Environmental Contaminants Report Number: R6/729C/14



U.S. FISH & WILDLIFE SERVICE REGION 6



ENVIRONMENTAL CONTAMINANTS PROGRAM

Migratory bird threats by surfactants and other contaminants in evaporation ponds associated with oilfield wastewater disposal facilities

By Pedro 'Pete' Ramirez, Jr. Environmental Contaminants Specialist

Project ID: 6F55



U.S. FISH AND WILDLIFE SERVICE
Ecological Services
Wyoming Field Office
Cheyenne, Wyoming

March 2014

Abstract

Increased exploration and production of oil and gas has resulted in a concurrent increase in the generation of oilfield wastes including produced water, drilling fluid wastes, and wastewater from hydraulic fracturing. In Wyoming, this increase has resulted in the expansion of existing commercial and centralized oilfield wastewater disposal facilities (COWDFs) and the permitting and construction of new COWDFs. These facilities typically contain one or more large ponds and rely on evaporation for water disposal. Although the risk of spills into surface water is low, spills flowing off-site could collect in natural depressions where the ponded water could be a risk to wildlife. The U.S. Fish and Wildlife Service (Service), the U.S. Environmental Protection Agency, and the Wyoming Department of Environmental Quality have conducted environmental compliance inspections of COWDFs since 1998. As part of this effort, the Service collected wastewater samples from nine COWDFs in 2009, 2010 and 2011 to determine if the wastewater contained salts, surfactants or other chemicals that posed risks to migratory birds. Boron concentrations ranged from 5,760 to 87,400 micrograms per liter (ug/L) and selenium concentrations ranged from below detection limits to 701 ug/L. At these concentrations, boron and selenium are toxic to ungulate wildlife and livestock. Surfactants in oilfield wastewater disposed in COWDFs could affect aquatic birds that land on the evaporation ponds by compromising the water repellency of their feathers through reductions in water surface tension. Surface tension measurements in wastewater from two COWDFs were below the level that could cause feather wetting in adult waterfowl in one facility, but slightly above the threshold level in the other. Four facilities contained hypersaline wastewater (total dissolved solids greater than 35,000 milligrams per liter) that also posed risks to aquatic birds due to sodium toxicity and/or salt encrustation. Field inspections also documented aerial drift of oilfield wastewater from the COWDFs onto adjacent lands resulting from the use of sprayers to enhance evaporation. This investigation demonstrates the need for additional data on the surface tension of oilfield wastewater and the impacts of aerial drift from COWDFs on air quality, soil, vegetation, and wildlife.

Acknowledgements: Thanks are extended to Randy Lamdin, U.S. Environmental Protection Agency, and Dennis Lamb, Wyoming Department of Environmental Quality, for the camaraderie we shared during countless field inspections, long days on the road and their commitment to the protection of wildlife. Manuscript reviewers included: George T. Allen, Kimberly Dickerson, Craig Giggleman, Anthony Velasco of the U.S. Fish and Wildlife Service. This study was funded by the Service's Environmental Contaminants Program (Project # 6F55).

Table of Contents

Figures and Tablesi
Introduction
Methods
Results
Surface Tension
Water Quality
Bird Mortalities
Discussion9
Management Recommendations
Literature Cited
Figures and Tables
Figure 1. Surface tension (in Dynes/cm) in wastewater collected from commercial oilfield
wastewater disposal facilities in Wyoming5
Figure 2. Sodium concentrations (in mg/L) in wastewater from five commercial oilfield wastewater disposal facilities in Wyoming
Figure 3. Aerial drift of evaporator spray extends beyond two commercial oilfield wastewater disposal facilities onto adjacent lands, Carbon County Wyoming (Sep 20, 2010 and Nov 8, 2012)
Table 1. Surface tension in water (in mN/m) collected from evaporation ponds in commercial oilfield wastewater disposal facilities in Wyoming
Table 2. Concentrations (in mg/L) of calcium, chlorides, sodium, salinity, and sulfates in wastewater collected from commercial oilfield wastewater disposal facilities in Wyoming6
Table 3. Total dissolved solids (TDS) (mg/L) in wastewater collected from commercial oilfield wastewater disposal facilities in Wyoming
Table 4. Trace element concentrations (in ug/L) in wastewater from commercial oilfield wastewater disposal facilities in Wyoming

Introduction

Commercial and centralized Oilfield Wastewater Disposal Facilities (COWDFs) use large ponds to dispose of the oilfield wastewater through evaporation. Commercial disposal facilities operated for profit receive produced water from one or more oil and gas operators. A centralized disposal facility is owned and operated by the same company that operates the wells that produce the water. Evaporation ponds at these facilities typically range in size from less than 0.4 to 2 hectares (ha) (\approx 1 acre to 5 acres) (Ramirez 2010).

Evaporation Ponds that have oil on their surfaces or that contain surfactants or high salt levels pose significant risks to migratory birds and other wildlife if not properly operated and maintained (Ramirez 2010). Although COWDF evaporation ponds may be free of oil, they may still present a hazard if surfactants or other oilfield chemicals are present in the wastewater or if the evaporation ponds are hypersaline (Ramirez 2010).

Long-term evaporative concentration of salts in the wastewater can create hypersaline conditions in the evaporation ponds and pose risks to migratory birds using them. Bird mortality due to salt crystallization is known to occur in hypersaline industrial wastewater ponds (Meteyer et al. 1997, Sladky et al. 2004, Jehl et al. 2012). Sodium in the hypersaline water can crystallize on the feathers of birds that land in the ponds. The crystals physically alter the feathers' thermoregulatory and buoyancy functions, and may cause birds to drown or die of hypothermia (Sladky et al. 2004). Birds that enter ponds with hypersaline water also may ingest the brine and die from sodium toxicity, although some species are more sensitive to saline conditions than others. Eared grebes (*Podiceps nigricollis*) are more likely to die from hypothermia due to salt crystallization than from the ingestion of hypersaline water (Jehl et al. 2012). Ingestion of water containing high sodium levels can also pose chronic effects to aquatic birds, especially if a nearby source of freshwater is not available. Birds preening the salt crystals from their feathers can ingest the salt. Salt toxicosis has been reported in ponds with sodium concentrations over 17,000 milligrams per liter (parts per million) (Windingstad et al. 1987). Ingestion of as little as 4 grams of salt crystals (NaCl) can be lethal for waterfowl (Meteyer et al. 1997). Sodium intoxication can cause neurological impairment that leaves the bird unable to hold its head upright so that it drowns (Meteyer et al. 1997).

Fifteen COWDFs were permitted by Wyoming Department of Environmental Quality (WDEQ) between 1980 and 1985 and have been operational for approximately 20 to 27 years. According to WDEQ, oilfield produced water disposed of at COWDFs has total dissolved solids (TDS) concentrations ranging from 9,232 ppm to 261,000 ppm (Kim Medina, WDEQ, personal communication, January 11, 2008). Wobeser and Howard (1987) documented salt encrustation of waterfowl in a hypersaline lake with a conductivity of 77,000 micromhos per centimeter (μmhos/cm, equivalent to microsiemens per centimeter or μS/cm). Other studies of hypersaline ponds with conductivities exceeding 100,000 µS/cm also have documented salt encrustation in waterfowl (Stolley and Meteyer 2004; Gordus et al. 2002; Meteyer et al. 1997). Water quality data from three COWDFs in Wyoming show increases in conductivity and TDS over time due to evaporative concentration to levels of more than 77,000 µS/cm, which could cause salt encrustation in aquatic birds landing on the ponds. We have salinity data from only three

Wyoming. Salinity data are needed from other evaporation ponds to determine which facilities are hazardous for migratory birds.

Oilfield wastewater also can contain oil and gas production chemicals such as corrosion inhibitors and surfactants, which can pose risks to migratory birds. When a bird comes into contact with water containing surfactants, the reduced surface tension of the water will allow water to penetrate through the feathers to the skin, thus compromising the thermoregulatory properties of the feathers and subjecting the bird to hypothermia (Stephenson 1997). The loss of feather water repellency will cause the bird to become water logged and drown. Stephenson (1997) reported that water surface tension reduced to approximately 38 to 50 mNm⁻¹ (milliNewtons per meter , equivalent to Dynes/cm) (compared to 72 mNm⁻¹ for pure water) will cause feather wetting in adult waterfowl and could result in mortality.

Some surfactants used for well stimulation can cause skin and eye irritation according to Material Safety Data Sheets. Surfactants remove natural moisturizers from the skin and can damage the skin to the extent that the permeability of the epidermis to water and toxicants is increased (Beradesca *et al.* 1992).

The increase in oil and gas development in western states is resulting in the permitting and construction of additional COWDFs. Increased production from this new development also will result in an increase in produced water volumes estimated at 8 billion barrels in 2007, and up to 10 billion barrels in 2024 (National Energy Technology Laboratory 2005). The WDEQ has permitted the construction of nine COWDFs since 2005 due to the increase in demand for oilfield wastewater disposal facilities (D. Lamb, personal communication, January 24, 2014). The WDEQ rules protect only surface water and groundwater specifically, and do not address the protection of wildlife. However, the WDEQ developed guidelines in 2008 for the design, operation and maintenance of COWDFs. The guidelines recommend measures for the protection of wildlife, such as keeping evaporation ponds free of oil and visible sheens and covering opentopped tanks with netting to prevent access by birds and other wildlife. Additional COWDFs may be permitted and constructed in the near future to handle produced water from the increase in oil and gas development and may result in an increase in migratory bird mortality if the facilities are not designed and managed properly.

The objectives of this study were to:

- determine if salts, surfactants and or other chemicals were present in COWDF evaporation ponds and posed a threat to migratory birds landing on them; and,
- determine average concentrations of TDS and other water quality indicators that can be used as a management decision tool to identify COWDF evaporation ponds that pose a threat to migratory birds.

Methods

Data collected in this investigation included compliance status of each COWDF; the number and type of migratory birds found in each evaporation pond; and other pertinent information such as other impacted wildlife, obvious breeches, spills, and condition of the site. Dead migratory birds in COWDFs were recovered using established field methods and submitted to Service Special Agents in Wyoming following strict line of evidence procedures. Thirty-five COWDFs were inspected from May 2009 through November 2012. Thirty-one of them were receiving oilfield wastewater. Three were under construction, and one was closed and not operational. The number of inspections at each facility ranged from 1 to 7 during the study period. Facilities with environmental compliance issues were inspected more frequently.

Wastewater samples from COWDF evaporation ponds were collected in 1-liter chemically-clean polyethylene jars with Teflon-lined lids. Water samples collected for trace element analyses were preserved by adding laboratory grade nitric acid until a pH of 2.0 was reached. Water samples for basic water chemistry analysis (cations, anions, TDS) were maintained at or below 4°C in an ice-filled cooler in the field and for shipping to the analytical laboratory. Prior to shipment to the analytical laboratory, they were stored at 4°C in a refrigerator at the U.S. Fish and Wildlife Service (Service) Wyoming Ecological Services Field Office laboratory.

Wastewater samples were submitted for trace element and ion analysis to Alpha Woods Hole Labs, Mansfield, Massachusetts, under contract with the Service's Analytical Control Facility (ACF) at Shepherdstown, West Virginia. Wastewater samples also were submitted to the Soil, Water and Plant Testing Lab at Colorado State University, Fort Collins, Colorado for basic water chemistry analysis. Trace element analysis included scans for arsenic, mercury, and selenium using atomic absorption spectroscopy and Inductively Coupled Plasma Emission Spectroscopy for analysis of a variety of elements including boron, barium, chromium, copper, lead, selenium, vanadium, and zinc. The ACF performed quality assurance and quality control on analyses conducted by Alpha Woods Hole Labs.

The surface tension of fluid samples from the COWDF evaporation ponds was measured using a surface tension apparatus comprised of an engraved 250 millimeter (mm) borosilicate glass capillary tube (graduated from 0 to 10 centimeters (cm) in 1-mm divisions) and an outer tube. Measurements were made by the Soil, Water and Plant Testing Lab at Colorado State University.

Additional water samples also were submitted to Dr. Jonathan A. Brant, University of Wyoming, Department of Civil and Architectural Engineering in Laramie, Wyoming for measurement of surface tension. Surface tension measurements were conducted using the Krüss Scientific Easy Drop Goniometer (Model DSA20E). The pendant drop technique was employed to calculate the surface tension of the liquid sample. The pendant drop method is an established technique for determining the surface tension of liquids; the method is based on the determination of the profile of a drop of one liquid suspended in air at hydromechanical equilibrium. From this profile it is possible to calculate the surface tension for the liquid using the Young-Laplace equation:

$$\Delta p = \sigma \left[\frac{1}{r_1} + \frac{1}{r_2} \right]$$

where Δp is the difference in pressure between the outside of the drop and its inside; r_1 and r_2 are the principle radii of the drop; and σ is the surface tension. Water samples were filtered through a 0.45-micrometer (µm) filter to remove large debris and suspended particulates. The filtered water was then loaded into a pre-cleaned syringe (dia. = 1.8 mm), which was inserted into the goniometer. The syringe was cleaned using acetone, hexane and doubly deionized water (DDW). The syringe was first flushed with DDW, then 3 cycles of either acetone or hexane, followed by a triple rinse of DDW. This procedure was followed anytime a new liquid sample was tested. This cleaning procedure is used to remove both apolar and polar contaminants that may accumulate within the syringe. A drop volume of approximately 17-microliter (µL) was dispensed from the syringe and analyzed by the Easy Drop® software to determine the surface tension of the sample. Ten samples were analyzed per water sample to determine an average surface tension value.

Results

Surface Tension

Surface tension measurements on samples submitted to the Soil, Water and Plant Testing Lab at Colorado State University are shown on Figure 1. Surface tension in all the wastewater samples was above the threshold of approximately 38 to 50 mNm⁻¹ or Dynes/cm. Surface tension measurements on COWDF wastewater samples submitted to the University of Wyoming are shown in Table 1. Surface tension in water from Sweetwater 3 COWDF was below the threshold level of 50 mNm⁻¹ that could cause feather wetting in adult waterfowl (Stephenson 1997). The surface tension of wastewater from the Sweetwater 2 COWDF was slightly above the threshold for feather wetting.

Water Quality

Oilfield wastewater disposed into COWDFs contains high concentrations of chlorides, sulfates, and TDS ((Figure 2, Table 2). Sodium in wastewater from one facility was above the 17,000 mg/L that Windingstad et al. (1987) considered the threshold for sodium toxicity in birds. Wyoming state regulations prohibit the discharge of oilfield produced water into surface waters if any of the following water quality criteria is exceeded: chlorides 2,000 mg/L; sulfates 3,000 mg/L; and TDS 5,000 mg/L.

Water samples from four COWDFs had high TDS and are classified as hypersaline, (salinity >35,000 TDS) (Table 3). Although salinity classifications for water salinity vary in the literature, most geoscientific literature uses the following terminology: freshwater <3,000 ppm TDS); saline 3,000 - 35,000 ppm TDS; and hypersaline > 35,000 ppm TDS (Last and Ginn 2005). The hypersaline conditions result from the continual concentration of dissolved solids (salts) due to evaporation over a period of years. Two of the four COWDFs with hypersaline water have been operational for over 25 years and the remaining two for 10 to 15 years.

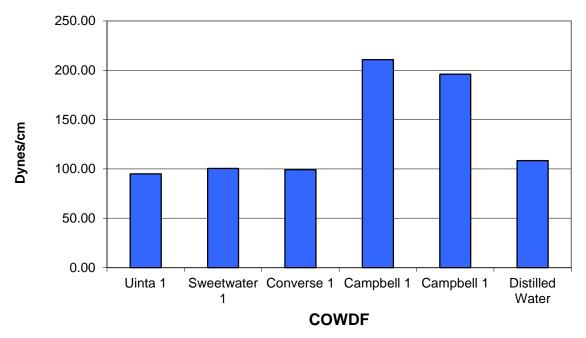


Figure 1. Surface tension in Dynes/centimeter in wastewater collected from five commercial oilfield wastewater disposal facilities in Wyoming.

Table 1. Surface tension in water in milliNewtons per meter collected from evaporation ponds at six commercial oilfield wastewater disposal facilities in Wyoming.

	Surface tension in mN/m						
COWDF#	Minimum	Maximum	Average	Standard deviation			
Converse 1	56.04	60.81	58.14	1.53E+00			
Converse 2	64.31	67.28	66.52	4.80E-01			
Sweetwater 1	58.13	59.74	58.97	5.08E-01			
Sweetwater 2	49.10	53.64	51.37	3.21E+00			
Sweetwater 3	39.27	40.81	40.19	5.98E-01			
Washakie 1	60.02	64.63	62.75	1.40E+00			

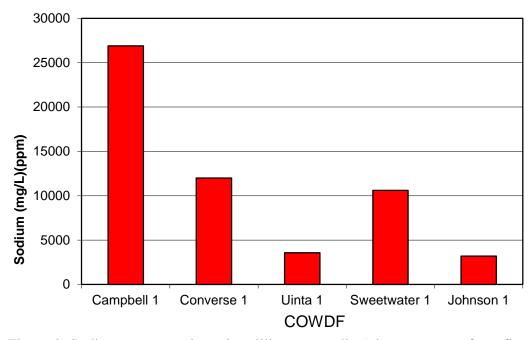


Figure 2. Sodium concentrations (in milligrams per liter) in wastewater from five commercial oilfield wastewater disposal facilities in Wyoming.

Table 2. Concentrations in milligrams per liter (mg/L) of calcium, chlorides, sodium, salinity, and sulfates in wastewater collected from 10 commercial oilfield wastewater disposal facilities in Wyoming. "nd" = no data.

		Ion Concentration in mg/L					
COWDF	Date Collected	Ca	Cl.	Na	Salinity	SO ₄ -2	
Campbell 1	13-Apr-09	53.6	43,000	26,900	73,000	210	
Converse 1	14-Apr-09	4,960	34,000	12,000	58,000	< 50.0	
Converse 2	26-May-11	261	nd	8,730	nd	nd	
Johnson 1	13-May-09	364	5,400	3,190	9,900	< 50.0	
Sweetwater 1	8-Jun-09	397	17,000	10,600	35,000	< 50.0	
Sweetwater 1	5-May-11	124	2,147	13,900	16,640	57.2	
Sweetwater 2	5-May-11	6.2	3,272	21,700	22,223	186	
Sweetwater 3	5-May-11	276	2,506	9,266	10,906	102	
Uinta 1	8-Jun-09	267	6,800	3,580	12,000	86	
Washakie 1	5-May-11	52.5	842	4,350	19,841	621	

Table 3. Total dissolved solids (TDS) in milligrams per liter (mg/L) in wastewater collected from nine commercial oilfield wastewater disposal facilities in Wyoming.

COWDF	Date Collected	TDS	Water Class
Converse 1	14-Apr-09	58,000	Hypersaline
Sweetwater 1	May 2011	57,115	Hypersaline
Campbell 1	13-Apr-09	73,000	Hypersaline
Sweetwater 2	May 2011	76,906	Hypersaline
Converse 2	May 2011	31,497	Saline
Sweetwater 3	May 2011	36,842	Saline
Uinta 1	8-Jun-09	12,000	Saline
Sweetwater 1	8-Jun-09	16,640	Saline
Washakie 1	May 2011	19,841	Saline

Analytical results for trace elements are shown in Table 4. Several trace elements exceeded toxicity thresholds recommended for livestock and ungulate wildlife species: 1,000 μ g/L for arsenic (As), 10,000 μ g/L for barium (Ba), 100 μ g/L for selenium (Se) (Raisbeck et al. 2011) and 5,000 μ g/L for boron (B) (Eisler 1990). Selenium concentrations were extremely elevated and ranged from below detection to 701 μ g/L. Iron concentrations ranged from 1,140 μ g/L to 62,600 μ g/L.

Bird Mortalities

Seventeen of 31 active COWDFs contained oil in the evaporation ponds during the field inspections conducted between 2009 and 2012. Typically the oil was removed after one or two follow-up inspections; however, oil was observed in the evaporation pond of one COWDF in Johnson County throughout the study period. Twenty-two bird carcasses were recovered from three COWDFs between September 2010 and October 2011. Fourteen songbird carcasses were recovered from skim pits adjacent to the COWDF evaporation ponds. Although the skim pits were enclosed with netting, holes in the netting allowed the songbirds to access the pits and become entrapped in the oily fluid. The remaining carcasses recovered from the evaporation ponds were ducks, eared grebes and shorebirds. Species identification of ducks and shorebirds was not possible due to severe oiling.

Table 4. Trace element concentrations in micrograms per liter in wastewater from 11 commercial oilfield wastewater disposal facilities in Wyoming.

	COWDF						
Element	Campbell 1	Conv	Converse 2	Johnson 1			
	13-May-09	13-May-09	26-May-11	26-May-11	13-May-09		
Aluminum	< 2,500	< 2,500	<1000	<1000	< 2,500		
Arsenic	168	99.7	107	36.9	<25		
Boron	50,600	32,100	35,400	25,500	5,760		
Barium	6,470	16,200	33,000	18,600	857		
Beryllium	< 25	< 25	<10	<10	<25		
Cadmium	< 25	< 25	<5	<5	<25		
Chromium	< 50	< 50	<20	<20	< 50		
Copper	497	363	249	138	< 50		
Iron	< 2,500	17600	15,400	9,920	8,560		
Mercury	< 0.05	< 0.05	< 0.25	< 0.25	< 0.05		
Magnesium	179,000	394,000	292,000	45,600	17,900		
Manganese	63.9	989	1,370	420	736		
Molybdenum	< 25	< 25	<10	18.3	<25		
Nickel	25.9	154	91.5	23.9	<25		
Lead	< 50	< 50	<20	<20	< 50		
Selenium	411	388	492	487	<250		
Strontium	12,800	65,900	61,300	21,800	7,020		
Vanadium	94	71	<100	<100	< 50		
Zinc	< 500	< 500	<200	<200	< 500		

	COWDF							
Element	Sweetwater 1		Sweetwater 2	Sweetwater 3	Washakie 1	Uinta 1		
	8-Jun-09	6-May-11	6-May-11	5-May-11	16-May-11	8-Jun-09		
Aluminum	< 2,500	<1000	<1000	<1000	<1000	< 2,500		
Arsenic	40.4	75.4	95.4	80.9	162	30.1		
Boron	28,700	53,700	87,400	33,900	56,300	30,900		
Barium	30,100	31,100	25,900	31,100	1,600	2,640		
Beryllium	< 25	<10	<10	<10	<10	< 25		
Cadmium	< 25	5.6	<5	<5	<5	< 25		
Chromium	< 50	29	22	43	67	< 50		
Copper	143	232	486	185	89	67		
Iron	3,580	2,210	5,320	32,500	1,140	62,600		
Mercury	< 0.05	< 0.25	< 0.25	0.32	< 0.25	< 0.05		
Magnesium	67,400	176,000	71,100	67,000	111,000	23,300		
Manganese	2,370	56	104	3,020	442	2,710		
Molybdenum	< 25	<10	15.4	28.3	31.6	47.5		
Nickel	36.4	53.2	178	45.2	35.3	25.7		
Lead	< 50	<20	<20	<20	<20	< 50		
Selenium	<250	330	701	440	<100	<250		
Strontium	19,700	20,300	7,590	31,500	5,980	13,800		
Vanadium	< 50	<100	<100	<100	<100	< 50		
Zinc	< 500	< 200	< 200	201	<200	< 500		

Discussion

Aquatic migratory birds are the primary wildlife species at risk at COWDFs due to oiling, salt encrustation, and surfactants. The high concentrations of several trace elements pose a risk to wildlife chiefly through direct ingestion of the wastewater as the evaporation ponds do not support food items such as aquatic vegetation and aquatic invertebrates. The high concentrations of several trace elements and metals detected are expected, given that the oilfield wastewater is disposed of into COWDFs because it does not meet water quality standards. These elevated concentrations reinforce the importance of ensuring that the evaporation ponds do not leak and contaminate the groundwater or surface water. However, the risk of wastewater spills into surface water is minimal as most COWDFs in Wyoming are not in close proximity to streams, ponds, or wetlands. Nonetheless, an off-site release could collect in natural depressions and would present a potential for exposure to wildlife and would likely contaminate soil and vegetation. Leaks from the evaporation ponds also could contaminate groundwater, with the potential to impact surface water.

Boron and barium were present in concentrations that may pose toxicity risks to wildlife. Boric acid (B(OH)₃), is used as a crosslinker in hydraulic fracturing fluid to increase the viscosity of the hydraulic fracturing fluid to enhance the transport of proppants into the formation (Montgomery 2013, Gulbis and Hodge 2000). Boron is toxic to plants and mammalian wildlife at concentrations exceeding 2,000 and 5,000 µg/L, respectively (Eisler 1990). Barium is used in drilling fluids and can be present in produced water (Raisbeck et al. 2011). According to Raisbeck et al. (2011) barium chloride (BaCl₂) is the more soluble form of barium and the most toxic; whereas barium sulfate (BaSO₄) is insoluble and thus less toxic. However, the microbial transformation of BaSO₄ to more toxic forms in ruminant wildlife is possible (Raisbeck et al. 2011). Although the boron and barium can be linked to oilfield wastewater (drilling fluid, produced water, and hydraulic fracturing flowback water), the source of selenium is less clear. The oil and gas reservoir source rocks are the most probable source of the high selenium concentrations in the oilfield wastewater. Marine Cretaceous shales are typically high in selenium in the western United States, so produced water from oil and gas-bearing shale formations can contain selenium (Seiler et al. 1999). Selenium concentrations higher than 100 μg/L pose a risk to sensitive species of livestock and potentially, ungulate wildlife (Raisbeck 2011). However, selenium in the wastewater does not exceed the level) known to cause immune suppression in mallards (2,200 µg/L organic selenium as selenomethionine, Fairbrother and Fowles 1990).

Drilling fluid wastes, formation water and water produced from enhanced oil recovery (EOR) operations are disposed of in COWDFs. The increase of hydraulic fracturing in well completions also has generated significant quantities of wastewater disposed of in COWDFs. Following the fracturing of oil and gas-bearing formations, some of the hydraulic fracturing fluid flows out of the well, and is termed "frac flowback." Estimates of frac flowback vary from 10 to 60 percent return of the fluid injected into the formation (American Petroleum Institute 2010). The frac flowback is transported from the well site to a disposal facility where it is disposed of by deep-well injection or release into evaporation ponds at COWDFs. Acidizing treatments in oil and gas wells to stimulate production can result in an increase in the amount of oil solubilized in the water caused by the formation of microemulsions (Ali and Hinkel 2000). The flowback

water from an acid treated well will contain higher amounts of oil, and the resulting microemulsions can impair the separation of oil and water at COWDFs. Ineffective oil-water separation will result in oiling of the COWDF evaporation ponds.

The ability of surfactants to solubilize, emulsify/demulsify, alter surface tension and viscosity, and reduce friction, are useful in the exploration and production of oil and gas and are used in drilling fluid, hydraulic fracturing fluid and in EOR operations (Schramm and Marangoni 2000). The presence of surfactants in COWDF wastewater can pose a risk to aquatic birds landing in the evaporation ponds (Ramirez 2010). The half-life of surfactants ranges from less than a day for alkyl aryl sulfonate and petroleum sulfonate surfactants to 10 days for alcohol ether sulfate surfactants (Britton 2000). Aquatic birds landing in a COWDF evaporation pond within a week following the disposal of wastewater containing surfactants could become water logged and succumb to hypothermia or the loss of buoyancy could cause the bird to drown. Anionic surfactants (sulfonated or phosphorylated forms) can cause dermal irritation in birds and cationic surfactants (Quarternary ammonium with alkyl or aryl substituent groups), if ingested by birds, can cause corrosive esophageal damage, collapse, or coma (Dumonceaux and Harrison 1994). Surfactants also vary in toxicity to aquatic organisms. Alkyl phenol ethoxylate (nonylphenol ethoxylate) surfactants are the most toxic and have estrogenic effects (Britton 2000). Aquatic organisms would likely risk exposure to toxic concentrations if a spill reached surface waters. Toxicity to birds landing in evaporation ponds containing alkyl phenol ethoxylate surfactants would depend on the concentration and the amount ingested by birds; however, the toxicity due to dermal exposure is unknown. Some surfactants used for well stimulation can cause skin and eye irritation according to Material Safety Data Sheets. Surfactants remove natural moisturizers from the skin and can damage the skin to the extent that the permeability of the epidermis to water and toxicants is increased (Beradesca et al. 1992). Observations of excessive preening by eared grebes swimming in the COWDF evaporation ponds may indicate that surfactants or other chemicals in the wastewater were irritating the birds.

Sources of iron in produced water or oilfield wastewater include dissolved iron in the formation water and from the corrosion of iron or steel in well casings or tubing (Kemmer 1988, Obeadalla and Abdelmagd 2013). Water containing colloidal iron sulfide has a black color (Obeadalla and Abdelmagd 2013) and was observed in several of the COWDF evaporation ponds. Bacteria growing in iron sulfide-rich water creates a thin biofilm on the pond surface resembling an oil sheen that fractures into small "plates" when the water surface is disturbed (Otton and Zielinski 2000). Although colloidal suspensions in water can lower surface tension (Dong and Johnson 2003), it is not known if iron sulfide colloids or the biofilms created by bacteria disrupt bird feathers' thermoregulatory and water-repellency functions.

Oil and other hydrocarbons in wastewater ponds are threats to birds and other wildlife (Ramirez 2010). Additionally, hydrocarbons in the wastewater can be a source of volatile organic compound (VOC) emissions from COWDFs and may affect air quality and lead to exceedances in ozone levels (Thoma 2009). In response to the increase in the generation of oilfield wastewater, and the concurrent demand for oilfield wastewater disposal, COWDF operators have constructed more evaporation ponds to accommodate the additional wastewater. Additionally, because hypersaline conditions decrease the evaporation rate of water (Hammer 1986), some COWDF operators use aerial sprayers to enhance evaporation thus freeing up pond capacity for

additional wastewater (Figure 3). These sprayers atomize the wastewater, which is dispersed as a fine mist over the evaporation pond. VOCs in the wastewater also are aerosolized by the sprayers and released into the air. The aerial drift of wastewater can deposit salts, naturally occurring radioactive material (NORM), hydrocarbons, and trace elements onto the vegetation and soils adjacent to the COWDF (Figure 3). Excessive salts deposited on adjacent land can kill vegetation and cause long-term damage to soils (Harris et al. 2005).

The development of guidelines by the WDEQ for the design, operation and maintenance of COWDFs in Wyoming appears to have had a positive impact on reducing wildlife mortality in COWDFs. However, mortalities of protected migratory birds occur when operators do not follow the guidelines. Continued site visits and enforcement of the standards for COWDFs are strongly encouraged.

Management Recommendations

The reduced surface tension documented by this investigation points to the need for additional data on oilfield wastewater surface tension, the presence of surfactants in COWDFs and the risk for bird mortality. Further investigation is needed on the extent of aerial drift of COWDF wastewater resulting from the use of sprayers and the impacts on soil, vegetation, and resident wildlife. More study is also needed on VOC emissions from COWDFs and impacts on air quality. This information is essential given the increase in oil and gas exploration and production along with the concurrent increase in the number of COWDFs to handle the associated increase in oilfield wastewater. Additionally, the exposure of aquatic birds to chemicals in flowback water disposed into COWDF evaporation ponds should be studied further to determine if contact with this wastewater can lead to avian mortality. Given the increase in the production of oilfield wastewater and the concurrent demand for COWDFs, frequent inspections by regulatory agencies are crucial to ensure that the facilities are operated properly to minimize risks to birds and other wildlife. Other states that permit the construction and operation of COWDFs with large evaporation ponds should develop guidelines or requirements for the design, construction, operation, and maintenance of COWDFs. States should implement an annual training program for COWDF personnel and provide them with a review of permit requirements, health and safety best management practices, and spill response procedures (Ramirez 2010).





Figure 3. Aerial drift of evaporator spray extends beyond two commercial oilfield wastewater disposal facilities onto adjacent lands, Carbon County Wyoming (Sep 20, 2010 and Nov 8, 2012).

Literature Cited

- Ali, SA and JJ Hinkel. 2000. Additives in acidizing fluids. Pages 15-1 15-20 in MJ Economides and KG Nolte, editors. Reservoir Stimulation. John Wiley & Sons, Ltd. New York, NY. 856 pp.
- API (American Petroleum Institute). 2010. Water Management Associated with Hydraulic Fracturing. API Guidance Document HF2, First Edition, American Petroleum Institute, Washington, DC. 22 pp.
- Berardesca, E, GP Vignoli, G Borroni, C Oresajo, and G Rabbiosi. 1992. Surfactant damaged skin: which treatment. Pages 283-286 in R. Marks and G. Plewig, editors. The environmental threat to the skin. Martin Dunitz, Ltd. London. 432 pp.
- Britton, LN. 2000. Toxicity and persistence of surfactants used in the petroleum industry. Pages 541-565 in L.L. Schramm, editor. Surfactants: fundamentals and applications in the petroleum industry. Cambridge University Press. New York. 630 pp.
- Dumonceaux G and GJ Harrison. 1994. Bird Toxins. Pages 1030-1050 in BW Ritchie, GJ Harrison, and LR Harrison, editors. Avian Medicine: Principles and Application. Wingers Publishing, Inc. Lake Worth, FL. 525 pp. Available at: http://avianmedicine.net/content/uploads/2013/03/37.pdf
- Dong, L and D Johnson. 2003. Surface tension of charge-stabilized colloidal suspensions at the water-air interface. Langmuir (19):10205-10209.
- Gulbis, J and RM Hodge. 2000. Fracturing fluid: chemistry and proppants. Pages 7-1 7-23 in MJ Economides and KG Nolte, editors. Reservoir Stimulation. John Wiley & Sons, Ltd. New York, NY. 856 pp.
- Eisler, R. 1990. Boron hazards to fish, wildlife, and invertebrates: a synoptic review. U. S. Fish Wildlife Service, Biological Report 85(1.20).
- Fairbrother, A and J Fowles. 1990. Subchronic effects of sodium selenite and selenomethionine on several immune-functions in mallards. Archives of Environmental Contaminants and Toxicology 19:836-844.
- Gordus, AG, HL Shivaprasad, and PKSwift. 2002. Salt toxicosis in ruddy ducks that winter on an agricultural evaporation basin in California. Journal of Wildlife Diseases 38: 124-131.
- Hammer, T. 1986. Saline ecosystems of the world. Dordrecht: Dr. W. Junk Publishers. 616 pp.
- Harris, TM, JB Tapp, and KL Sublette. 2005. Remediation of oil-field brine-impacted soil using subsurface drainage system and hay. Environmental Geosciences 12:101-113.

- Jehl, JR Jr, AE Henry, and J St Leger. 2012. Waterbird mortality in hypersaline environments: the Wyoming trona ponds. Hydrobiologia 697:23-29.
- Kemmer, FN. 1988. The NALCO water handbook. McGraw-Hill Book Co. New York. 1120 pp.
- Last, WM and FM Ginn. 2005. Saline systems of the Great Plains of western Canada: an overview of the limnogeology and paleolimnology. Saline Systems 1:10. Available at: http://salinesystems.org/content/1/1/10
- Meteyer CU, RR Dubielzig, FJ Dein, LA Baeten, MK Moore, JR Jehl Jr and K Wesenberg. 1997. Sodium toxicity and pathology associated with exposure of waterfowl to hypersaline playa lakes of southeast New Mexico. Journal of Veterinary Diagnostics Investigation 9: 269-280
- Montgomery, C. 2013. Fracturing fluid components. Pages 25 45 in AP Bunger, J McLennan, and R Jeffrey, editors. Effective and Sustainable Hydraulic Fracturing. InTech Publishing. Available at: http://www.intechopen.com/books/effective-and-sustainablehydraulic-fracturing (Accessed February 2014).
- NETL (National Energy Technology Laboratory). 2005. Produced water from oil and natural gas operations – setting the context. Program Facts. U.S. Dept. Energy, Office of Fossil Energy. Available at: http://www.netl.doe.gov/technologies/oilgas/publications/AP/Program063.pdf (Accessed July 2007).
- Obeadalla, LE and SE Abdelmagd. 2013. Beneficial uses of the produced water from palogue oil field for injection to enhance oil recovery. Archives of Applied Science Research 5(4):69-75. Available at: http://www.scholarsresearchlibrary.com
- Otton, JK and RA Zielinski. 2000. Simple techniques for assessing impacts of oil and gas operations on Federal lands – a field evaluation at Big South Fork National River and Recreation Area, Scott County, Tennessee (online edition). Open-File Report 00-499. U.S. Geological Survey, Lakewood, CO. Available at: http://pubs.usgs.gov/of/2000/ofr-00-499/
- Raisbeck, MF, SL Riker, CM Tate, R Jackson, MA Smith, KJ Reddy, and JR Zygmunt. 2011. Water quality for Wyoming livestock and wildlife – a review of the literature pertaining to health effects of inorganic contaminants. Univ. Wyoming Dept. Veterinary Sciences and Renewable Resources, Wyoming Dept Game and Fish, Wyoming Dept Environ. Quality. Laramie, Wyoming. Available at: http://www.wyomingextension.org/agpubs/pubs/B1183.pdf
- Ramirez, P. 2010. Bird mortality in oil field wastewater disposal facilities. Environmental Management 46:820-826.

- Schramm, LL and DG Marangoni. 2000. Surfactants and their solutions: basic principles. Pages 3 – 50 in L.L. Schramm, editor. Surfactants: fundamentals and applications in the petroleum industry. Cambridge University Press. New York. 630 pp.
- Seiler, RL, JP Skorupa, and LA Peltz. 1999. Areas susceptible to irrigation-induced selenium contamination of water and biota in the western United States. U.S. Geological Survey Circular 1180. U.S. Geological Survey, Denver, CO 36 pp.
- Sladky, KK, FJ Dein, P Ramirez and CF Quist. 2004. Investigation of migratory bird mortality associated with exposure to soda ash mine tailings water in southwest Wyoming. Unnumbered Final Report, Biological Resources Division, US Geological Survey, National Wildlife Health Center, Madison, WI. 46 pp.
- Stephenson, R. 1997. Effects of oil and other surface-active organic pollutants on aquatic birds. Environmental Conservation 24:121-129
- Stolley, DS and CU Meteyer. 2004. Peracute sodium toxicity in free-ranging black-bellied whistling duck ducklings. Journal of Wildlife Diseases. 40: 571-574.
- Thoma E. 2009. Measurement of Emissions from Produced Water Ponds: Upstream Oil and Gas Study #1. U.S. Environmental Protection Agency Final Report /600/R-09/132. Air Pollution Prevention and Control Division, National Risk Management Research Laboratory, Research Triangle Park, NC, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 70 pp.
- Windingstad, RM, FX Kartch, RK Stroud, and MR Smith. 1987. Salt toxicosis in waterfowl in North Dakota. Journal of Wildlife Diseases 23:443-446.
- Wobeser, G and J Howard. 1987. Mortality of waterfowl on a hypersaline wetland as a result of salt encrustation. Journal of Wildlife Diseases 23: 127-134.