

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

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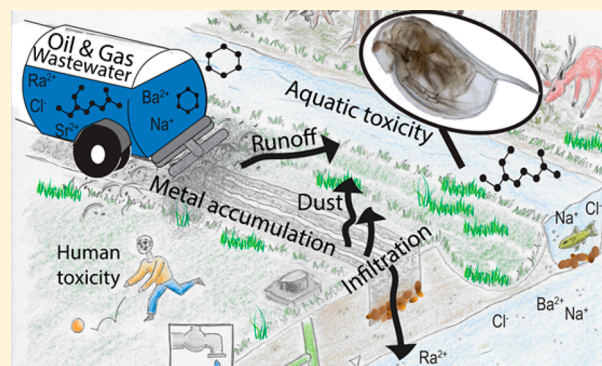
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Supporting Information

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 Pennsylvania

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 $REF = DCM \text{ extraction enrichment factor} / \text{dilution factor in bioassay}$.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: $\% \text{ effect} = (\text{response} - Max_{ref}) / (Max_{ref} - Min_{control})$. 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: $BEQ = \text{slope}_{\text{unknown sample}} / \text{slope}_{\text{reference compound}}$. 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.

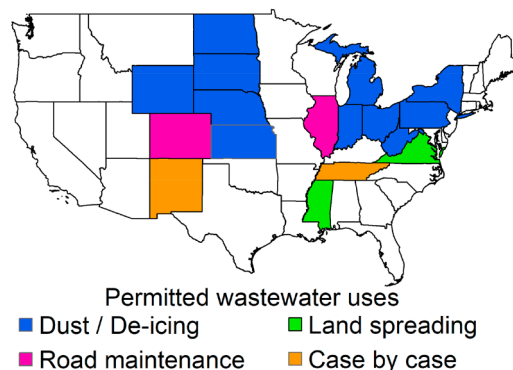


Figure 1. U.S. states with regulations for spreading oil and gas (O&G) wastewaters on roads.

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

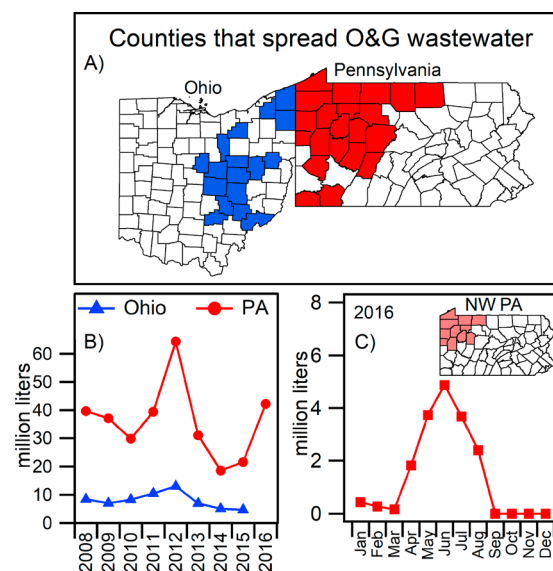


Figure 2. A) Counties in Pennsylvania and Ohio that spread O&G wastewaters on roads since 2008.⁶ B) Volumes of O&G wastewater spread on roads in PA and Ohio. C) Monthly volumes of O&G wastewater spread in NW PA.

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

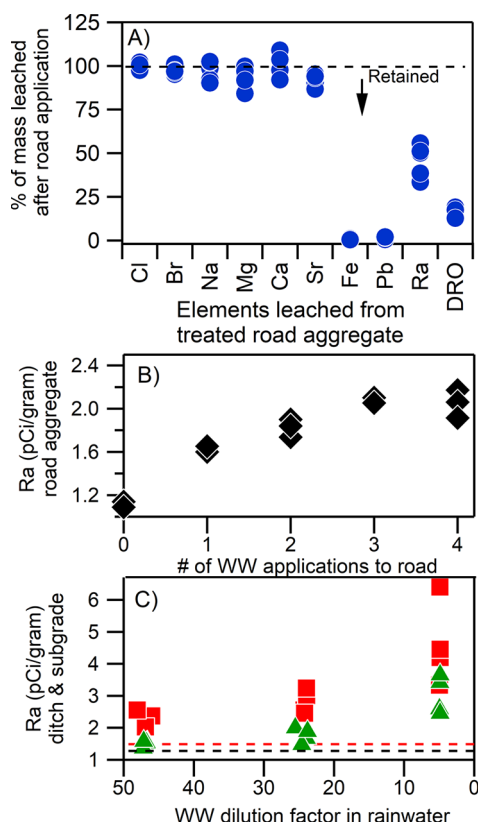


Figure 3. A) Lab experiments showing the percent of contaminant mass that was leached from road aggregate after O&G wastewater application, drying, and leaching with synthetic rainwater. Values below 100% indicate mass retention in the road aggregate. B) Radium in road aggregate after multiple O&G wastewater 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

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 \times 256 spills \times 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

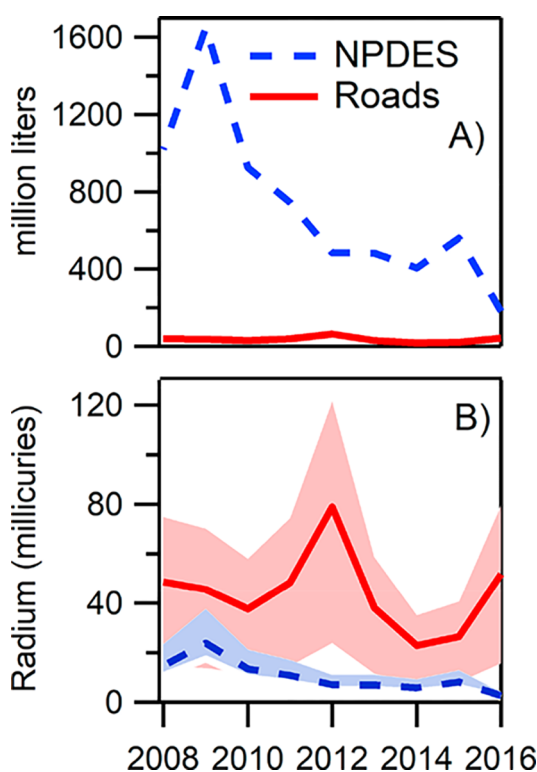


Figure 4. A) Volumes of O&G wastewater spread on roads or discharged through wastewater treatment plants with NPDES permits in Pennsylvania.⁶ B) Annual radium loads to the environment based on radium effluent concentrations reported for O&G wastewater treatment facilities⁴¹ and radium concentrations 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.

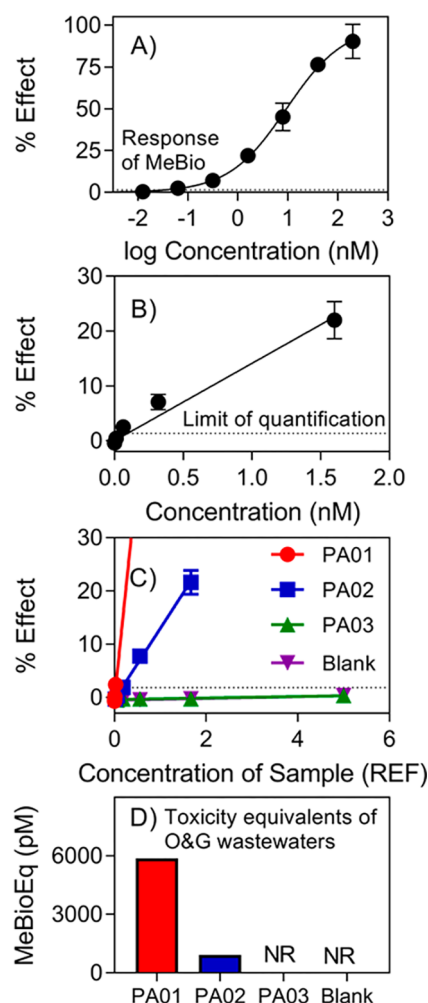


Figure 5. Induction to AhR human receptor by O&G wastewaters (PA01, PA02, and PA03). The response curve for the 1-methyl-6-bromoindirubin-3'-oxime (MeBio) reference compound is shown in parts A) and B). The % effect curves for the O&G wastewater samples are normalized to the minimum and maximum responses 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).

(NfκB) (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

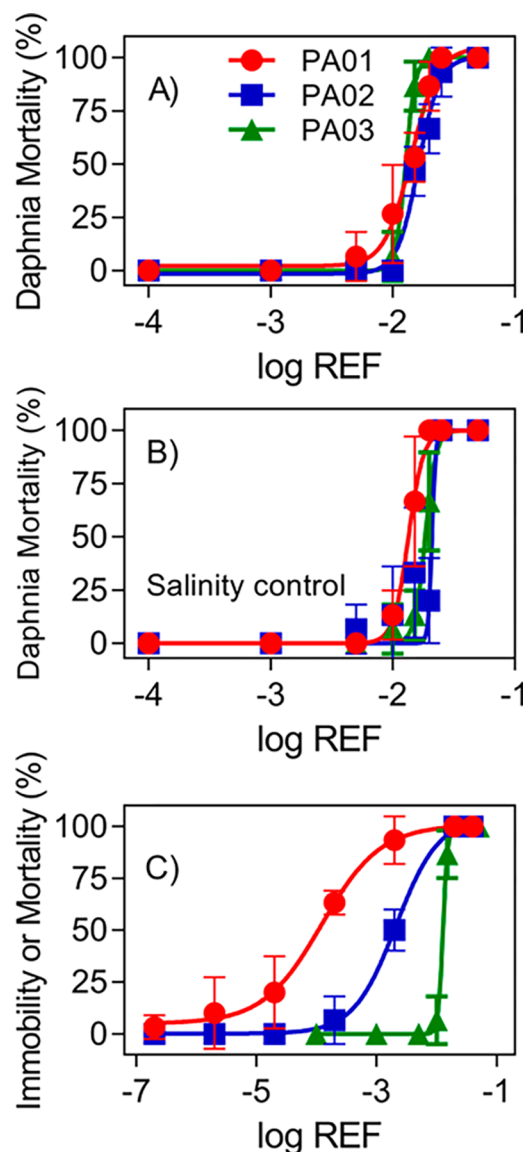


Figure 6. Acute lethal toxicity (Figure 6A) in *Daphnia magna* neonates after 48 hour exposure to oil and gas wastewater samples. *Daphnia* toxicity was also tested after exposure to control samples containing salinities that matched the O&G wastewaters (Figure 6B). The % immobile or dead *D. magna*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