Organic compounds present in the OGPW samples only elicited quantifiable responses in the XM panel. The GW4064 equivalent concentrations for OGPW 1–3 ranged from 1.7 to 4.3 nM. Activation of the

XM panel was possibly driven by the alkanes, PAHs, and phenolic compounds quantified in the OGPW samples ([Table 4](#)). These compounds were measured in the parts-per-billion range, which could explain the low observed responses.

Organic compounds extracted from Soybean Oil generated the highest response for the LEM panel. Soybean Oil generated an elevated LEM response of 21.0 nM triiodothyronine equivalents. The number of quantifiable targeted organic compounds was limited in Soybean Oil ([Table 4](#)), possibly due to the Florosil cleanup step used during sample preparation. The manufacturer of the Soybean Oil used in this study reported it as >95% fatty acid, which is likely a combination of palmitic, stearic, oleic, linoleic, and linolenic acids ([Clemente and Cahoon, 2009](#)). Peroxisome Proliferator-Activated Receptors (PPARs) comprised the LEM panel. PPARs are useful in environmental monitoring studies as they are involved in inflammatory responses to organic contaminants exposure, but they are primarily activated by lipids, pathogenic lipoproteins, and essential fatty acids ([Varga et al., 2011](#)). In the case of Soybean Oil, the high concentration of fatty acids is likely responsible for the strong activation of this panel.

Though organic compounds extracted from UltraBond induced the highest toxic responses for the EDC, OS, and XM panels, none were

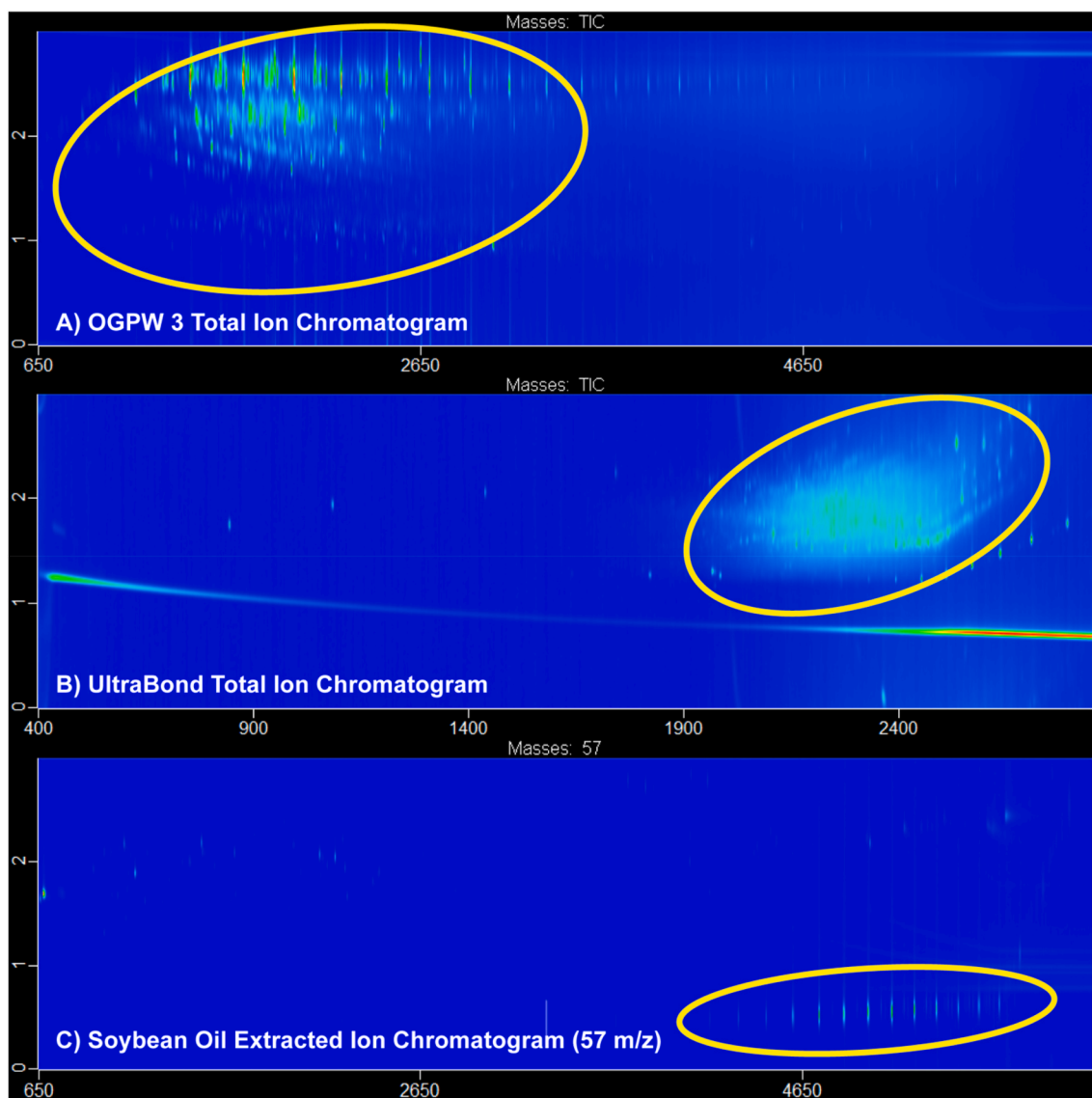


Fig. 2. Two-dimensional chromatograms of road palliatives that elicited toxic responses. A) OGPW 3 total ion chromatogram. Circled region indicates resolved but unidentified petroleum hydrocarbons. B) UltraBond total ion chromatogram. Circled region indicates unresolved matrix, likely heavy naphthenic distillate compounds. C) Soybean Oil extracted ion chromatogram (57 m/z). Circled region indicates heavy alkanes (>C20). Differences in x-axis are reflective of different chromatographic methods used to analyze samples.

positively identified by GCxGC-ToFMS (Table 4). However, an unresolved matrix was detected in the two-dimensional gas chromatogram (Fig. 2, panel B). In its associated material safety data sheet, UltraBond is described as a petroleum extract and contains heavy naphthenic distillates and proprietary ingredients. These compounds likely comprise the observed unresolved matrix. Heavy naphthenic distillates are a complex mixture of cyclic alkane hydrocarbons typically between C20–C50 (U.S. Environmental Protection Agency). Of particular concern are naphthenic acids, a mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids commonly associated with petroleum products and have many industrial applications (though use for dust suppression has not been previously reported) (Clemente and Fedorak, 2005). Naphthenic acids, specifically pentacyclic and polycyclic monoaromatic acids, were modeled to have reproductive and developmental affects (Scarlett et al., 2012). They have also been shown to activate the AhR nuclear receptor and the nuclear factor Nrf2, indicating induction of xenobiotic metabolism and oxidative stress pathways, respectively (Marentette et al., 2017; Wiseman et al., 2013). Naphthenic acids are analytically challenging to resolve even when using two-dimensional

gas chromatographic techniques (Jones et al., 2012). Though it was beyond the scope of this study to confirm the presence of naphthenic acids in UltraBond, it is possible that these compounds are inducing the observed sublethal effects.

4. Conclusions

Because high volumes of road palliatives are applied to road surfaces each year, investigation of the chemical composition and toxic effects of these products is necessary to understand their potential environmental and human health risks. Salts, the most common material used for road maintenance, are sourced from geologic formations that may contain heavy metal impurities (Fay and Shi, 2012). However, few studies report the concentration of metals in these products (Li et al., 2019) but instead focus on heavy metal mobilization from roadside soils (Schuler and Relyea, 2018a). In toxicological studies, toxic effects to aquatic organisms from rising salinity has been well documented (Nazari et al., 2015; Schuler and Relyea, 2018b; Schuler et al., 2017). The toxic effects of organic additives or organic products, however, has received less

attention (Kunz et al., 2022; Schuler and Relyea, 2018a). In this study, organic and inorganic composition of seventeen road palliatives were characterized and their potential toxicities were profiled.

Chloride-based products have the highest concentrations of salt ions, which are necessary for dust suppression and deicing activities. However, they also have elevated concentrations of trace metals (Cu, Sr, Li, Zn) that could pose risks to human and environmental health. Radium was elevated in the OGPWs and calcium chloride brines. Though elevated radium was not measured in sodium chloride products in the present study, they have been reported in other studies (Titler and Curry, 2011). Therefore, chloride-based road palliatives could be a significant source of radium to the environment because of their widespread application. The organic composition of brine-based products likely poses little risk to human health. Only organic compounds extracted from the OGPWs activated nuclear receptors associated with xenobiotic metabolism at low levels. Conversely, organic-based dust suppressants induced the highest toxic responses. Soybean Oil activated nuclear receptors in lipid metabolism, which is likely due to its high concentration of fatty acids. UltraBond, a petroleum emulsion used for dust suppression, activated pathways involved in xenobiotic metabolism, endocrine disruption, and oxidative stress, which could be due to the presence of naphthenic acids. UltraBond likely poses the largest health risks to road maintenance workers handling the dust suppressant during application.

Credit roles

James Farnan: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **John P. Vanden Heuvel:** Formal analysis, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Frank L. Dorman:** Resources. **Nathaniel R. Warner:** Conceptualization, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing. **William D. Burgos:** Conceptualization, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.122184>.

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Appendix 4 - Stallworth et al., 2020

key findings: A laboratory-scale method to measure dust generated from gravel roads was validated in the field using the same equipment mounted on the back of a car while driven along a gravel road.

Synthetic brines of sodium chloride, calcium chloride, and magnesium chloride were tested to compare their ability to reduce dust generation. The presence of sodium decreased or eliminated the efficacy of dust suppression.

Laboratory Method to Assess Efficacy of Dust Suppressants for Dirt and Gravel Roads

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Abstract

Particulate matter (PM) generated from dirt and gravel roads is a concern for both human and environmental health. To help reduce the amount of PM generated, many states allow the use of water coproduced from oil and gas wells (i.e., brines) as road dust suppressants. However, few methods exist to quantify the effectiveness of these brines and other dust suppressants. Here we designed and tested a bench-scale method to test the efficacy of dust suppressants on dirt and gravel road materials. The Standard Proctor test was modified to create discs of road aggregate that could be treated with dust suppressant, dried, and then tumbled in a mechanical drum attached to an aerosol monitor that measured PM generated within the drum. Using two types of road aggregate (DSA and 2RC) and a combination of nine simulated brines, the effects of brine total dissolved solids (TDS), and sodium adsorption ratio (SAR) on dust suppression were calculated. The effects of moisture content and aggregate type were also observed. Higher TDS and lower SAR were found to be good predictors of dust-suppression effectiveness, with the degree of effectiveness partially dependent on the type of road aggregate. The test method provides a means to quickly and reproducibly compare effectiveness of dust suppressants, with other variables such as aggregate type and moisture content, to accurately estimate dust suppression. Comparisons of dust measurements collected within the laboratory and vehicle-based measurements offer the ability to relate laboratory results to conditions encountered on dirt and gravel roads.

Dust generated from dirt and gravel roads accounts for the emission of an estimated 35% of total particulate matter (PM) with a diameter of 10 μm or less (PM_{10}) in the United States (1, 2), where around 40% of roads are unpaved (3). PM can be generated from the road surface as a result of vehicle traffic, where large amounts of PM reduce visibility (4) and the deposition on private property can be an aesthetic issue for community members. Roads generate varying amounts of PM based on road maintenance, vehicle traffic, relative humidity, and road aggregate material. Although much of the PM creates hazards locally, PM_{10} or less can travel tens to thousands of kilometers (5). The U.S. Environmental Protection Agency (EPA) regulates both PM_{10} and $\text{PM}_{2.5}$, PM with a diameter of 10 or 2.5 μm or less, respectively. The deposition of suspended PM is of concern to aquatic and vegetative health (6–8), as is the interception of airborne PM by the human respiratory system (9). Although PM_{10} is referred to as the “coarse particulate” fraction, it can settle into the trachea or bronchi, exacerbating conditions such as asthma, chronic obstructive pulmonary

disease, and emphysema (5, 10). Particles between 1 μm and 5 μm are small enough to enter the bloodstream through the lungs, where they can cause cardiovascular issues and contribute to premature death (5).

The negative impacts of PM from dirt and gravel roads have motivated the usage of dust suppressants, which through several means control the generation and release of PM from a road surface. Water, the most basic suppressant, temporarily aggregates small particles, making them harder to entrain; organic (both petroleum and non-petroleum) products bind small particles; lignin products (such as paper industry byproducts) physically suppress dust by creating a barrier between the road

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surface and vehicle impact (11). One of the most common dust suppressants is brine (11). Brines contain high concentrations of metal salts (>34,000 parts per million total dissolved solids [TDS] [12]), including cations such as calcium, magnesium, and sodium. These ions are hygroscopic, and retain ambient moisture on the road surface (4), which aggregates smaller particles. Because of their divalent charge, calcium and magnesium can bridge/flocculate clay particles by attaching to negative binding sites on more than one clay particle (13). Typical commercial brine dust suppressants include magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$). In contrast, sodium chloride ($NaCl$) is not as hygroscopic as the divalent cations and cannot bridge clays; instead, monovalent sodium neutralizes clays as a result of the single-bond limit, which can cause dispersion (13), making it easier for these particles to be released as dust (14).

Although effective, commercial dust suppressants can be expensive, with in-place costs ranging from \$4,000 to \$10,000 per mile per application. For comparison, the Pennsylvania gas tax provides rural townships with approximately \$4,000 per mile of road, annually (15). Dirt and gravel roads occur primarily in rural areas, and the townships in charge of maintaining these roads often have small budgets and other priority road maintenance tasks, such as deicing and repair. Therefore, commercial products are seldom used. The need for low-cost dust suppression has led to a less expensive alternative—byproduct usage. In states with oil and gas development, regulations have developed to allow the disposal of oil and gas-produced water (OGPW) on dirt and gravel roads (16–18). OGPWs are fluids that often contain high concentrations of salts, natural radioactivity, and trace metals of concern that are brought to the surface along with the oil or gas that is extracted. Oil and gas drilling in the United States generates large volumes of produced water, around 21 billion barrels annually (in 2011) (19). The majority of OGPW is disposed via injection back into the ground, but in some areas disposal of this water can be challenging because treatment can be costly, and well injection options may be limited depending on the state (20). Use as a dust suppressant is an attractive beneficial use of OGPW because although its composition varies by source and region (19, 21, 22), it is generally high in TDS (21), and often contains high concentrations of calcium and magnesium.

Although OGPW may contain high concentrations of calcium and magnesium, several other constituents have led to concerns over its use on rural roads. First, naturally occurring constituents in OGPW such as lead, arsenic (17), diesel range organics (17, 23), and radium (12, 21, 22, 24) pose potential health risks to exposed populations near the treated roads. Although recent studies have investigated the health and environmental

risks of OGPW spreading (17, 25), it appears that little to no historical evidence exists on the efficacy of using OGPW as a dust suppressant (16, 26). The composition of OGPW varies widely by region (21, 27), and therefore the effectiveness of dust suppression likely also varies regionally (16, 26). For instance, OGPWs from the Appalachian Basin are typically high in sodium, which is not an effective dust suppressant. Although valuable, the current research method of field application and vehicle-based dust-generation measurements has limitations. Field studies are expensive, require large volumes of dust suppressant, do not always provide equivalent conditions for each test section, and can expose the environment to controversial test materials such as OGPW. A laboratory method was recently developed by University of Alaska Fairbanks to test dust-suppressant efficacy using dust column settling times (28). In this test, dust suppressants are added to road aggregate, the dust is released from the top of an 8-in. air-filled column, and the settling times for PM_{10} are measured. The faster the PM_{10} concentrations return to background levels, the greater the efficacy of the dust suppressant. For a more robust understanding of dust suppressant efficacy, additional test methods are needed.

The objectives of this study were: (1) design a bench-scale method to evaluate the efficacy of dust suppressants, (2) evaluate the method relative to vehicle-based methods, and (3) determine predictors of brine dust-suppressant effectiveness, to inform the potential for beneficial use of OGPW as a dust suppressant across the United States.

Materials and Methods

Materials

Two road aggregate materials were obtained for this study (Table 1). The first, driving surface aggregate (DSA), is a high-quality aggregate that meets Pennsylvania Department of Transportation (PennDOT) specifications for the distribution of particle sizes, as well as other quality and characteristic standards (29, 30). The DSA used in this study was mined from a limestone quarry in central Pennsylvania. The second road aggregate, specified by PennDOT as 2RC (29, 30), was obtained from a quarry in NW Pennsylvania where the majority of OGPW spreading for dust suppression historically occurred. DSA material was the aggregate to which suppressants were applied for all conditions, with the exception of six test conditions that were applied to discs made of 2RC material to examine the effects of road aggregate on dust generation. DSA has strict quality specifications on distribution of fine particle sizes, whereas 2RC specifications are more relaxed (29). Road aggregates DSA and 2RC were measured to quantify

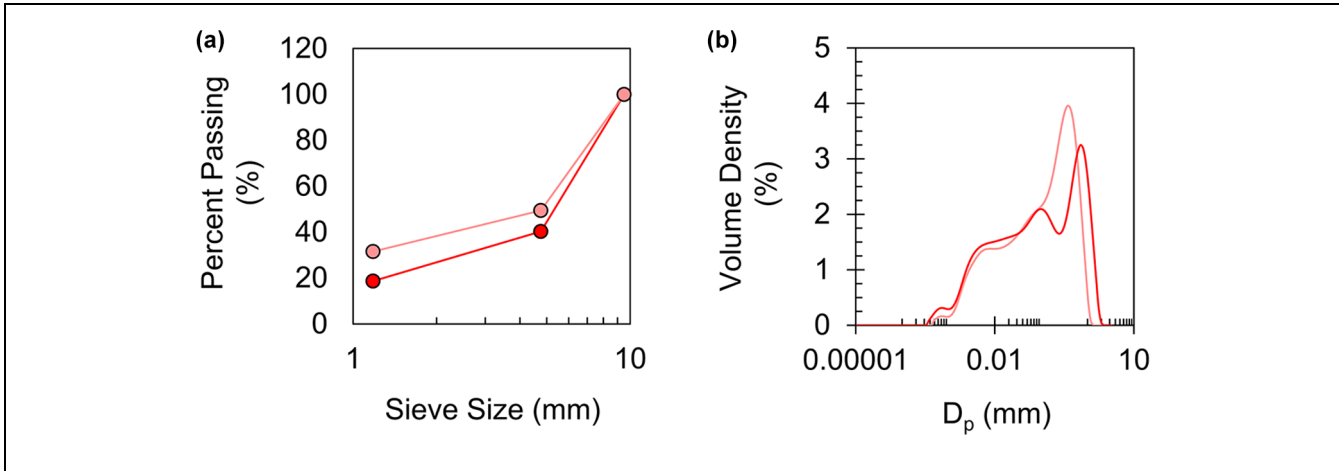


Figure 1. (a) Percent passing sieves for both driving surface aggregate and 2RC material and (b) volume density of the sand, silt, and clay fractions from Malvern Mastersizer. DSA is represented in red; 2RC is represented in light red.

Table 1. Particle Size Distributions of DSA and 2RC Road Aggregate Materials Used to Create Discs for Dust Generation Measurements

Bulk aggregate analysis ^a		DSA		2RC	
Mesh	Size (mm)	% Passing		% Passing	
		Original sample	Corrected sample	Original sample	Corrected sample
2"	50.8	100	na ^b	100	na ^b
3/8"	9.51	62	100	63	100
No. 4	4.76	40	40	49	49
No. 16	1.18	19	19	32	32
Pan	<1.18	0	0	0	0

Fine-grain particle analysis		DSA	2RC
Classification	Size range (mm)	Volume density (%)	Volume density (%)
Sand	0.05–2.00	58	62
Silt	0.002–0.05	37	35
Clay	<0.002	5	3

Note: DSA = driving surface aggregate; na = not applicable.

^aBased on averaged samples ($n_{\text{DSA}}=45$, $n_{\text{2RC}}=37$).

^bOriginal sample analysis discards any material < 50.8 mm; thereby none is present in the corrected sample analysis.

bulk aggregate and fine-grain size distribution. For bulk aggregate size distribution, during road aggregate disc synthesis (detailed in the following section), mass retained on the 50.8 mm (2"), 9.51 mm (3/8"), 4.76 mm (No. 4), and 1.18 mm (No. 16) sieves, and mass passing the 1.18 mm sieve were measured (Figure 1a and Table 1). For fine-grain particle size distribution, samples were first sieved to < 1.18 mm and sonicated for 1 min before analysis. Sand (0.05–2.00 mm), silt (0.002–0.05 mm), and clay (<0.002 mm) size fractions were then measured by laser diffraction using a Malvern Mastersizer 3000 (Figure 1b).

Both DSA and 2RC road aggregate material had relatively even distributions of the sieved size fractions

>1.18 mm, as well as silt, sand and “clay”-sized fractions (Table 1). The DSA material is almost exclusively limestone, so although clay-sized particles were detected, these particles are fine limestone. Compared with the DSA, the 2RC material is more heavily weighted to both the larger size fraction (>9.51 mm) and sand, silt, and clay-sized fractions. Within the sand, silt, and clay fractions, the 2RC had a higher percentage of sand (62%), but less clay (3%) than the DSA. As the 2RC material is primarily glacial till, the clay-sized fraction should represent specimen clay minerals (e.g., illite, smectite).

Metal chloride salts (NaCl, MgCl₂, CaCl₂) were prepared at varied concentrations and compositions with

Table 2. Composition of Simulated Brines used in this Study

Brine ID	SAR	TDS	Ca	Mg	Na	Cl	Ca	Mg	Na
		mg/L	mg/L	mg/L	mg/L	mg/L	meq/L	meq/L	meq/L
CaCl ₂	0.12	614,000	222,000	0	0	392,000	11,100	17	9
MgCl ₂	0.13	422,000	0	108,000	0	314,000	10	8,860	9
NaCl	1,410	299,000	0	0	118,000	181,000	10	17	5,110
High SAR	79	181,000	15,700	5,740	45,300	114,000	784	472	1,970
Mid SAR	14	163,000	40,900	5,610	11,100	106,000	2,040	462	482
Low SAR	2	160,000	48,300	5,570	1,830	104,000	2,410	458	80
Mid SAR–High TDS	15	299,000	69,900	15,700	17,300	196,000	3,490	1,290	751
Mid SAR–Low/Mid TDS	14	75,100	10,900	6,660	7,440	50,100	542	548	324
Mid SAR–Low TDS	15	24,400	3,000	1,550	3,940	15,900	150	128	171

Note: SAR = sodium adsorption ratio; TDS = total dissolved solids.

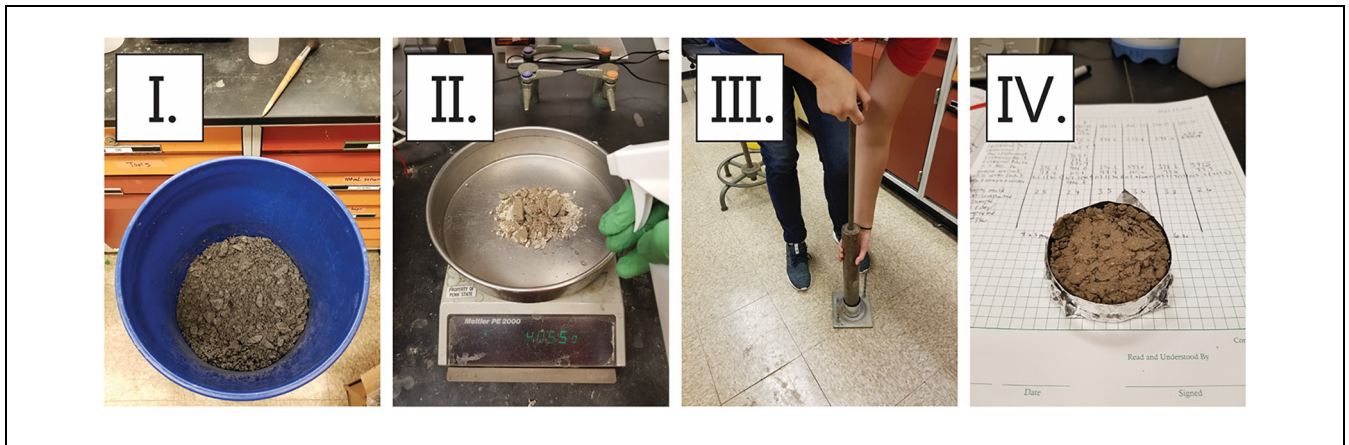


Figure 2. Road aggregate disc synthesis method; from (I) stock material collection and sieving; (II) moisture content equilibration; (III) modified Proctor compaction; and (IV) drying (finished road aggregate disc).

18 MΩ ultrapure water to represent commercial dust suppressants and OGPW, hereafter referred to as simulated brines. Nine simulated brines with a varying range of ratios of sodium, magnesium, and calcium chlorides were created to mimic combinations of TDS and sodium adsorption ratio (SAR) that might be encountered in OGPW. Concentrations of major elements in both milligrams per liter (mg/L) and milliequivalents per liter (meq/L) for each simulated brine are included in Table 2. Three different variables influencing brine dust-suppression effectiveness were investigated using simulated brines: moisture content of the road aggregate, the SAR of the brine, and the TDS of the brine. Moisture tests were conducted by adding water to oven-dried, desiccated road aggregate discs. The SAR was calculated based on dissolved metal concentrations as follows:

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

TDS was calculated based on the sum of all dissolved ion concentrations (all in mg/L). Although the moisture content of the road and the SAR and TDS of a brine will likely covary across field sites, these variables were independently fixed for method development purposes.

Methods

Road Aggregate Discs. Cylindrical discs of road aggregate material were created using a modified version of ASTM D698, the Standard Proctor test, in conjunction with PennDOT PTM-106, to model a gravel road surface (Figure 2). First, 100 g of dry aggregate was sieved using the 50.8 mm (2"), 9.51 mm (3/8"), 4.76 mm (No. 4), and 1.18 mm (No. 16) sieves. Material greater than 50.8 mm was discarded. The mass of material greater than 9.51 mm was recorded, discarded, and replaced with a stock material of the aggregate with particles less than 9.51 mm and greater than 4.76 mm, biasing each disc toward smaller grain sizes than the true distribution of

the raw material, but maintaining the ratio of dust producing clay and sil-sized fractions to larger material. The mass retained on each sieve was recorded for one of every five discs synthesized to approximate the average distribution of particle sizes for each aggregate material (Table 1). The dried and sieved aggregate was then wetted, using 18 M Ω ultrapure water, to a specified moisture content, based either on specification or operational/field conditions. For DSA, samples were wetted to 5% moisture content, and 2RC samples were wetted to 8% moisture content (each approximately 1% lower than optimal field-recommended moisture content). Wetted samples were stirred to homogenize the water and aggregate. Homogenized samples were transferred to a mold with a diameter of 6.35 cm (2.5 in.) and an average height of 1.5 cm. Molds were created by wrapping aluminum foil around a steel cylinder. Once transferred, samples were then compacted using a soil Proctor hammer to provide a standardized application of compaction effort. The compaction effort was calculated as follows:

$$E = \frac{B * W_H * H_D}{V_M} \quad (2)$$

where

$E =$ Compaction Energy ($\frac{kN \cdot m}{m^3}$)

$B =$ No. of hammer blows (per layer of material)

$L =$ No. of layers of material

$W_H =$ Weight of hammer (kN)

$H_D =$ Height of drop (m)

$V_M =$ Volume of mold (m^3)

A compaction energy of 13,000 kN-m/ m^3 was delivered to all road aggregate discs. For a 100 g sample ($L = 1$; total aggregate volume, $V_M = 6.0 \times 10^{-5} m^3$), a total of $B = 5$ blows was used, where the hammer weight was $W_H = 24.47$ N, and the hammer drop height was $H_D = 304.8$ mm. The Standard Proctor compaction energy is 12,000 kN-m/ m^3 (ASTM D698). Once samples

were compacted, they were dried for 24 h at 60°C until samples reached constant weight. Dried samples were stored in an airtight container with desiccant until use.

Application of Dust Suppressants. Three variables influencing brine dust-suppressant effectiveness were investigated: road moisture content ($n = 6$ test conditions), SAR ($n = 6$), and TDS ($n = 4$). All test conditions were conducted in duplicate. For the moisture content tests, DSA samples were treated topically by wetting to 5% moisture content with 18 M Ω ultrapure water, allowing time for these, and then drying at 60°C until the discs were either 0.0%, 0.25%, 0.75%, 1.5%, 2.3%, or 3.0% moisture content (m/m). Moisture content tests did not include the addition of any salts. Six simulated brines were created to model a range of SAR values (Equation 1), from 0.12 to 1,410, and common commercial dust-suppressant products such as calcium chloride, magnesium chloride, and sodium chloride (Table 2). The Ca, Mg, and Na concentrations in the simulated brines were calculated based on the mass of calcium, magnesium, sodium chloride, or any combination of these, added to 18 M Ω ultrapure water. SAR values for simulated brines that did not contain Na, Ca, or Mg were calculated using a minimum detection limit in a brine of 100 mg/L for sodium, calcium, or magnesium. Three additional simulated brines were created to represent a range of brines with similar SAR values (14–15) but with varied TDS values (24,400–299,000 mg/L). In each simulated brine, major element ratios were chosen to mimic combinations of TDS and SAR that might be encountered in OGPW.

Road aggregate discs were topically treated with simulated brines in 1 mL increments using a pipette (Figure 3), allowed time for treatment to fully penetrate the road disc, and then oven-dried. For each material (DSA or 2RC), the amount of liquid required to penetrate a 100 g sample disc without causing liquid pooling at the bottom of the sample was operationally defined

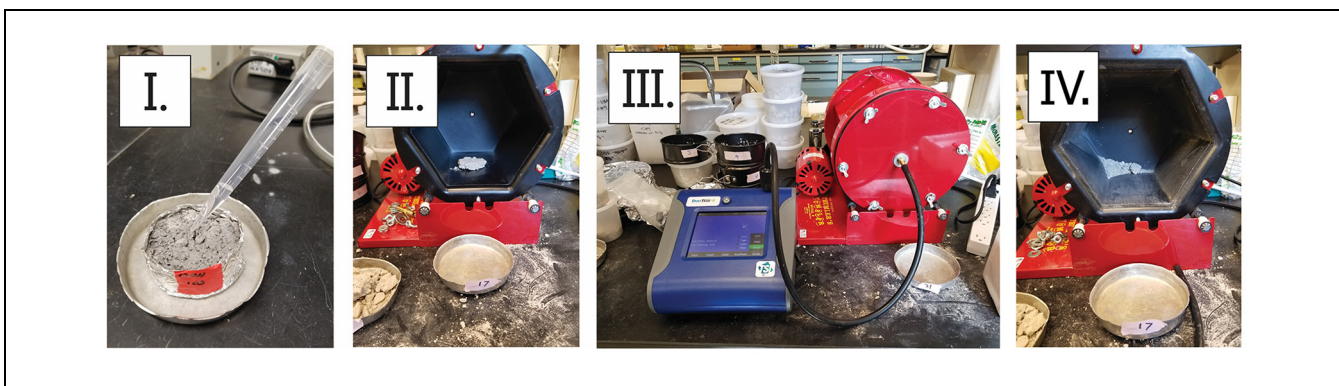


Figure 3. Dust-suppressant efficacy testing method; from (I) treatment of road aggregate discs with dust suppressants; (II) sample setup in rotary drum; (III) vehicle impact simulation and aerosol measurement, and (IV) aggregate disc at conclusion of test.

(analogous to water-holding capacity). For DSA discs, 5 mL of brine was applied and allowed to absorb for at least 10 min before drying. For 2RC discs, 8 mL of brine was applied and allowed to absorb for 40 min. These values were similar to application rates proposed by regulatory agencies. For example, the recommended CaCl_2 spreading rate is 1.6 L/m^2 (4). For a 6.35 cm disc as used in this study, this corresponds to a volume of 5 mL. The recommended rate for MgCl_2 is 2.3 L/m^2 (4), which corresponds to an applied volume of 7 mL. Former Pennsylvania regulations for OGPW spreading specified 0.5 gal/yd^2 (2.3 L/m^2) (17), which corresponded to 7 mL for a 6.35 cm disc. Following application of the simulated brines, samples were dried for 24 h at 60°C .

Mechanical Rotating Drum and Aerosol Measurement. A mechanical rotating drum (Model B Rotary Tumbler; Thumler's Tumbler) was chosen to model the impact of vehicle tires on a dirt and gravel road surface. The tumbler consisted of a hexagonal steel barrel with a removable rubber liner (20 cm deep, 9.53 cm each side). A hole was drilled into the center of the faceplate of the tumbler to attach a barbed nozzle, which did not rotate with the tumbler. A 3.18 mm hole was also drilled into the back of the tumbler liner to allow air entry. Mechanical rotating drums have been used in other studies to generate dust from rock samples (31). Other lab techniques that have measured dust-suppressant effectiveness either did not model vehicle traffic, or used vehicle-based instrumentation that may be difficult to obtain (32–34).

Treated and dried road aggregate discs were unwrapped from aluminum foil molds, placed into the tumbler, and once the faceplate was secured, a 3/16" (4.76 mm) inner diameter hose was attached to the barbed nozzle on the faceplate (Figure 3). The hose connected to an aerosol monitor (DustTrak II Aerosol Monitor 8530; TSI) with an impactor plate attached to exclude particles greater than PM_{10} . The rotary drum and aerosol monitor were positioned as to minimize kinks in the tubing. The DustTrak sampling rate was 3 L/min, and measurement frequency was every second. Background concentrations inside the tumbler were measured for 30 s before starting the tumbler. Once the tumbler was rotating, aerosol concentrations were measured for 3 min before ending aerosol sampling and tumbling. Three minutes was operationally defined to allow samples to reach a local equilibrium of dust generation as well as to avoid overwhelming the filter capabilities of the DustTrak, for maintenance purposes. The tumbler rotational speed was approximately 21 rpm. Ambient humidity in the lab was monitored using a digital hygrometer; although most tests were run at 25% humidity or less, values ranged from 25% to 70%.

Data Processing. With this laboratory setup, dust generation typically asymptotically approached a maximum value within 3 min (Figure 4). Based on this temporal response, dust-suppressant efficacy was calculated as the operationally defined "Average Maximum PM_{10} , or AM PM_{10} ." For each road aggregate disc, the dust concentration readings recorded every second between run time

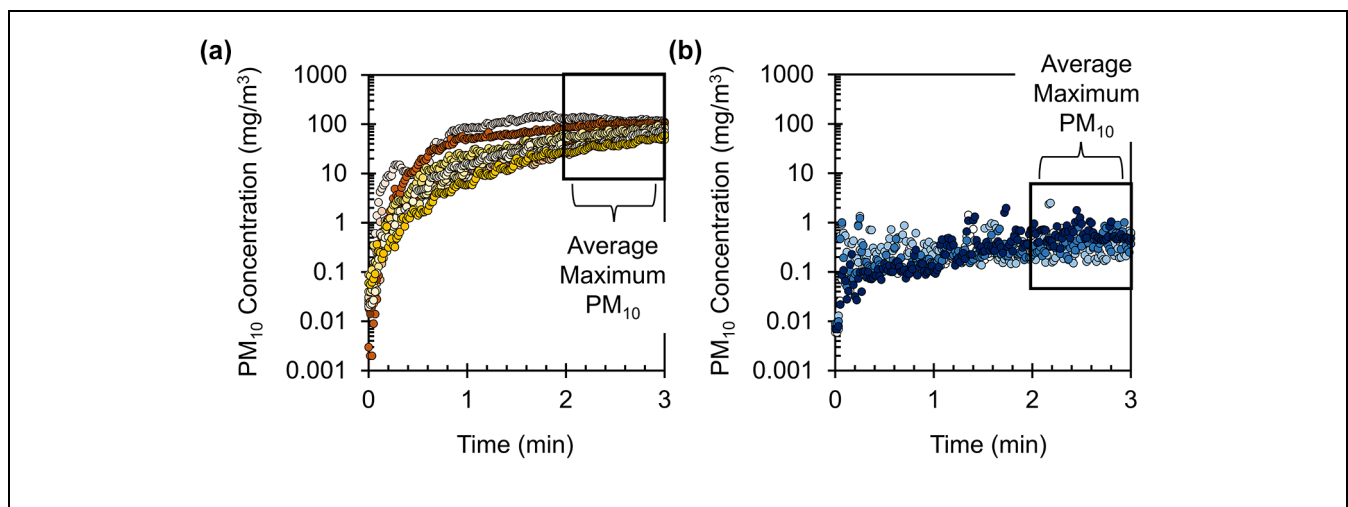


Figure 4. Schematic of data processing to compare dust-suppressant efficacy. Panel (a) shows results from nine replicate samples of the untreated control. Panel (b) shows results from four replicate samples of the CaCl_2 -treated samples. All readings were collected from individual road aggregate discs of driving surface aggregate (shown as unique colors). For the untreated samples, the mean \pm standard deviation of the Average Maximum PM_{10} was $68 \pm 15 \text{ mg/m}^3$. For the CaCl_2 -treated samples, the mean \pm standard deviation of the Average Maximum PM_{10} was $0.4 \pm 0.1 \text{ mg/m}^3$.

2:00 and 3:00 min:sec were averaged ($i = 61$) to calculate the “Average Maximum PM_{10} .” For most samples, this value represented a local maximum level of dust generation (Figure 4). However, other samples did not reach a plateau or in some cases dust concentrations exceeded the upper detection limit of the DustTrak instrument (400 mg/m^3). For both cases, the AM PM_{10} was still calculated as the average of $i = 61$ readings. For very dusty samples, the maximum detection value of 400 mg/m^3 was input for every data point missing within the 2:00–3:00 min run time for that sample.

Statistical Analysis of Results. Several representative test conditions (e.g., no-treatment control or treatment with calcium chloride brine) were tested with several replicates to ensure repeatability of the method. In these cases the 61 readings of dust concentration (mg/m^3) reported from 2:00 to 3:00 of the test were averaged to determine AM PM_{10} for each test condition. Each individual test condition had an AM PM_{10} and associated standard deviation. In cases in which multiple samples under the same test condition were averaged to present a mean AM PM_{10} value, the standard deviation was calculated. Subsequent test conditions were run in duplicate. A linear regression was completed for the SAR, TDS, and moisture variables on the AM PM_{10} using the Data Analysis Toolpack from Microsoft Excel. Field moisture and aggregate material comparisons were also analyzed using linear regression. A p -value < 0.05 was considered significant.

Field Comparison Test. Field measurements of dust production from a DSA-surfaced road at different moisture contents were conducted to compare with laboratory-based measurements. Dust production was measured along a DSA-surfaced road in the Penn State University Experimental Forest in Huntingdon County, Pennsylvania using an integrated vehicle-mounted particulate-monitoring system. The primary monitoring instruments consist of two TSI DustTrak 8530 aerosol monitors (same model used for aerosol measurements in the laboratory), which have been used successfully by other researchers to assess dust emissions from unpaved roads (35–39). The integrated dust-monitoring system captures dust generation from both aerosol monitors, GPS location, and speed of the vehicle, as well as infrared road surface temperature and ambient air temperature. All data streams were processed through an Arduino microcontroller, compiled into a single data string, and recorded every second on a laptop computer (Figure 5).

During this study, the aerosol monitors were mounted on the back of a Chevy Traverse with the inlets set at approximately 1 m above the road surface to measure the dust concentration within the wake of the vehicle, similar to Edvardsson and Magnusson (38). The aerosol monitor

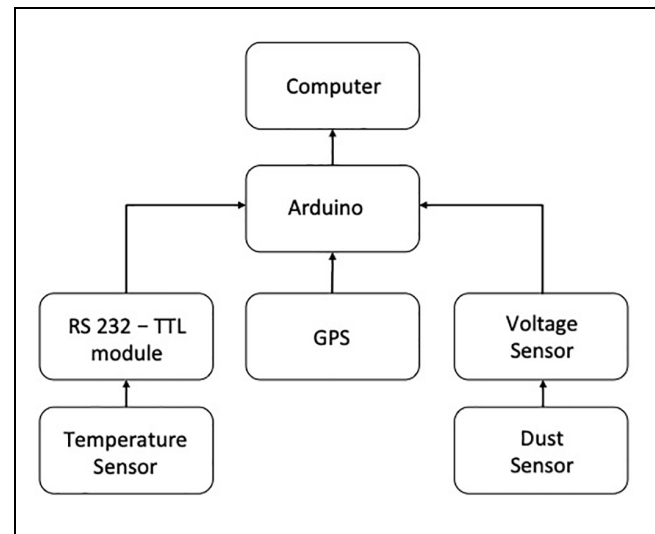


Figure 5. Schematic of data collection sensors for field aerosol monitoring.

was equipped with an impactor plate to exclude particles greater than PM_{10} . The vehicle maintained an average speed of 40 km/h (25 mph) during each test to control one variable known to increase dust generation (35). All testing was conducted between 1:00 p.m. and 3:00 p.m. each day to control weather variables such as temperature and humidity as presented in Table 3. Dust monitoring was conducted on three different days, and each day three consecutive vehicle sampling runs were made all in the same direction. The values for the three runs each day were then averaged to create spatially located data that represented the PM_{10} for each approximately 35 ft interval along the road. The road surface samples were sealed in airtight containers and returned to the laboratory, where moisture content (m/m) of the material was determined by oven-drying samples at 60°C until samples reached constant weight.

Results and Discussion

Variables Influencing Efficacy

Three primary variables influencing dust suppression effectiveness—moisture content of the road surface, and the SAR and TDS of the brine—were investigated using simulated brines. These factors were systematically varied to validate our proposed method of measuring dust generation potential, and to establish a baseline for future comparisons of OGPW dust suppression efficacy.

Moisture. Water, a dust suppressant in its own right, reduces dust generation by aggregating particles so that they are less likely to become airborne (11). Based on six laboratory test conditions with moisture contents that

Table 3. Shading, Moisture Content, Road and Air Temperature, and PM₁₀ Generated during Field Tests on DSA Road Aggregate

Shading	Road moisture content (%)	PM ₁₀ (mg/m ³)	Average road temp. (F)	Average air temp. (F)
No canopy	1.25	1.57	111	73
No canopy	0.73	1.51	127	87
No canopy	0.67	1.47	121	87
Full canopy	2.98	0.04	78	73
Full canopy	2.95	0.01	87	87
Full canopy	2.29	0.01	91	87
Full canopy	1.88	0.23	83	87

Note: DSA = driving surface aggregate; PM = particulate matter; temp. = temperature.

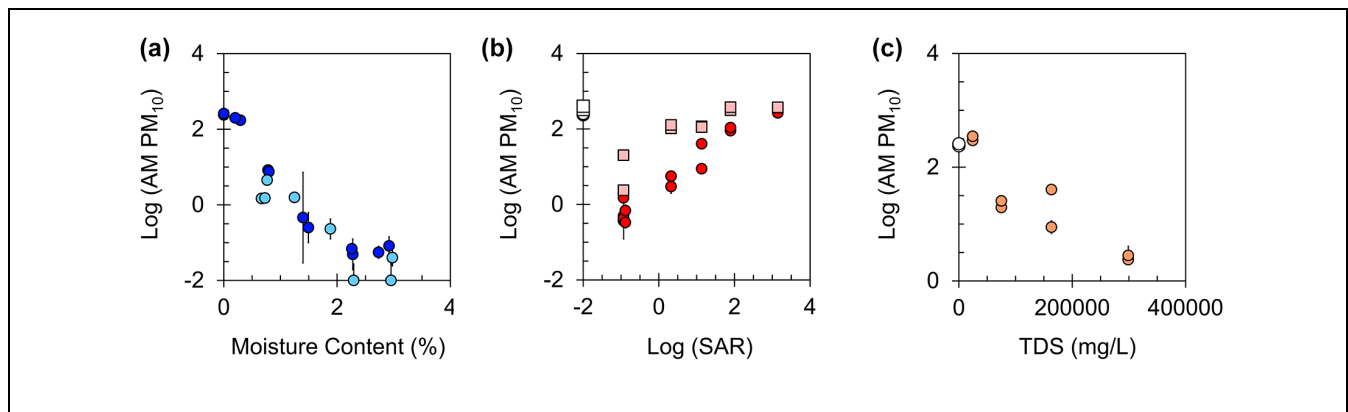


Figure 6. Summary of the effects of dust-suppressant treatments on dust generation. Factors varied in each test are plotted on the x-axis, and Average Maximum PM₁₀ values (AM PM₁₀) are plotted on the y-axis. All test conditions were carried out in duplicate with DSA or 2RC aggregate, as noted. Factors tested include: (a) Moisture content of untreated road aggregate (in %), (b) SAR, and (c) TDS. In (a), dark blue circles represent values collected using the laboratory method and light blue circles represent values collected using the field method. In (b), dark red circles represent DSA samples, and light red squares represent 2RC samples, with empty symbols representing data from untreated control samples (arbitrarily plotted at log [SAR] = -2). In (c), orange circles represent TDS test conditions, and empty circles represent data from untreated control samples.

Note: AM PM₁₀ = average maximum particulate matter with a diameter of 10mm or less; DSA = driving surface aggregate; PM = particulate matter; SAR = sodium adsorption ratio; TDS = total dissolved solids.

Table 4. Summary of Mechanistic Controls (Moisture Content, SAR, TDS) on Dust Generation for Both DSA and 2RC Road Aggregate

Variable	Aggregate material	AM PM ₁₀ (y)	Variable (x)	Model equation	p-value	R ²
Moisture	DSA (lab)	log	linear	$y = -1.4 \times x + 2.2$	1E-06	0.92
Moisture	DSA (field)	log	linear	$y = -1.0 \times x + 1.1$	1E-03	0.83
SAR	DSA	log	log	$y = 0.71 \times x + 0.42$	2E-09	0.96
SAR	2RC	log	log	$y = 0.41 \times x + 1.6$	2E-03	0.73
TDS	DSA	log	linear	$y = -6.6E-06 \times x + 2.3$	3E-03	0.80

Note: DSA = driving surface aggregate; SAR = sodium adsorption ratio; TDS = total dissolved solids.

ranged from 0% to 3.0%, dust generation decreased as moisture content increased (Figure 6a). The relationship appears to be significant ($p < 0.05$) and log-linear; linear changes in water content correspond to log change in dust generation, and can be modeled by the regression equation presented in Table 4. Samples that had a 0% moisture content had an AM PM₁₀ of $248 \pm 11 \text{ mg/m}^3$

dust ($n = 2$). At a relatively low moisture content of 1.5%, the dust generation was minimal (PM₁₀ of $0.4 \pm 0.6 \text{ mg/m}^3$), plateauing at a minimum dust generation between 2.3 and 3.0% moisture content (Figure 6a). Our results for samples with moisture contents of 1.5–3% correspond well with field results for suspended PM near gravel roads reported in Roberts et al. that showed

mean dust from 0.05 to 0.46 mg/m³ (40). Unfortunately, no moisture contents were reported in Roberts et al. (40). Road aggregate moisture content is pertinent to brines because they are aqueous solutions; roads newly wetted from the application of brines and OGPWs would produce less dust than roads that had not been treated for several days, weeks, and so forth. Likewise, small rain events that increase the moisture content of the road aggregate will suppress dust until the water evaporates. Based on these results with DSA aggregate, increasing moisture content to $\geq 2.3\%$ will lead to essentially complete dust suppression with quantifiable suppression at moisture contents as low as 0.25%. Trends measured in laboratory tests (dark blue circles) were consistent with the field tests (light blue circles) (Figure 6a, discussed below).

SAR. Six different simulated brines with SAR values that ranged from 0.12 to 1,410 were used to determine if SAR could predict dust-suppressant efficacy. As the ratio of monovalent sodium to divalent calcium and magnesium (i.e., SAR) increased, dust generation was also expected to increase (13, 14). As expected, the application of the magnesium and calcium chloride brines with no measurable sodium (lowest SAR values) resulted in the lowest dust generation (Figure 6b); 0.4 ± 0.1 mg/m³ and 0.5 ± 0.1 mg/m³, respectively. In contrast, a concentration of 317 ± 17 mg/m³ dust ($n = 2$) was measured after treating with sodium chloride, a value that surpassed even that of the untreated control (248 ± 11 mg/m³). In other words, sodium chloride destabilized the road aggregate or potentially crystalized and became part of the PM₁₀ measured in the instrument. The relationship between SAR and AM PM₁₀ follows a log-log relationship and can be modeled by the regression equation presented in Table 4. The relationship was significant ($p < 0.05$). These results are consistent with previous field-based studies (14) and highlight that the sodium content of dust suppressants must be considered in product selection. The influence of SAR applied to an alternative aggregate type (2RC) (Figure 6b, light red squares) was consistent with results from DSA (discussed below).

TDS. Although the effect of increasing SAR (and sodium) on dust generation was expected (13, 14), TDS values should also influence dust generation. Increasing the total application of calcium and magnesium can cause flocculation of fine particles (13). Four simulated fluids with similar SAR values (14–15) but varying TDS values (24,400–299,000 mg/L) were applied to road aggregate discs and tested for dust production. Overall, for brines with similar SAR, dust generation decreased as TDS increased (Figure 6c). The relationship follows a somewhat linear-log trend, is significant ($p < 0.05$), and

can be modeled by the regression equation presented in Table 4.

Field Test: Relating Lab Measurements to Field Measurements using Moisture Content

A field test was conducted to compare dust concentrations generated with the laboratory method with dust concentrations generated from an unpaved road. The road aggregate material (DSA) was the same for both laboratory and field tests with the notable exception that the laboratory aggregate was augmented as described in the methods (above). The moisture content of the DSA material was used to compare between field and laboratory tests. The trend of decreasing PM₁₀ generation with increasing moisture content was also observed in the field and is modeled by the relationship presented in Table 4 ($p < 0.05$). Notably, PM₁₀ levels generated in the laboratory were similar to PM₁₀ levels measured in the field at moisture content between 1% and 2%, but slightly higher than field measurements at both low (~0.7 %) and high (~3%) moisture content (Figure 6a). The estimation of PM₁₀ from the laboratory indicates that this method is valuable for providing *relative* comparisons between different dust suppressants and road conditions, and should not be used to predict exact concentrations of dust generated from unpaved roads. Importantly, the relative humidity could influence the dust generated from treated roadways (28).

Influence of Aggregate Material

The type of road aggregate material varies nationwide, based on locally available materials (41), and therefore the distribution of particle sizes, mineral composition, and interaction of aggregate particles with a dust suppressant may influence dust generation differently nationwide. It is desirable to maintain a small percentage of fines in a road aggregate to bind larger particles together, but too many fines in an aggregate leads to dust production when the road aggregate dries (4, 42, 43). To examine the effect of road aggregate material on dust generation, the same six simulated brines with varying SAR values that were applied to DSA samples were applied to 2RC road aggregate discs and measured. In all cases, the 2RC road aggregate discs generated more dust than the DSA road aggregate discs (Figure 6b). As with DSA, increasing dust generation with increasing SAR was observed with the 2RC road aggregate. However, at the high end of the SAR spectrum (NaCl), one of two 2RC road aggregate discs tested produced more dust than the maximum detection limit of the instrument (400 mg/m³) within the 3 min run time. Based on visual observations, the 2RC road aggregate discs

generally held together after mechanical impact, whereas the DSA samples tended to disintegrate. This was true even though the DSA samples produced less aerosol dust as compared with the 2RC samples. The greater mechanical integrity of 2RC could reflect its greater clay mineral content (Table 1). Although DSA had a higher content of clay-sized particles, these particles were fine limestone particles. Clay-sized particles in the 2RC samples included a high fraction of specimen clay minerals. We note that aggregate type could include many sub-factors, including clay content, optimal moisture/compaction conditions, and liquid-suppressant retention capacity. Our results reinforce the presumption that road aggregate material is a factor in dust generation. Therefore, it is necessary to test specific road materials with candidate dust suppressants because results will vary across road material.

Limitations

Future experiments could help eliminate limitations of the current method. First, in some cases the PM_{10} generated from an aggregate sample, usually in the case of the 2RC material, reached the DustTrak's upper limit of detection. The decision to input the maximum value, 400 mg/m^3 for any data points unable to be collected in the 2–3 min window may skew results for more dusty materials. Therefore, smaller cut points ($PM_{2.5}$, $PM_{1.0}$) in the aerosol-monitoring equipment could be used, as these particles are usually generated in smaller quantities than PM_{10} (almost 40% the level of emissions) (44). Another factor to consider when comparing dust suppressant effectiveness is relative humidity. Not presented in the main work, several test conditions run during a period of higher relative humidity within the laboratory produced similar trends, but with a narrower distribution of results between the two extremes of dust generation, calcium chloride-treated versus sodium chloride-treated samples. Relative humidity has implications for future laboratory tests, as well as the prediction of brine dust-suppressant efficacy. An expansion of aggregate materials tested with this method would also be beneficial. Finally, a more robust comparison across a variety of dust-suppressant candidates should be completed between the laboratory method presented here and dust measured in the field.

For laboratory testing, it would serve the user best to test batches of suppressants consecutively to limit variables such as ambient humidity and temperature. Performance controls should also be run with each batch of test conditions; for example, “new” batches of runs should include untreated control, NaCl, and $CaCl_2$ -treated samples to correct for changes in PM_{10} generation resulting from varying testing factors, such as ambient humidity. We estimate that researchers could perform the tumbler aerosol measurements on roughly

four discs per hour. Discs could be prepared and compacted in batches of 24–30, dried overnight, and then treated with dust suppressant. Thus, over a 3-day period, 24–30 road disc samples could be prepared, tested, and data analyzed.

Conclusion

The amount of PM generated from dirt and gravel roads can be reduced with dust suppressants. Decreased emissions of PM from roadways can reduce safety and human health risks, but few methods exist to quantify the efficacy of treatments in a relatively quick, economical, and reproducible method. Here, we designed a bench-scale method to test the efficacy of dust suppressants on dirt and gravel road materials. Field measurements of dust production at different moisture contents compared favorably with laboratory-based measurements. The results demonstrate a reproducible and efficient laboratory evaluation procedure that could analyze several test conditions per day. Higher TDS and lower SAR in simulated brines applied to road aggregate material generated less dust than fluids with lower TDS and higher SAR.

Dust-suppressant efficacy is affected not only by the chemical composition of the dust suppressant (e.g., SAR, TDS) but also by characteristics of the road aggregate material (e.g., particle size distribution and mineralogy). OGPWs that are candidates to be applied as dust suppressants should be tested in the laboratory before field applications. Laboratory test conditions should be performed with specific combinations of suppressants and road aggregates to mimic expected field conditions and demonstrate effectiveness on a case-by-case basis. This type of testing will save money relative to field testing methods, improve transportation safety by reducing dust generation, and protect the environment by limiting the application of ineffective suppressants.

Author Contributions

The authors confirm contribution to the paper as follows: study conception and design: AMS, EHC, WDB, and NRW; data collection: AMS, EHC; analysis and interpretation of results: AMS, EHC, WDB, and NRW; draft manuscript preparation: AMS, EHC, WDB, and NRW. All authors reviewed the results and approved the final version of the manuscript.

Declaration of Conflicting Interests

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Appendix 5 - Farnan et al., 2024

key findings: As a dust suppressant, oil & gas produced waters failed to meet the USEPA's criteria for beneficial use of industrial waste.



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Oil and gas produced waters fail to meet beneficial reuse recommendations for use as dust suppressants

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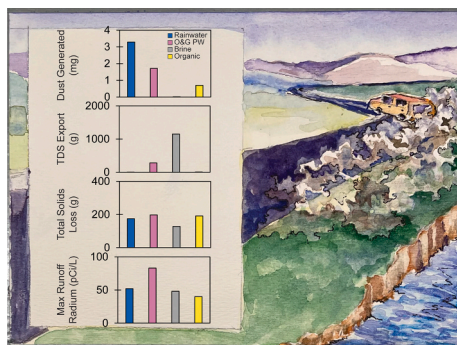
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HIGHLIGHTS

- Commercial dust suppressants were more effective than oil and gas produced water.
- High sodium concentrations in produced water destabilized the roadbed.
- All radium in produced water applied to roads was mobilized during storm events.
- Most salt ions were flushed from brine-treated roadbeds during storm events.
- Produced water does not meet the recommended criteria for beneficial reuse.

GRAPHICAL ABSTRACT



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ABSTRACT

Produced water from conventional oil and gas wells (O&G PW) is beneficially reused as an inexpensive alternative to commercial dust suppressants which minimize inhalable particulate matter (PM₁₀) from unpaved roads. The efficacy and environmental impacts of using O&G PW instead of commercial products have not been extensively investigated, although O&G PW has been used for dust suppression for decades and often has elevated concentrations of environmental pollutants. In this study, the effectiveness of O&G PW is compared to commercial products under variable humidity conditions by measuring total generated PM₁₀ emissions from treated road aggregate discs. To measure environmental impacts, model roadbeds were treated with six O&G PW and commercial products then subjected to a simulated two-year, 24-h storm event. Generated runoff water was collected and characterized. In efficacy studies, O&G PW offered variable dust reduction (10–85 %) compared to rainwater controls under high humidity (50 %) conditions but performed similarly or worse than controls when

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humidity was low (20 %). Conversely, all but two commercial products reduced dust emissions by over 90 % regardless of humidity. In rainfall-runoff experiments, roads treated with O&G PWs and CaCl₂ Brine generated runoff that was hypersaline, indicating that mobilization of soluble salts could contribute to freshwater salinization. Though most runoff concentrations were highest from roadbeds treated with CaCl₂ Brine, runoff from roadbeds treated with O&G PW had the highest concentrations of combined radium (83.6 pCi/L), sodium (3560 mg/L), and suspended solids (5330 mg/L). High sodium concentrations likely dispersed clay particles, which increased road mass loss by 47.2 kg solids/km/storm event compared to rainwater controls. Roadbeds treated with CaCl₂ Brine, which had low sodium concentrations, reduced solid road mass loss by 98.1 kg solids/km/storm event. Based on this study, O&G PW do not perform as well as commercial products and pose unique risks to environmental health.

1. Introduction

Industrial processes in the United States generate approximately 7.6 billion tons of waste and byproducts each year (Beneficial Use of Waste Materials: State of the Practice 2012, 2013). These waste streams can be difficult and expensive to manage, but they offer an opportunity for significant materials recovery. Rather than send these products directly for disposal, usually by landfilling (U.S. Environmental Protection Agency, 2006), they can be beneficially reused for energy production, construction materials, or as a substitute for raw materials in manufacturing operations. Beneficial reuse of waste products can reduce costs for both the waste generator and the manufacturer while decreasing energy usage and the need for continual extraction of virgin materials, resulting in significant environmental benefits. Guidance from the United States Environmental Protection Agency (US EPA) recommends that waste products proposed for beneficial reuse meet two criteria: 1) they perform as well as or better than the material being replaced, and 2) using the waste product does not increase the risk of harm to either the environment or human health (Methodology for Evaluating Beneficial Uses of Industrial Non-Hazardous Secondary Materials, 2016).

The oil and gas industry beneficially reuses approximately 47 % of the 3.3 trillion liters of produced water generated each year in the United States (Veil, 2015). Produced water returns to the surface alongside the extracted hydrocarbon after a well has been in production for a few weeks, and the composition of produced water typically reflects the source rock of the target formation (Tasker et al., 2020). Most (46 %) of the reused produced water is reinjected into producing wells for enhanced oil recovery (Veil, 2015). The remaining 1 % of recycled produced water is beneficially reused outside of the energy industry in a variety of ways, including irrigation, stream augmentation, livestock watering, and wildlife propagation (Veil, 2015; Cooper et al., 2022; Appendix B to 10 CFR 20, n.d.). Because the composition of produced water is highly variable both within and between formations, its management is a function of the water quality, location where it was generated, and regulations regarding its disposal or reuse.

As of 2018, 13 states permit produced water from conventional wells (wells drilled into permeable formations that permit hydrocarbons to readily flow to the surface) to be spread on roads for dust suppression (Tasker et al., 2018). An additional four states permit road spreading of conventional oil and gas produced water (O&G PW) on a case-by-case basis (Tasker et al., 2018). Where road spreading is permitted, O&G PW is often offered as a low-cost alternative to commercial dust suppressants which can be prohibitively expensive. The cost of calcium and magnesium brines, the two most common commercial dust suppressants, ranges from \$283–\$2020/acre. Organic products, such as ligno-sulfonate, vegetable oils, or petroleum emulsions, are more expensive (\$6700–\$24,300/acre) (Piechota et al., 2002). Annual dust suppression operations using commercial products can cost between \$4000 and \$10,000 per road mile per application (Chase, 2022). Over 1 million miles of unpaved roads in the United States could be treated with dust suppressants (Bureau of Transportation Statistics, 2020), and oftentimes unpaved roads require multiple treatments per dry season. Therefore, cost effectiveness is the primary consideration when selecting a dust

suppressant (Kociolek, 2013), and cheaper alternatives to commercial products are desirable.

Though expensive, reducing dust emissions from unpaved roads is critical in order to minimize the negative human and environmental health impacts of particulate matter (PM). Unpaved roads generate over one-third of inhalable PM (<10 µm, PM₁₀) in the United States (Bureau of Transportation Statistics, 2012), which can aggravate respiratory illnesses (U.S. Environmental Protection Agency, 2023a). PM smaller than 2.5 µm (PM_{2.5}) can penetrate deeper into the lung tissue, posing more serious health risks including decreased lung function (Zhang et al., 2020a), heart arrhythmia (Zhang et al., 2020b), heart attacks (Khosravipour et al., 2022), and premature death in at-risk populations (Fang et al., 2013). PM specifically from roadways has been shown to be more toxic than PM from other sources because of the co-contaminants associated with vehicular traffic (Park et al., 2018) such as trace metals from brake wear and corrosion of vehicle components (Haynes et al., 2020; Huber et al., 2016), tire wear particles (Baensch-Baltruschat et al., 2020), or toxic organic compounds from exhaust emissions (Hou and Li, 2020). To reduce human health risks from exposure to PM, the US EPA established 24-h average National Ambient Air Quality Standards enforceable through the Clean Air Act for PM₁₀ (150 µg/m³) and PM_{2.5} (35 µg/m³) (40 CFR 50, n.d.).

Dust suppressants reduce the amount of PM mobilized from the roadbed by changing the physical nature of the road surface. Generally, dust suppressants increase moisture retention or bind dust particles together (Piechota et al., 2002). O&G PW typically has high total dissolved solids (TDS) concentrations in states where it can be spread on roads (Veil, 2015), and is therefore assumed to be a suitable replacement for commercial brines (e.g., calcium and magnesium chloride). The salts in these brines are deliquescent and hygroscopic (Piechota et al., 2002), which improves the moisture retention of the roadbed and reduces dust emissions. Additionally, divalent cations like calcium and magnesium can act as bridges between negatively charged clay particles (Payne, 2018), further stabilizing the roadbed. Organic-based products, however, do not improve moisture retention but instead agglomerate road particles together and form a crust on the driving surface. This crust acts as a barrier between fine particles and vehicle tires or wind (Piechota et al., 2002; Steevens et al., 2007).

Although O&G PW has been used as a dust suppressant for the last 70 years (Payne, 2018), no scientific study has evaluated how well O&G PW meets the two criteria of beneficial reuse. O&G PW often contains elevated concentrations of environmental pollutants like radioactivity (mean 1095 pCi/L) (Blondes et al., 2019), TDS (100–400,000 mg/L) (McLaughlin et al., 2020), and petroleum hydrocarbons (up to 2000 mg/L) (Benko and Drewes, 2008) which complicates its reuse for other applications. Most recent studies focus on treatments like advanced oxidation processes (Alomar et al., 2022) or membrane technologies (Amakiri et al., 2022; Chen et al., 2022; Goh et al., 2022) to remove these contaminants of concern from O&G PW prior to reuse to reduce pressure on freshwater resources. Most discussion on potential reuse applications focus on agriculture (Samuel et al., 2022) or future drilling operations (Zhang et al., 2022) and only one recent review article mentions spreading O&G PW on roads for dust control (Cooper et al., 2022). Reuse of O&G PW as a dust suppressant remains understudied

despite its potential risks to environmental and human health.

Studies conducted in the last 5 years have begun to cast doubt on the effectiveness of O&G PW as a dust suppressant. One study found that roads treated with O&G PW in North Dakota produced the same amount of dust as roads left untreated (Graber et al., 2017). Similarly, Stallworth et al. (2020) determined that O&G PW underperformed compared to calcium and magnesium brines and organic products using a field-validated laboratory method that could be used to determine the efficacy of dust suppressants (Stallworth et al., 2020). However, those authors noted that variable humidity conditions could have affected some of their measurements (Stallworth et al., 2021).

While fugitive dust emissions pose risks to air quality and respiratory health, no study has investigated the fate of O&G PW-associated contaminants from roadbeds during storm events under real-world conditions. Tasker et al. (2018) found that pollutants in O&G PW (Cl, Br, Ca, Mg, Na, Sr, Ra) were leachable from loose road aggregate mixed with synthetic rainwater (Tasker et al., 2018), though the experimental conditions of this study were designed to maximize mobilization from the aggregate during multiple leaching events. Similarly, previous research has shown that the conductivity of surface water and groundwater increases near roads treated with commercial chloride brines and O&G PW (Goodrich et al., 2009a; Bair and Digel, 1990). However, the mobilization of contaminants from unpaved roads during single storm events is still unknown.

The objective of this study was to determine if O&G PW meets the recommended criteria for beneficial reuse, i.e., effective dust suppression with no increased risk to human health or the environment. In this study, experiments were conducted to evaluate: 1) dust suppressant efficacy and 2) mobilization of contaminants in runoff from treated roads during rain events. For efficacy experiments, O&G PW were compared to commercial dust suppressants using a modified method (i.e., with humidity control) based on the one presented in Stallworth et al. (2020) (Stallworth et al., 2020) to measure PM₁₀ emissions from roadbed aggregate. To test the second objective, a model roadbed was constructed and subjected to a simulated storm event. The generated runoff was collected and analyzed for a variety of chemical parameters to characterize the potential threats to water quality in freshwater resources adjacent to treated unpaved roads. The parameters for both efficacy and runoff experiments were chosen to reflect conditions in northwestern Pennsylvania, though the results are applicable to the broader Appalachian region and beyond. A portion of these data were compiled into a report submitted to the Pennsylvania Department of Environmental Protection (Burgos et al., 2022).

2. Methods

2.1. Dust suppressants

Twenty-one dust suppressants were evaluated that represent some of the major classes of dust suppressants used in the United States (Table S1). Five of the dust suppressants were calcium and magnesium chloride brines. One of these, CaCl₂ Brine, was prepared in the lab by dissolving solid calcium chloride (Fisher Science Education, >95 % mass/vol assay range) in distilled water. Because of kinetic limitations, this solution did not reach full saturation (~35 % m/m). Instead, the concentration of the CaCl₂ Brine ranged from 17.2 % to 25.4 %. The other four brines were commercial products sourced directly from the manufacturers (Commercial Brine 1–4). Ten dust suppressants were O&G PWs from Pennsylvania and acquired under nondisclosure agreements. Prior to use in efficacy experiments, the pH of acid-preserved O&G PW was increased to >4.2 with a combination of sodium hydroxide and calcium carbonate to minimize any effect on dust suppression. Addition of sodium hydroxide and calcium carbonate resulted in TDS increases of 1.3–4.0 % and changes in the sodium adsorption ratio (SAR) of ±0.03–0.32 %. The remaining five dust suppressants were organic products. Soybean Oil was reported as mechanically extracted,

degummed, and > 95 % fatty acid. The remaining four commercial organic products were either mixtures of hydrocarbons or synthetic polymers sourced from the manufacturers (see Table S1 in Appendix A for more details). Finally, Synthetic Rainwater was prepared by adding a 60/40 % (wt/wt) mixture of sulfuric acid/nitric acid to distilled water until pH = 4.2 according to US EPA Method 1312 (U.S. Environmental Protection Agency, 1994a). Experiments using synthetic rainwater represented natural wetting of the roadbed in dust suppression efficacy experiments and runoff generated from untreated roadbeds in rainfall-runoff experiments and was therefore used as a control for all comparisons.

2.2. Dust suppressant efficacy experiments

In efficacy experiments, road discs were tumbled and the PM₁₀ emissions were measured as described in Stallworth et al. (2020) (Stallworth et al., 2020). 2RC roadbed aggregate (100 g) was compacted into road discs using a modified Standard Proctor test. 2RC aggregate is a well-graded mix of crushed stone (48.3 % m/m), sand (42.2 % m/m), silt (6.6 % m/m), and clay (2.9 % m/m) sourced from a quarry in northwestern Pennsylvania. The dominant mineral phases were albite, calcite, clinocllore, dolomite, kaolinite, muscovite, and quartz. Gravel >9.51 mm prevented adequate compaction and was replaced with an equivalent mass of material in the second-largest size fraction (4.75 to 9.51 mm). The compacted disc was treated with 6 mL of dust suppressant, reflecting a 2 L/m² application rate. This application rate falls within the recommended range (1.4 to 4.5 L/m²) for most commercial dust suppressants (Piechota et al., 2002). The treated disc was then dried in a 60 °C oven until constant weight.

Experiments were conducted in a humidity-controlled chamber that was constructed from a plastic container securely attached to the laboratory bench equipped with a humidifier regulated by a humidity feedback sensor (Fig. S1). A mechanical rotating drum (Model B Rotary Tumbler, Thumler's Tumbler) was placed inside the chamber and connected to an aerosol monitor (DustTrak II Aerosol Monitor 8530; TSI) outfitted with an impactor plate to exclude particles >10 μm. The manufacturer-supplied impactor plate controls the airflow into the instrument so that 50 % of particles below the threshold (i.e., 10 μm) enter the photometer while the remaining particles are retained on the plate. The mechanical rotating drum was left open to equilibrate with the chamber's humidity level before sealing the tumbler and starting the test.

The aggregate disc was tumbled until PM₁₀ measurements stabilized, which usually took between two and three minutes. These data were averaged according to Eq. (1) to determine the Average Maximum PM₁₀ (AMPM₁₀):

$$AMPM_{10} (mg/m^3) = \sum_{i=1}^{61} \frac{(Observed PM_{10})_i}{61} \quad (1)$$

where (Observed PM₁₀)_i is the PM₁₀ (mg/m³) measured *i* seconds between the two- and three-minute marks (*n* = 61). For some tests, generated dust concentrations exceeded the maximum detection limit of the aerosol monitor (400 mg/m³). In these instances, the instrument detection limit was used to calculate AMPM₁₀ and for total PM₁₀ generation calculations.

Total PM₁₀ generated was calculated with a mass balance according to Eq. (2):

$$Total PM_{10} Generated (mg) = \sum_{i=1}^{180} C_{dust,i} \times V_i \quad (2)$$

where C_{dust,i} is the dust concentration and V_i is the volume of air measured at time *i* seconds throughout the entire 3-min test. The flow rate for the aerosol monitor was set to 3 L/min and the test was run for 180 s.

Efficacy experiments were conducted under low (20 %) and high (50 %) relative humidity conditions to represent roadbeds exposed to direct sun and those that are partially shaded, respectively. Ambient humidity partially controls roadbed moisture, which in turn affects dust generation. To determine the most representative daytime summer month humidity conditions for dust generation testing, historical climatological data were analyzed within northwestern Pennsylvania (see Appendix A).

2.3. Rainfall-runoff experiments

A laboratory-scale, stainless steel-lined frame (2.7 m long, 0.9 m wide, 0.3 m tall) was used to construct roadbeds for all rainfall-runoff experiments (Fig. S2). The 2RC aggregate used in the efficacy experiments was also used to construct each roadbed. The roadbed frame was initially filled with 23 cm of loose lift aggregate (6.5 % moisture content), then compacted to a 15 cm depth (95 % compaction minimum) using a motorized vibrating plate compactor. Roadbed compaction was verified in accordance with ASTM D6938 – Density and Moisture Content of In-Place Soil and Soil Aggregates Using Nuclear Methods (Shallow Depth). During compaction, a solid plastic insert was placed at the downgradient end of the frame to retain the aggregate. After compaction, the plastic insert was removed, and the aggregate was retained by a heavy gage stainless-steel screen with 6.4 mm openings.

A subset of six dust suppressants used in the efficacy experiments were chosen for rainfall-runoff experiments: O&G PW1, O&G PW2, O&G PW3, CaCl₂ Brine, Soybean Oil, and Synthetic Rainwater (as the control; Table S1). Dust suppressants were chosen based on sample availability, and in the case of the three O&G PWs, SAR and TDS values representative of O&G PW across the Appalachian Basin. The dust suppressant was applied to the constructed roadbed at a rate of 2.7 L/m² except for Soybean Oil, which was heated to 49 °C and applied at 1.4 L/m² to reflect typical field conditions (Chase, 2022). Once the roadbed was constructed and treated, it was positioned at a 5 % slope, representing the typical grade of an unpaved road from the crown to the edge. The treated roadbed rested under ambient conditions for ca. 20 h before the start of the rain event.

A rainfall simulator was designed to spray rainwater evenly over the roadbed, simulating a 2-year, 24-h, National Resources Conservation Service (NRCS) Type-II storm event (6.2 cm total precipitation) for Warren County, Pennsylvania (Technical Release 55: Urban Hydrology for Small Watersheds, 1986). A NRCS Type-II storm event was selected because: 1) it allowed contaminant mobilization to occur under varied rainfall intensities (starting at 0.62 mm/h, increasing to 26 mm/h, and ending at 0.62 mm/h; Table S3) and 2) its extended duration allowed long-term contaminant fate to be evaluated. The rainfall simulator included a supply tank, submersible pump, constant head feed tank with supply tank, diaphragm pump, manifold, pressure gauges, solenoid valves, and spray nozzles (details in Appendix A). To ensure the amount of rainwater delivered at a given time corresponded to the Type-II storm event, the hyetograph (Fig. S3) was discretized into 5-min intervals to calculate the volume of rain to be delivered during each interval. A microcontroller was programmed to open the solenoid valves at the start of each 5-min interval, hold the valves open until the calculated rainfall volume was delivered, then close the valves for the remainder of the 5-min interval. Generated runoff was directed into a flow-through sampling bucket connected to a stainless-steel chute at the downstream end of the roadbed frame (Fig. S2).

A model 6712 Portable ISCO sampler collected 500 mL grab samples after every 1/24th of the total storm volume (ca. 6.4 L) was applied to the roadbed (Table S3). Runoff samples collected using the ISCO sampler were analyzed for a variety of water quality parameters (Table S4). Since the ISCO sampler was programmed to collect a sample after every 1/24th of the storm volume had been distributed, the time between sampling events was variable. This time was shortest (ca. 6 min) during peak rainfall intensity and longest (up to 3.6 h) during the initial and final

phases of the rainstorm event (Table S3).

2.4. Chemical analyses

For the entirety of each rainfall-runoff experiment, a Hanna HI98195 Multiparameter Waterproof Meter positioned in the flow-through sampling bucket measured pH, electrical conductivity (EC), and temperature every 10 s.

Dust suppressants and runoff samples collected with the ISCO sampler were filtered (>0.45 μm) and acidified (pH < 2) prior to metals analysis. Major cations (Ca, K, Mg, Na, Sr) were measured using a Thermo iCap 7400 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and trace metals (Al, As, B, Ba, Co, Cr, Fe, I, Li, Mn, Ni, Pb, V, Zn) were analyzed using a Thermo iCap RQ Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (U.S. Environmental Protection Agency, 2018; U.S. Environmental Protection Agency, 1994b). Dissolved anion (Cl⁻, Br⁻, SO₄²⁻, NO₃⁻) concentrations were analyzed on a Dionex ICS 1100 ion chromatograph using filtered (>0.45 μm) but unacidified samples (U.S. Environmental Protection Agency, 1993). Internal standard solutions (Lu and Sc) were used to monitor ICP instrument performance. Certified reference materials (CRM; USGS M-220, EPA 200.7, and NIST 1640 A) were used to confirm instrument accuracy (<10 % difference from reported values) for all analyses.

Bulk solids were characterized for all runoff samples. TDS were calculated from the sum of the concentrations of Cl⁻, SO₄²⁻, Br⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, Sr²⁺, Ba²⁺ and reported as mg/L TDS. Total suspended solids (TSS) were measured photometrically with a portable HACH DR2800 spectrophotometer following HACH method 8006.

Radioactivity was measured in the dust suppressants and select runoff and roadbed samples using a Canberra small-anode germanium gamma ray spectrometer. Acid-preserved, unfiltered runoff samples and dust suppressants were transferred to 24 mL plastic tubes sealed with paraffin tape. Loose aggregate samples were collected before roadbed construction (pre-treatment), after the dust suppressant was applied (post-treatment), and after the rainfall-runoff experiment (post-rainfall). All samples were dried overnight in a 60 °C oven, crushed in a mortar and pestle, and sieved to four size fractions: bulk material (<1.18 mm), sand (90 μm to 1.18 mm), silt (between 45 and 90 μm), and clay (<45 μm). Only data from the clay fraction are presented. Each size fraction was packed into 24 mL plastic tubes and sealed with tape. All sealed samples were incubated for at least 21 days to establish secular equilibrium (Parekh et al., 2003). ²²⁶Ra was measured using the average ²¹⁴Pb (351 and 295 keV) and ²¹⁴Bi (609 keV) peak activities. ²²⁸Ra was measured using the ²²⁸Ac (911 keV) and ²¹²Pb (239 keV) peaks. Samples were counted until all counting errors were typically <5 % for all energy channels and the Gaussian ratio was between 0.9 and 1.1. Efficiencies for each energy peak were calculated using standards measured in the same geometry, volume, and matrix.

2.5. Mass balance calculations

A mass balance approach was used to calculate the retention of chemicals from the dust suppressants applied to the roadbed after the rainfall event according to Eq. (3):

$$M_{j,\text{retained}} = V_{DS} \times C_{j,DS} - \sum_i^{24} C_{j,i} \times V_i \quad (3)$$

where $M_{j,\text{retained}}$ is the mass of element j retained in the roadbed (g), V_{DS} is the volume of dust suppressant applied to the roadbed (L), $C_{j,DS}$ is the concentration of chemical j in the dust suppressant (g/L), $C_{j,i}$ is the concentration of chemical j in the i^{th} runoff sample (g/L), and V_i is the volume of runoff (1/24th of the total storm volume; L). In cases where $M_{j,\text{retained}}$ was <0, the roadbed aggregate was considered the source of chemical j .

3. Results and discussion

3.1. Dust suppressant efficacy

O&G PW did not reduce PM₁₀ emissions as effectively as commercial brine (CB) or commercial organic (CO) products, though most road discs treated with O&G PW did reduce PM₁₀ compared to discs treated with synthetic rainwater at 50 % humidity (Fig. 1). The effectiveness of the O&G PW was highly variable. O&G PW-treated road discs reduced dust emissions between 10 % and 84 % compared to road discs treated with synthetic rainwater. However, when humidity was low (20 %), O&G PW did not significantly reduce PM₁₀ compared to rainwater controls, and in some cases, increased total PM₁₀ generation (Table 1). The 50 % and 20 % relative humidity levels represent shaded and unshaded portions of an unpaved road, respectively, during summer months in Pennsylvania (see Appendix A for further discussion).

Most of the commercial products effectively suppressed PM₁₀ emissions regardless of ambient humidity. CB were the most effective class of dust suppressants. Road aggregate discs treated with CB reduced PM₁₀ by at least 99.4 % compared to discs treated with synthetic rainwater at 50 % relative humidity (Fig. 1), and over 90 % less PM₁₀ at 20 % relative humidity (Table 1). Though the CB were the most effective class of dust suppressants, three of the CO products performed comparably. In fact, road discs treated with CO2 generated the least amount of PM₁₀ and reduced 100 % of PM₁₀ emissions compared to discs treated with synthetic rainwater (Fig. 1). CO3 and CO4, however, were the least effective commercial products and only reduced dust emissions by 41 % and 53 % relative to synthetic rainwater, respectively.

Relative humidity influenced the total mass of dust generated during the experiment. Generally, experiments run at 50 % relative humidity had less PM₁₀ production from discs treated with CB and O&G PW compared to 20 % relative humidity (Table 1). This effect was strong and independent of other factors such as aggregate moisture content. The CO products were less affected by changes in relative humidity (Table S5).

3.2. Dust suppressant influence on road stability

While dust suppression goals may not be directly tied to achieving roadbed stability, commercial products do often influence roadbed strength. In fact, commercial calcium chloride brines are often marketed as soil stabilizers or for road refurbishment projects. Previous studies have shown that untreated unpaved roads can lose mass up to three

Table 1

Total dissolved solids (TDS) and sodium adsorption ratios (SAR) for the brine-based dust suppressants used in this study. Organic products did not have measurable concentrations of dissolved ions and are not shown. Total generated PM₁₀ calculated at 20 % and 50 % relative humidity conditions were averaged across all trials and reported errors represent standard error of the mean (n = 1 to 4).

Dust Suppressant	TDS (g/L)	SAR	Total PM ₁₀ (mg)	
			20 % Humidity	50 % Humidity
SR	0.0	0.0	2.5 ± 0.09	3.28 ± 0.05
CaCl ₂ Brine	270	1.4	0.072 ± 0.04	0.001 ± 0.000
CB1	380	17	0.020 ± 0.02	0.005 ± 0.002
CB2	390	2.1	0.045 ± 0.02	0.020 ± 0.009
CB3	340	1.4	0.220 ± 0.05	0.007 ± 0.002
CB4	370	0.2	0.170 ± 0.03	0.010 ± 0.002
O&G PW1	84	67	2.80 ± 0.21	2.30 ± 0.26
O&G PW2	82	68	3.20 ± 0.00	2.90 ± 0.18
O&G PW3	85	69	3.10 ± 0.12	2.00 ± 0.09
O&G PW4	140	83	1.80 ± 0.52	1.40 ± 0.47
O&G PW5	330	89	2.00 ± 0.05	0.54 ± 0.16
O&G PW6	51	50	3.10 ± 0.10	2.20 ± 1.00
O&G PW7	300	84	2.20 ± 0.15	0.70 ± 0.05
O&G PW8	280	80	2.00	1.30 ± 0.17
O&G PW9	340	110	2.60	0.84 ± 0.28
O&G PW10	140	63	3.00 ± 0.02	2.00 ± 0.00

times faster than those treated with chloride salts for dust suppression (*Gravel Roads Construction and Maintenance Guide*, 2015). Therefore, the ability to stabilize roadbeds should be considered when assessing dust suppressants' efficacy.

The calcium chloride brine (CaCl₂ Brine) was the only dust suppressant to significantly reduce the TSS concentrations in runoff and material loss from the roadbed during the rainfall-runoff experiments compared to the rainwater control (Fig. 2; *P* < .05). On average, CaCl₂ Brine reduced total material loss from the roadbed by 16 %, and the maximum runoff TSS concentration from roadbeds treated with the CaCl₂ Brine was 60 % lower than the rainwater control (2510 mg/L compared to 4290 mg/L; Fig. 2). The high concentration of divalent calcium ions (78,200 mg/L; Table 2) could explain why CaCl₂ Brine was the only dust suppressant to significantly reduce total solids loss from the roadbed. Divalent metals can serve as a cation bridge between negatively charged clay particles, which improves the bulk strength of the roadbed and makes finer particles more difficult to mobilize even under the high flow conditions during maximum rainfall intensity (Payne, 2018). The O&G PWs and Soybean Oil had relatively minor concentrations of divalent cations, and the bridging effect was therefore diminished (Table 2). The maximum TSS concentrations in runoff samples for roadbeds treated with soybean oil (4460 mg/L), O&G PW1 (4550 mg/L), O&G PW2 (5330 mg/L), and O&G PW3 (4480 mg/L) were not significantly different than roadbeds treated with rainwater (Figs. 2 and S11).

Though soybean oil effectively reduced dust generation (Fig. 1), it did not lead to improved road stability like CaCl₂ Brine (Fig. 2). This could be due in part to the experimental design. Many of the CO product application notes specify a “grow in” time of up to two weeks before the dust suppressant achieves maximum effectiveness. In this study, roadbeds were dried at ambient conditions for only 24 h, so it is possible that the soybean oil was not fully cured at the onset of the rainfall simulation. Nonetheless, previous studies on organic-based dust suppressants have reported increased TSS concentrations in runoff which could have resulted from larger clods of aggregate being mobilized from the roadbeds during higher rainfall intensities (Singh et al., 2003).

The differences in solids lost or retained in the roadbed with different dust suppressants become ecologically and economically important at scale. Increased turbidity in surface waters can decrease light penetration into the water column, which in turn decreases the productivity of aquatic ecosystems. Additionally, elevated suspended solids have been

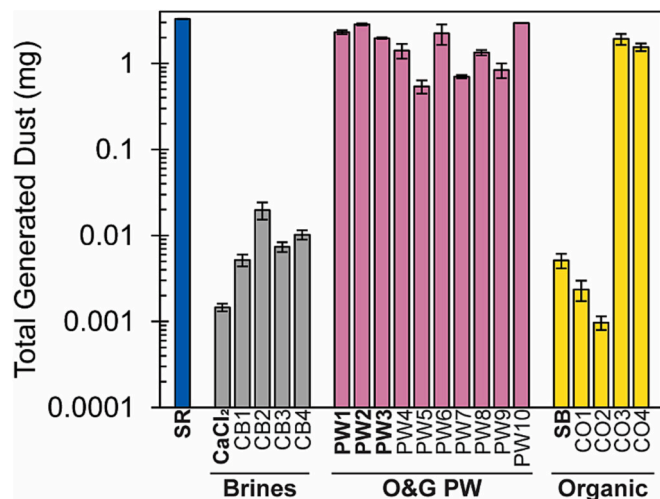


Fig. 1. Average total generated dust calculated for each dust suppressant according to Eq. (2) at 50 % relative humidity. Error bars are standard error of the mean (n = 2 to 5). Bolded dust suppressants were used in rainfall-runoff experiments.

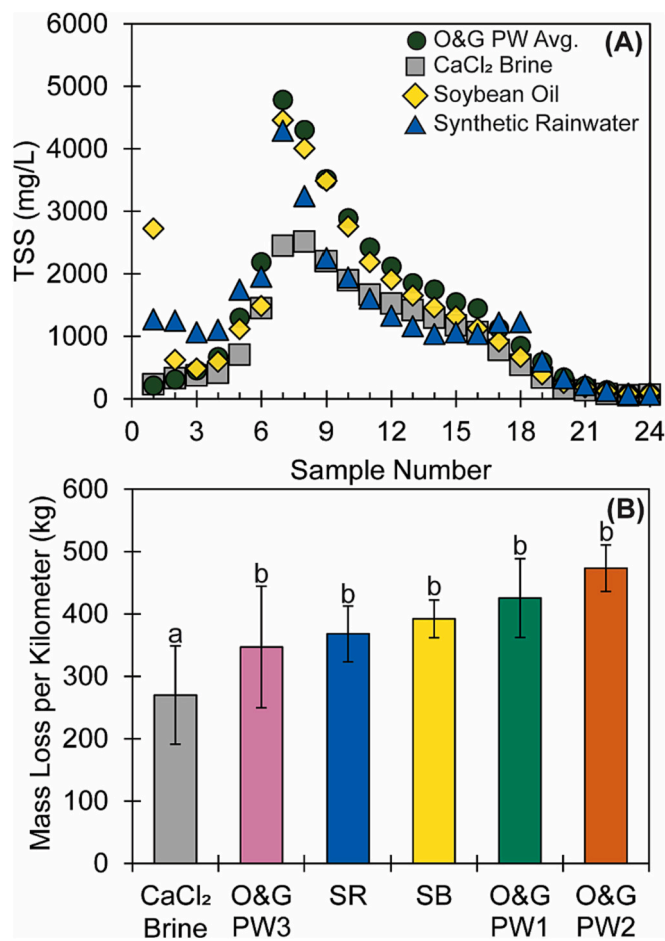


Fig. 2. (A) Total Suspended Solids (TSS) measured in runoff from gravel roadbeds treated with synthetic rainwater, CaCl₂ Brine, and averaged TSS concentrations across all O&G PW experiments. Samples were collected after 1/24th of the storm volume was rained onto the roadbed. Results shown are average values across all trials, and error bars are not shown for clarity. (B) Extrapolated mass lost from roadbed during one storm event calculated from volume-integrated TSS concentrations (Eq. (3)) with roadbed dimensions adjusted to 5.4 m wide and 1 km long. SB represents Soybean Oil. Different letters denote significant differences from the synthetic rainwater (SR) control at the 95 % confidence level.

shown to decrease the survival of salmonid eggs, serve as vectors for environmental pollutants, and reduce the efficiency of water treatment operations (Bilotta and Brazier, 2008; U.S. Environmental Protection Agency, 2012). Significant material losses from unpaved roads can increase the frequency of road maintenance and associated annual maintenance costs. Unpaved roads lose an estimated one ton of aggregate per road mile per vehicle passing daily (Gravel Roads Construction and Maintenance Guide, 2015). Though many factors control material losses (rainfall, traffic, gravel quality, etc.), improving aggregate retention through effective dust control can result in significant cost reductions for road managers (Légère and Bradley, 2019).

Solids lost per Type-II storm event per kilometer of two-lane gravel road were calculated from these lab tests by accounting for the length (i.e., doubled for 5.4 m wide carriageway) and width (i.e., 0.9 m extended to 1000 m) of the test frame. Compared to solid mass lost from the rainwater control, calcium chloride brine reduced solid mass loss by 98 kg solids/km/storm event while O&G PWs increased solid mass loss by 47 kg solids/km/storm event (Fig. 2, panel B). During the latter part of the rain event, the export of solids from roadbeds treated with CaCl₂ Brine was comparable to the rainwater control, suggesting that loss of calcium during the first flush reduced its stabilization effects on the

roadbed (Fig. 2, panel A). Previous work has shown that dust suppressants with soluble components (i.e., O&G PW and brines) lose efficacy after storm events, and often these products need to be applied multiple times per dust season (Stallworth et al., 2021).

3.3. Predicting dust suppressant efficacy

The chemistry of a brine-based dust suppressant can be used to predict its efficacy. A high dissolved ion concentration (i.e., EC or TDS) is considered the first measure of a brine's potential effectiveness as a dust suppressant. High salinity is required to induce the “salting out” of clays (Payne, 2018), which typically happens in soil solutions above 4 mS/cm (Graber et al., 2019).

A low SAR can also be used to predict the efficacy of a brine as a potential dust suppressant (Stallworth et al., 2020; Graber et al., 2019). The SAR is a measure of the abundance of divalent ions (i.e., calcium and magnesium) to monovalent ions (i.e., sodium; Eq. (4)):

$$SAR = \frac{[Na^+]}{\sqrt{0.5 \times ([Ca^{2+}] + [Mg^{2+}])}} \quad (4)$$

where all concentrations are in meq/L. Previous research has consistently shown that brines dominated by divalent cations are the most effective (Edvardsson et al., 2012; Monlux and Mitchell, 2007; Rushing and Tingle, 2007). Brines with a low SAR have higher concentrations of divalent cations which act as a cation bridge between negatively charged clay particles and can lead to roadbed stabilization and improved dust suppression.

The ten evaluated O&G PW samples had lower TDS concentrations and SAR values approximately 500-times greater than the CB samples (Table 1), which could explain why they did not effectively reduce total PM₁₀ emissions or solids losses from treated roads (Figs. 1 and 2). Of all O&G PWs, those with TDS concentrations comparable to the CB (O&G PW 5, 7, 8, and 9; Table 1), were the most effective at 50 % relative humidity (Fig. 1). Notably, these samples did not have the lowest SAR of the O&G PW, suggesting that SAR may be secondary to TDS when predicting efficacy when ambient humidity is high.

TDS concentrations also explain the variability amongst O&G PW evaluated in the efficacy studies. There was a strong negative correlation between TDS and total PM₁₀ generated at 50 % relative humidity ($r^2 = 0.82, P < .001$). The relationship between SAR and TDS was weaker ($r^2 = 0.59$) but still significant ($P = .009$). Together, these data further support the hypothesis that, while both influence efficacy, TDS is more important than SAR when predicting the effectiveness of a dust suppressant.

SAR did however play more of a role under low humidity conditions (20 %). O&G PW9, which had both the highest TDS concentration (343 g/L) and SAR value (110) of the tested O&G PW, reduced dust emissions by 75 % when the humidity was high but increased emissions by 4 % when the humidity was low. O&G PW8, which had both the lowest TDS (278,000 mg/L) and the lowest SAR (79.7) of the four effective O&G PW, reduced total PM₁₀ emissions by 59 % under high humidity conditions but still reduced total emissions by 19 % when the humidity was low (Table 1).

CaCl₂ Brine had the lowest TDS concentration (272 g/L) that still reduced nearly 100 % of all PM₁₀ emissions relative to the synthetic rainwater control. O&G PW8 had the highest SAR value (79.7) that was still able to offer some amount of dust suppression regardless of ambient humidity conditions. Using these conditions as minimum criteria that would indicate modest dust suppression under high and low humidity conditions, only 17 % of O&G PW in Pennsylvania listed in the USGS Produced Water Database (Blondes et al., 2019) would be predicted to be moderately effective. Further, no O&G PW found in the database have SAR and TDS values that would indicate dust suppression efficacy comparable to any of the CB tested in this study.

Table 2
Chemical characterization of dust suppressants applied to a gravel road constructed for the rainfall-runoff experiments.

Analyte	O&G PW1	O&G PW2	O&G PW3	CaCl ₂ Brine	Soybean Oil	Synthetic Rainwater	Regulatory Criteria
EC (mS/cm)	120 ± 1.4	120 ± 1.1	125 ± 1.5	197 ± 4.0	NA	0.023 ± 0.0	3.0 ^g
TDS* (mg/L)	84,100 ± 988	82,000 ± 1090	85,300 ± 6610	272,000 ± 41,700	0.14 ± 0.0	2.39 ± 0.1	500 ^b
²²⁶ Ra (pCi/L)	212 ± 118	52 ± 2	1800 ± 929	159 ± 42	BQL	BQL	60 ^c
²²⁸ Ra (pCi/L)	148 ± 88	33 ± 6	696 ± 455	72 ± 42	BQL	BQL	60 ^c
Combined Ra (pCi/L)	360 ± 147	84 ± 6	2500 ± 1035	230 ± 59	BQL	BQL	5 ^b
Chloride (mg/L)	49,700 ± 1250	48,000 ± 1330	49,000 ± 6630	176,000 ± 30,000	NA	BQL	250 ^{h,i} , 230 ^c
Bromide (mg/L)	922 ± 188	753 ± 253	592 ± 110	3770 ± 1071	NA	BQL	6 ^d
Iodide (mg/L)	14 ± 0.37	11 ± 1.3	15 ± 0.72	0.22 ± 0.04	NA	0.0 ± 0.0	
Nitrate (mg/L)	324 ± 78.7	BQL	BQL	735 ± 242	NA	0.7 ± 0.02	10 ^{a,i}
Sulfate (mg/L)	1480 ± 407	1350 ± 389	2000 ± 291	7210 ± 1680	NA	2.14 ± 0.06	250 ^{b,i}
Calcium (mg/L)	6760 ± 116	6860 ± 48	7150 ± 66	78,200 ± 9400	0.41 ± 0.0	BQL	401 ^g
Magnesium (mg/L)	1360 ± 26	1310 ± 8	1310 ± 5	BQL	0.10 ± 0.004	BQL	61 ^g
Strontium (mg/L)	112 ± 2	112 ± 2	453 ± 4	1480 ± 113	BQL	0.0 ± 0.0	4 ^{f,h,i}
Barium (mg/L)	1.58 ± 0.1	4.38 ± 0.1	417 ± 19	1.57 ± 0.9	BQL	0.0 ± 0.0	2 ^{a,i}
Sodium (mg/L)	23,600 ± 410	23,500 ± 230	24,300 ± 31	1460 ± 265	BQL	0.14 ± 0.01	20 ^h , 920 ^g
Potassium (mg/L)	117 ± 1.6	125 ± 2.3	132 ± 8.8	3120 ± 550	BQL	0.1 ± 0.01	
Lithium (mg/L)	2.48 ± 0.1	2.92 ± 0.1	13.3 ± 0.1	58 ± 9	BQL	BQL	0.01 ^f , 0.069 ⁱ
SAR ⁻ (meq/L) ^{1/2}	69 ± 0.6	68 ± 0.5	69 ± 0.2	1.4 ± 0.2	NA	BQL	9 ^g
Aluminum (mg/L)	BQL	BQL	BQL	BQL	BQL	BQL	0.05 to 0.2 ^{b,i}
Manganese (mg/L)	4.2 ± 0.1	4.8 ± 0.1	4.9 ± 0.5	0.1 ± 0.1	BQL	BQL	0.05 ^b , 0.3 ⁱ
Iron (mg/L)	15 ± 16	1.4 ± 0.9	44 ± 43	3.4 ± 1.4	BQL	0.02 ± 0.0	0.3 ^{b,i} , 1 ^c
Nickel (mg/L)	0.09 ± 0.04	0.09 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	BQL	BQL	0.052 ^c , 0.1 ^{h,i}
Zinc (mg/L)	1.83 ± 0.09	1.93 ± 0.19	2.21 ± 0.15	1.84 ± 0.75	BQL	0.44 ± 0.02	5 ^b , 0.12 ^c , 2 ^h
Lead (mg/L)	0.11 ± 0.00	0.13 ± 0.02	0.11 ± 0.00	0.4 ± 0.63	BQL	BQL	0.015 ^a , 0.0025 ^c
Boron (mg/L)	0.77 ± 0.11	0.99 ± 0.15	1.26 ± 0.01	22 ± 3.65	BQL	BQL	2.4 ^d , 6 ^{h,i}
Arsenic (mg/L)	0.06 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.02 ± 0.01	BQL	BQL	0.01 ^{a,i} , 0.15 ^c
DRO (mg/L)	14.7 ± 3.2	10.8 ± 0.2	1650 ± 322	0.5 ± 0.0	6.5 ± 0.7	1.1 ± 0.9	
GRO (mg/L)	1.3 ± 0.04	2.6 ± 0.08	1.1 ± 0.27	0.6 ± 0.06	22.8 ± 6.98	BQL	
TOC (mg/L)	88.3 ± 8.33	81.1 ± 11.7	76.6 ± 14.5	8.27 ± 1.29	NA	1.75 ± 0.5	
TIC (mg/L)	1.1 ± 0.5	1.5 ± 0.9	13.1 ± 8.3	0.6 ± 0.02	NA	0.6 ± 0.7	
pH (std units)	6.42 ± 0.16	6.15 ± 0.14	6.50 ± 0.04	9.95 ± 0.19	NA	4.29 ± 0.10	6.5–8.5 ^b

*Calculated as sum of Cl, SO₄, Br, Ca, Mg, Na, K, Sr, Ba concentrations.

BQL – Below quantification limit.

NA – Not analyzed.

[^]Calculated using Eq. (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.

3.4. Risks to water quality from treated roads

3.4.1. Chemical composition of dust suppressants

The chemical compositions of the investigated dust suppressants and, when applicable, regulatory criteria for each analyte are presented in Table 2. Criteria for drinking water, aquatic life, irrigation water, and groundwater were all considered because roadway runoff could impact each of these systems. CaCl₂ Brine and the O&G PWs had the highest salinity levels. Though CaCl₂ Brine never reached full saturation, it was 4- and 8-times more saline than average seawater when comparing EC and TDS, respectively. Typical seawater has an EC of 55 mS/cm and a TDS concentration of 35,000 mg/L (State Water Resources Control Board, D. o. W. Q, 2004) compared to an EC of 197 mS/cm and TDS of 272,000 mg/L measured in the CaCl₂ Brine (Table 2). Calcium was the dominant cation, with relatively minor amounts of potassium, sodium, and magnesium (Table 2). The cations were primarily balanced by chloride and, to a lesser degree, bromide. The O&G PWs had similar salinities to each other and were not as saline as the calcium chloride brine. The EC of the O&G PWs ranged from 120 to 125 mS/cm while the TDS concentrations ranged from 82,000 mg/L to 85,300 mg/L (Table 2), approximately two-times more saline than typical seawater. Sodium was the dominant cation for each O&G PW, counterbalanced primarily by chloride and bromide. Notably, the O&G PWs used in this study are

roughly two times less saline than O&G PWs typically generated in the Appalachian Basin (Tasker et al., 2020; Tasker et al., 2018). The soybean oil and synthetic rainwater both had very low dissolved ion concentrations (Table 2).

The calcium chloride brine and O&G PWs had elevated concentrations of trace metals that exceeded regulatory thresholds (Table 2). Radium is a naturally occurring radioactive metal with a primary drinking water standard of 5 pCi/L and an industrial effluent standard of 60 pCi/L for ²²⁸Ra and ²²⁶Ra (Table 2) (Appendix B to 10 CFR 20, n.d.; U.S. Environmental Protection Agency, 2023b). O&G PW3 had a combined radium activity of 2500 pCi/L (summed ²²⁸Ra and ²²⁶Ra activities), which was the highest of all tested dust suppressants, but still representative of O&G PWs from the Appalachian Basin. For comparison, the 25th, 50th, and 75th percentile values (n = 25) for combined radium activity in Appalachian O&G PWs were 961, 2030, and 4220 pCi/L, respectively (Tasker et al., 2018; Rowan et al., 2011). Another study on O&G PW in NW PA reported an average (n = 38) combined radium activity of 1418 pCi/L (NORM Survey Summary, 1992). O&G PW1 and CaCl₂ Brine had lower combined radium activities of 350 pCi/L and 230 pCi/L, respectively, while O&G PW2 had the lowest radium activity of the measured brines at 84 pCi/L (Table 2).

Strontium, barium, iron, and manganese concentrations in CaCl₂ Brine and O&G PWs also exceeded regulatory criteria. These metals are

commonly reported in conventional produced waters from the Appalachian Basin (Tasker et al., 2018), but their abundance in CaCl_2 Brine was surprising. To ensure that the calcium chloride brine used in this study was representative of calcium chloride brines used in the field, two other commercial calcium chloride brines (CB1 and CB2) were characterized (Table S1). The compositions of the commercial products and CaCl_2 Brine were comparable (Table S6), suggesting that commercial brine products contain impurities that may be of concern. Neither the soybean oil nor rainwater had measurable trace metal concentrations (Table 2).

While soybean oil did not have high concentrations of inorganic analytes, it did have the highest concentration of gasoline range organics (22.8 mg/L; Table 2) and the second highest concentration of diesel range organics (6.5 mg/L; Table 2). More discussion on the organic composition of the dust suppressants can be found in Appendix A.

3.4.2. Water quality of runoff from treated roads

The water quality of runoff was generally proportional to the dust suppressant applied to the roadbed. For example, the EC was highest in runoff waters from roadbeds treated with CaCl_2 Brine (59 mS/cm; Fig. 3) followed by runoff from roadbeds treated with each of the O&G PWs (O&G PW1: 23 mS/cm, O&G PW3: 20 mS/cm, O&G PW2: 19 mS/cm; Fig. 3). Roadbeds treated with soybean oil had the lowest EC (0.1 mS/cm). The EC of runoff from roadbeds treated with CaCl_2 Brine and O&G PW was significantly higher than the rainwater control (0.2 mS/cm; $P < .05$) which was expected because the composition of the calcium chloride and O&G PWs was dominated by highly soluble salt ions that are easily mobilized from the roadbed during storm events. Conversely, the soybean oil had minimal dissolved ions and the EC of runoff from these roads was not significantly different than the synthetic rainwater control ($P > .05$).

The shapes of the EC curves highlight important stages of runoff water quality during the storm event (Fig. 3). Initially, no runoff was generated because small volumes were rained onto the roadbed. After this lag period, the initial runoff from the roadbed had high concentrations of dissolved ions reflected by the sharp increases in runoff EC (Fig. 3). High concentrations during this “first flush” period were primarily caused by the dissolution and mobilization of chemical constituents from the dust suppressant and possibly caused by secondary reactions (e.g., ion exchange) with roadbed minerals. Though the soybean oil and rainwater contained small amounts of dissolved ions, the highest EC and TDS concentrations also occurred in the initial runoff samples, likely from the dissolution of minerals in the road aggregate material (Fig. S4). As rainfall intensity increased, the concentration of ions in the runoff decreased, reaching a minimum during this “maximum

flush” period. Decreased EC during the maximum flush period could be due to dilution during heavier rainfall, the loss of easily soluble ions following the first flush period, and a decreased rainfall residence time in the roadbed. The inverse relationship between EC and rainfall intensity is consistent with results from a US EPA report on potential water quality impacts from dust suppressants used in the southwestern US (U. S. Environmental Protection Agency, 2008).

Similarly, the concentrations of individual ions in runoff from treated roads was proportional to their concentration in the original dust suppressant (Fig. 4; note data are plotted against sample number collected after every 1/24th of the storm volume, not time. See Fig. S5 in Appendix A for more details). For example, calcium was most concentrated in CaCl_2 Brine, and runoff from these roadbeds had significantly higher maximum calcium concentrations than any other treated roadbed (14,800 mg/L; Fig. 4; $P < .05$). Conversely, the O&G PWs were sodium-dominated, and runoff from roadbeds treated with the O&G PWs had significantly higher sodium (2500 to 3500 mg/L; Fig. 4; $P < .05$).

Chloride was the dominant anion in the brine-based dust suppressants (Table 2), and chloride concentrations in runoff from roadbeds treated with these dust suppressants were significantly higher than the rainwater control (Fig. 4; $P < .05$). CaCl_2 Brine had the highest chloride concentrations (176,000 mg/L; Table 2), and runoff from roadbeds treated with this dust suppressant also had the highest chloride concentrations (26,100 mg/L; Fig. 4). The chloride concentrations in the O&G PWs were comparable to each other, and chloride concentrations in runoff from roadbeds treated with these dust suppressants ranged from 6800 to 8500 mg/L (Fig. 4). Soybean oil was not analyzed for anion concentrations because it is a non-aqueous phase liquid, but runoff from roadbeds treated with this dust suppressant contained very little chloride. Low chloride concentrations in these samples suggests soybean oil added negligible amounts of these ions to the roadbed. Runoff from roadbeds treated with soybean oil, however, did have the highest concentrations of organic compounds, which notably occurred during both the first and maximum flush periods of the storm event (see Appendix A for more detailed discussion).

The ecological impacts resulting from freshwater salinization have long been recognized as a threat to environmental health (Kaushal et al., 2018; Hintz and Relyea, 2019; *Roadspreading of Brine for Dust Control and Road Stabilization*, 2011), though the contribution from chloride-based dust suppressants has been relatively understudied compared to salt applied to paved surfaces for snow and ice management in colder climates. Runoff samples from roadbeds treated with CaCl_2 Brine and O&G PWs were hypersaline (Figs. 3 and 4). High salinity in soils can reduce soil permeability (Singh et al., 2003), hinder plant growth (van den Ende et al., 1975), and induce foliar burns in roadside vegetation (Goodrich and Jacobi, 2012; Goodrich et al., 2009b). Chloride is of particular concern because elevated concentrations in surface water resulting in salt application to roadways alters aquatic systems at the species, community, and ecological levels (Hintz and Relyea, 2019). The EPA guideline for chloride concentrations in freshwaters is 230 mg/L to protect the health of aquatic systems (Table 2), suggesting the runoff waters from roadbeds treated with the calcium chloride brine in this study would have to be diluted up to 113-fold and those treated with O&G PWs would require a 37-fold dilution (Tables S9 and S10). However, chloride has been shown to induce toxic effects on aquatic organisms at concentrations far below the current 230 mg/L limit (Arnott et al., 2020), suggesting that episodic pulses of hypersaline runoff water could negatively impact sensitive aquatic organisms even after anticipated mixing and dilution with receiving waters (Bair and Digel, 1990).

Though the chemistry of the dust suppressant originally applied to the roadbed often reflected the concentration of contaminants of concern in the runoff, this was not the case for every analyte. Secondary geochemical reactions with roadbed minerals could occur during the storm event to mobilize contaminants from the aggregate used to construct the roadbed. For example, roadbeds treated with CaCl_2 Brine generated runoff that had the highest concentrations of barium (31 mg/

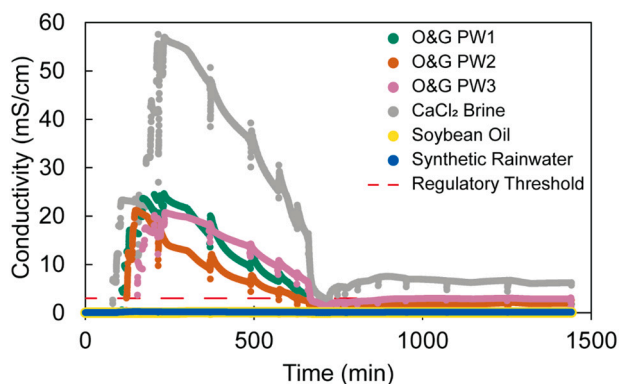


Fig. 3. Electrical conductivity of runoff from gravel roadbeds treated with various dust suppressants. Results shown are average values across all trials, and error bars are not shown for clarity. The regulatory threshold shown is 3.0 mS/cm from USDA Irrigation Water Quality Guidelines. The EPA chronic aquatic life benchmark value for conductivity in central Appalachian streams is 0.30 mS/cm.

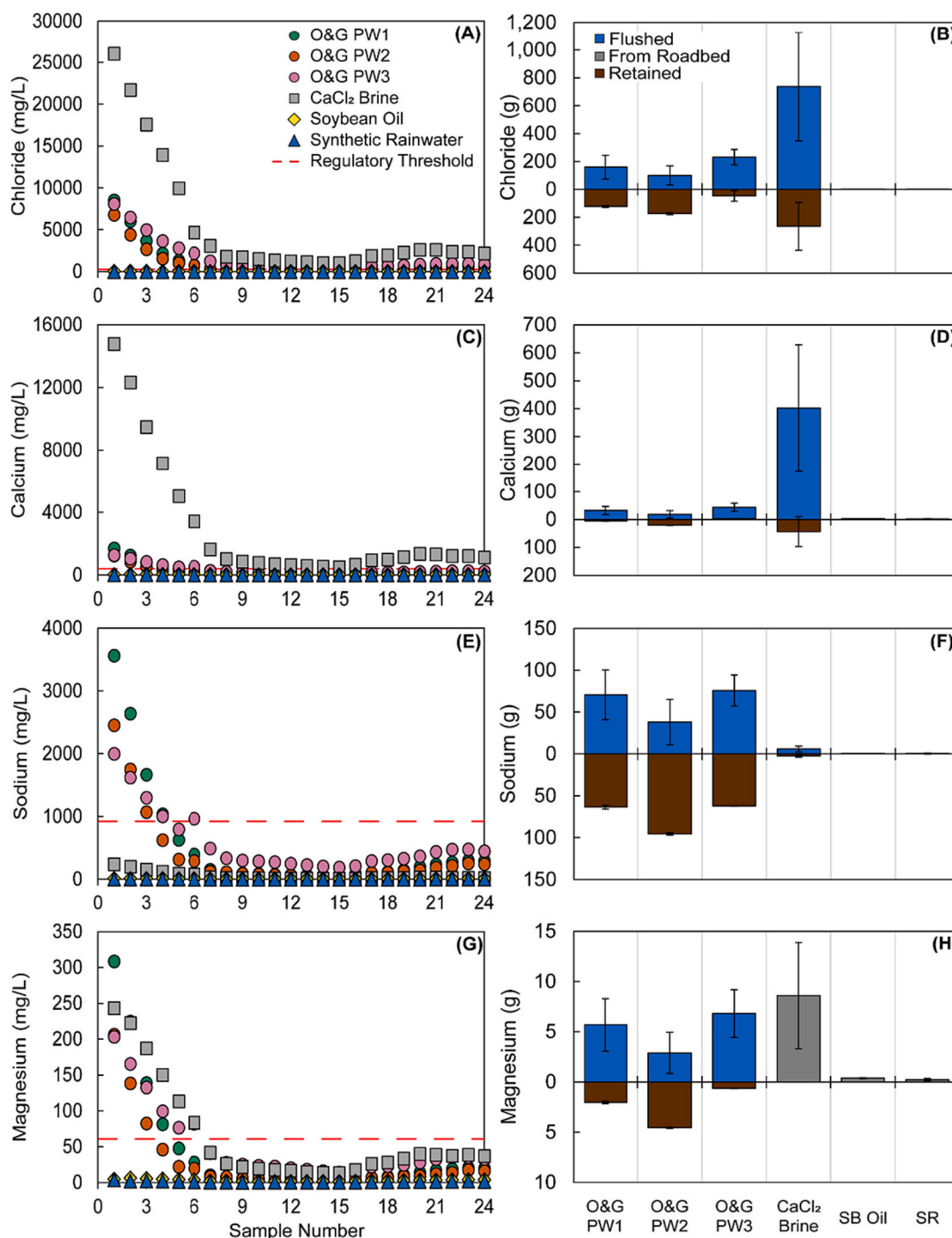


Fig. 4. (A) Chloride, (C) calcium, (E) sodium, and (G) magnesium measured in runoff from gravel roadbeds treated with various dust suppressants. Samples were collected after every 1/24th of the storm volume. The regulatory thresholds shown are (A) 250 mg/L Cl from EPA Secondary Drinking Water Standards. The EPA chronic aquatic life benchmark value for chloride is 230 mg/L, (C) 401 mg/L Ca, (E) 920 mg/L Na, and (G) 61 mg/L Mg from the USDA Irrigation Water Quality Guidelines. Masses of (B) chloride, (D) calcium, (F) sodium, and (H) magnesium retained, flushed, or sourced from the roadbeds.

L) even though the concentration of barium in the calcium chloride brine was low relative to the other brines (Table 2, Fig. S8). High calcium concentrations in this dust suppressant could have displaced barium from sorption sites in the aggregate through competitive ion exchange (Bair and Digel, 1990). While chemical characterizations of the dust suppressants help predict runoff concentrations, the mineralogy of the aggregate and site-specific conditions may contribute other unsuspected contaminants to the runoff.

3.4.3. Fate of radium

Because radium is a known hazard to human health, it is important to understand its fate in the roadbed during a storm event in areas where O&G PWs are used as dust suppressants. The O&G PWs and calcium chloride brine were enriched in radium, yet O&G PWs from the Appalachian Basin can have much higher radium activities than the brines used in this study (Tasker et al., 2020). Radium activities in the roadbed aggregate were measured before and after treatment with each dust suppressant and at the conclusion of the rainfall-runoff experiment. Only O&G PW1 and O&G PW3 added a measurable amount of combined

radium activity to clay-sized particles (<45 μm) in the roadbed aggregate (Figs. 5 and S9). Focus was given to the radium activities of clay-sized particles because they preferentially sorb radium (Chen and Kocar, 2018) and, because of their small size, are more easily mobilized in runoff and as dust. All other dust suppressants did not raise the combined radium activities above the background roadbed aggregate (4 pCi/g; Fig. S9). At the end of the experiments, the radium activity of roadbed samples from roadbeds treated with O&G PW1 and O&G PW3 were comparable to background road aggregate, suggesting that most or all added radium was flushed from the roadbed (Fig. 5).

Radium activities in runoff were analyzed for samples corresponding to the first flush (sample numbers 1 and 2) and maximum flush (sample numbers 7 and 8) periods of the storm event (Figs. 5 and S10). O&G PW3 had the highest combined radium activity, and roadbeds treated with O&G PW3 generated runoff with the highest measured combined radium activities which occurred during the first flush (72 pCi/L) and maximum flush (83 pCi/L) periods (Fig. 5). O&G PW1 had the second highest combined radium activity (Table 2), and roadbeds treated with this dust suppressant generated runoff with elevated radium activities, but only during the maximum flush period (62 pCi/L; Fig. S10). Combined radium activity in runoff from roadbeds treated with CaCl₂ Brine and soybean oil ranged from 18 to 48 pCi/L and 16 to 39 pCi/L, respectively (Fig. S10), which were not significantly different from combined radium activities measured in runoff from the roadbed treated with rainwater (40 to 52 pCi/L; P > .05; Fig. 5).

Mobilization of radium from the roadbed during storm events likely explains why previous radiation surveys of unpaved roads in north-western Pennsylvania found little radiation above background readings (NORM Survey Summary, 1992; Protection, P. D. o. E, 2016). The transport of radium in the environment is controlled by sorption to mineral phases or mineral precipitation (Tasker et al., 2018). Transport by clay minerals is likely a dominant mechanism of radium transport from the roadbed. However, the high ionic strength of porewater during the first flush period could increase the solubility of free Ra²⁺, allowing for advective transport of dissolved radium (Chen and Kocar, 2018). Similarly, the pH runoff water can control the transport of radium. Radium tends to exist in the dissolved phase in water with pH < 5 (Beck and Cochran, 2013). Though the pH of the various dust suppressants and O&G PW varied (pH = 4.3 to 10; Table 2), the pH of runoff water was similar (Appendix A, Fig. S12). Therefore, mobilization of radium-laden clay particles and high-salinity porewater are likely the dominant mechanisms controlling the transport of radium from the roadbed.

Once geochemical conditions change, i.e., dilution of high-salinity runoff, radium could sorb to clay minerals or metal (hydr)oxides or could co-precipitate with insoluble sulfate minerals like barite (Warner et al., 2013; Van Sice et al., 2018). Radium has been shown to accumulate in soils adjacent to roads treated with O&G PWs as deicing agents (Skalak et al., 2014). Long-term spreading of O&G PWs could raise radium activities to levels that harm roadside ecosystems.

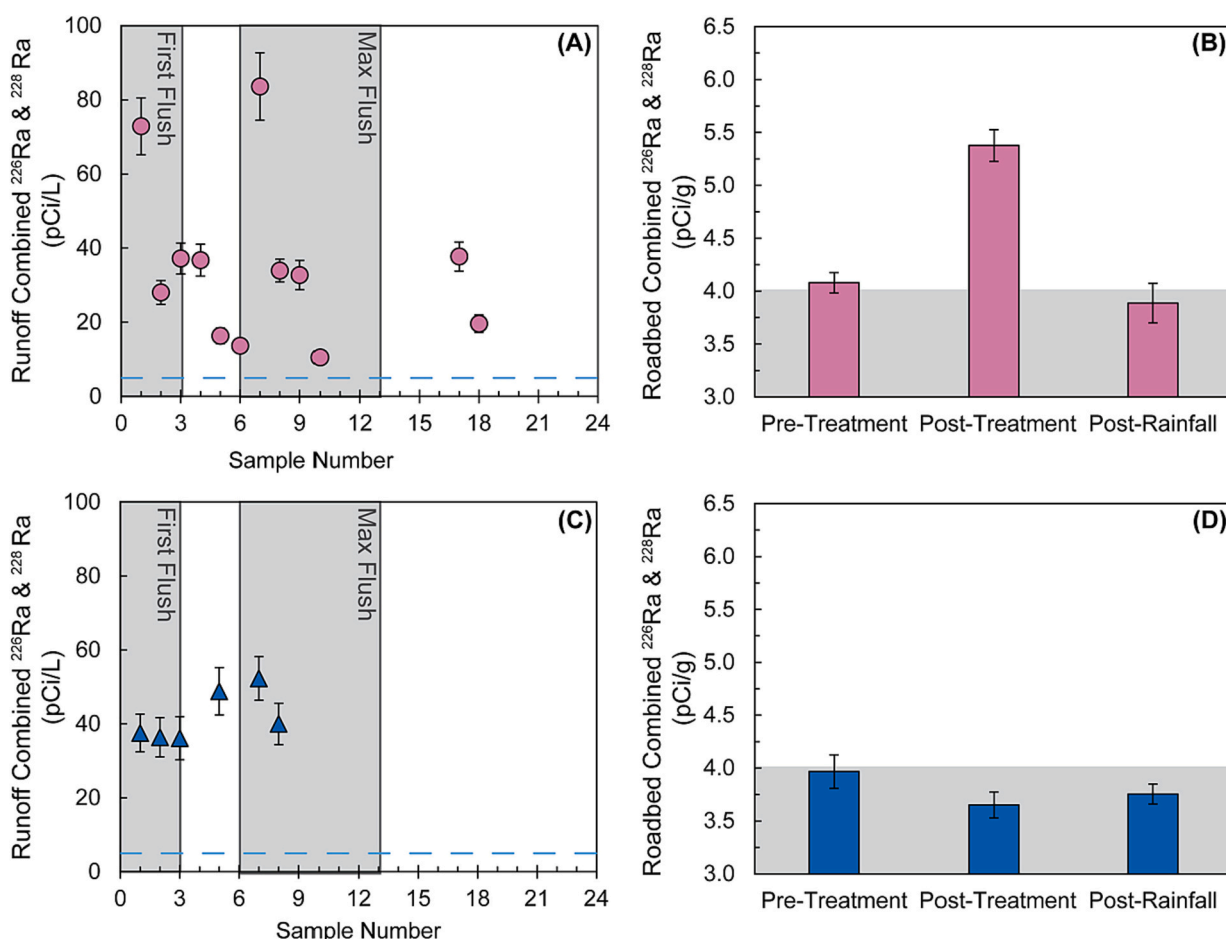


Fig. 5. Combined radium activities measured in runoff from roads treated with (A) O&G PW 3 and (C) synthetic rainwater. Results shown are from single tests and error bars illustrate instrument uncertainty. Blue dashed line represents the EPA and PA DEP Primary Drinking Water Standard for combined radium activity (5 pCi/L). Combined radium measured in roadbed samples (< 45 μm) treated with (B) O&G PW 3 and (D) synthetic rainwater collected before dust suppression application, after dust suppressant application, and after the simulated storm event. Results are shown for triplicate samples collected from the roadbed at each stage. Grey shaded area represents the average activity of untreated 2RC aggregate (4 pCi/g).

3.5. Evaluation of the beneficial reuse of O&G PW for dust suppression

For a waste product to be a suitable candidate for beneficial reuse, it should meet two criteria: 1) the waste product performs as well as or better than the product it is replacing and 2) use of the waste product presents no greater risk to human or environmental health (Methodology for Evaluating Beneficial Uses of Industrial Non-Hazardous Secondary Materials, 2016). Based on results of this study, O&G PW does not meet either of the recommended criteria for beneficial reuse as a dust suppressant.

To study efficacy, an improved version of the procedure presented in Stallworth et al. (2020) that controlled for humidity was developed, improving method precision and detection limits. Using this refined method, the road discs treated with O&G PW samples did not perform as well as the commercial brines or commercial organic products. Under high humidity conditions, road discs treated with O&G PW generated between 10 % to 84 % less PM₁₀ compared to road discs treated with synthetic rainwater (Fig. 1). However, under the same humidity conditions, the commercial brines and three of the commercial organic products reduced total PM₁₀ emissions over 99 %.

The chemistry of the O&G PW likely explains why they were ineffective at suppressing dust compared to most of the commercial products. Though the O&G PW were hypersaline, which is critical for dust suppression using brines, they had high SAR values, meaning sodium ions were more abundant than divalent calcium and magnesium ions. Divalent cations are critical for adequate dust suppression because they bridge negatively charged particles together, stabilizing the roadbed. Because sodium is monovalent, it does not bridge road particles together and instead can lead to destabilization of the roadbed. Based on TDS and SAR values of effective dust suppressants in this study, few O&G PW listed in the USGS Produced Water Database could be predicted to offer even modest dust suppression.

Spreading O&G PW on roads could decrease roadbed stability because the high sodium concentrations present in O&G PW can cause clay dispersion. Destabilization of the roadbed was observed during the rainfall-runoff experiments. On average, runoff from roadbeds treated with O&G PW had higher TSS concentrations and did not reduce total solids lost from the roadbed compared to roadbeds treated with synthetic rainwater. In contrast, CaCl₂ Brine significantly reduced solids lost during the storm event compared to the rainwater controls (Fig. 2).

O&G PW also pose unique risks to environmental and human health compared to the commercial products. The O&G PW3 used in the rainfall-runoff experiments was enriched in radium, a known carcinogen. All the radium from O&G PW3 that was added to the roadbed during application was mobilized in the runoff, suggesting that roadbeds treated with O&G PW could be a source of radium to adjacent freshwater resources or roadside soils following rain events.

It is important to note that roads treated with either CaCl₂ Brine or O&G PW both generated runoff that poses risks to adjacent freshwater quality, either through salinization or transport of trace metals (Figs. 3, 4, and S8). Contaminant concentrations in runoff exceeded thresholds designed to protect human and environmental health for over 8 h during the storm event. Because the chemistry of runoff waters generally reflected the original composition of the dust suppressant applied to the road, any brine-based dust suppressant, including commercially available CaCl₂ and MgCl₂ products, should also be evaluated for contaminants of concern (e.g., radium) prior to use.

Roadbeds treated with Soybean Oil, however, did not generate runoff that contributed appreciable amounts of salinity, trace metals, or radioactivity observed for the brine-based dust suppressants. Despite the lack of inorganic contaminants, runoff from the roadbeds treated with Soybean Oil contained elevated concentrations of organic compounds relative to the rainwater controls (Fig. S6). Runoff with high concentrations of labile organic molecules can increase the oxygen demand of receiving waters, potentially inducing eutrophic conditions. However, the organic compounds measured in runoff were closely associated with

the road aggregate (Figs. S6 and S7). Solids laden with organics are likely to be trapped in roadside ditches typically constructed alongside unpaved roads rather than exported to adjacent water resources. Though Soybean Oil did not appear to stabilize the roadbed during storm events, it is possible this is due to insufficient curing time. Longer curing times before the onset of precipitation could lead to less solids losses. Therefore, runoff from roadbeds treated with Soybean Oil likely poses little environmental harm.

Nonetheless, it is important to consider the limitations of this study and the applicability of these results to other environmental settings. First, all experiments were conducted with one road aggregate representing a limited geographic region (northwestern Pennsylvania). Interactions between contaminants and the mineral assemblage of this road aggregate may affect contaminant retention. Second, experiments were conducted with O&G PWs representative of the Appalachian Basin. The chemical characteristics of O&G PWs vary considerably between formations and across regions. Therefore, different O&G PWs may present different contaminants of greatest concern. Third, all experiments were conducted using a single storm event. Different rainfall patterns may affect contaminant retention, runoff, and material loss from the roadbed. Future work investigating these variables is necessary to better understand the transport of dust suppressants' constituents from unpaved roads.

4. Conclusions

Results from this study demonstrate that O&G PW do not meet the recommended criteria for beneficial reuse as a dust suppressant. Though O&G PW did suppress PM₁₀ under high humidity conditions relative to rainwater controls, commercial brines and most commercial organic products consistently performed more effectively. Similarly, the high sodium concentrations present in O&G PW likely led to clay dispersion and destabilized the roadbed, which could exacerbate dust emissions during dry conditions or increase TSS concentrations in runoff during storm events. Both scenarios pose risks to human and environmental health.

In road-runoff experiments, measured concentrations in runoff generally reflected the concentration of the dust suppressant originally applied to the road. The highest concentrations were usually measured in runoff from roadbeds treated with CaCl₂ Brine, and runoff from these roadbeds could contribute to freshwater salinization in roadside waterbodies. Runoff from roads treated with O&G PW was similarly hypersaline, though less so compared to roads treated with CaCl₂ Brine. O&G PWs from the Appalachian Basin often contain elevated radium, and all excess radium added to the roadbed during O&G PW application was mobilized during the storm event. Therefore, runoff from roads treated with O&G PW could be a significant source of radium to roadside ecosystems.

Roads treated with Soybean Oil generated runoff that did not have elevated concentrations of salinity or radioactivity but did have the highest concentration of organic molecules. Though export of organics can have environmental consequences, most organic carbon was bound to solids which are likely to get trapped in roadside ditches typically constructed alongside unpaved roads. Soybean Oil was also an effective dust suppressant, reducing over 99.9 % of PM₁₀ relative to rainwater controls. Therefore, Soybean Oil likely poses the lowest risks to human or environmental health of all dust suppressants and O&G PW evaluated in this study.

CRedit authorship contribution statement

James Farnan: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andrew Eck:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andrew Kearney:**

Writing – review & editing, Validation, Investigation, Formal analysis. **Frank L. Dorman:** Resources. **Hassan Ismail:** Methodology. **Eric Chase:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Xiaofeng Liu:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Nathaniel R. Warner:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Formal analysis, Conceptualization. **William D. Burgos:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.170807>.

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