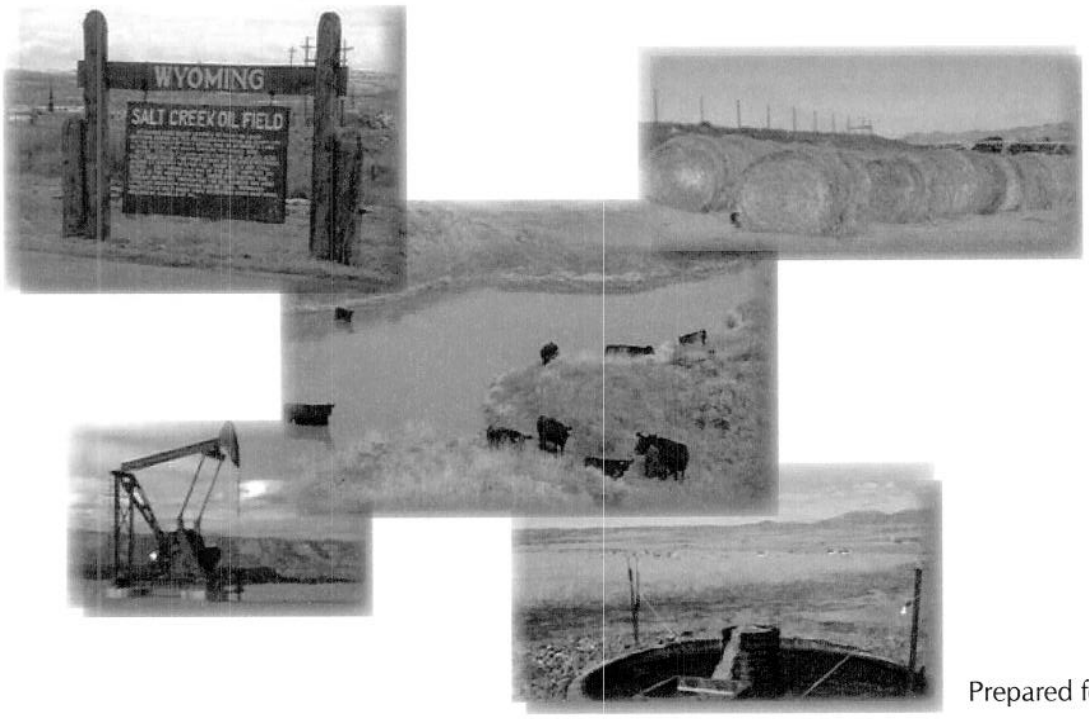
Water Quality Effects and Beneficial Uses of Wyoming Produced Water Surface Discharges



Prepared for:

Petroleum Association of Wyoming
951 Werner Court, Suite 100
Casper, WY 82601

January 16, 2007

GEOMEGA

GOOD SCIENCE • HARD WORK • CREATIVE THINKING

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Executive Summary

The Wyoming Department of Environmental Quality (WDEQ) is reviewing a petition to change the current Wyoming effluent limits for total dissolved solids (TDS) and sulfate, and to add an effluent limit for barium for coal bed natural gas (CBNG) industry produced water. The petitioners argue that current effluent limits for produced water are not "protective of stock and wildlife."

In addition to evaluating injuries to livestock and wildlife, effects on the well-being of the people of Wyoming should be carefully weighed, consistent with Wyoming statute W.S. 35-11-302(vi). Changing current effluent limits would not only impact water *quality*, but also ultimately water *quantity*. This is because unnecessarily stringent effluent limits for produced water discharges would likely result in reduced discharge to surface water bodies; the economics of treating large quantities of produced water to meet stringent effluent limits are such that injection/re-injection, deep disposal and/or reduced exploration and development are likely results of additional treatment requirements.

The adequacy of the current effluent limits and the validity of the proposed limits were analyzed by Geomega, who performed an ecological risk assessment of TDS, sulfate and barium water quality to livestock and wildlife, reviewed social and economic benefits to Wyoming residents, and evaluated potential injuries caused by changes in effluent limits.

This report addresses water quality effects of both CBNG and conventional oil and gas produced water. Although the petition targets only CBNG production in Wyoming, conventional oil production operations could also be affected by state-wide amendments to water quality effluent limits, because constituent concentrations of many conventional produced water surface discharges is greater than the petitioners' proposed limits. Hence, impacts to this sector of the oil and gas industry were also considered.

Geomega's analysis shows that current WDEQ effluent limits pose no measurable adverse effect to the health and well-being of domestic livestock and wildlife. Furthermore, there would be no incremental reduction in wildlife or livestock injury if water quality effluent limits were changed to the petitioners' requested limits.

In addition, associated social and economic impacts of reduced water discharges and/or reduced exploration and development would be harmful to Wyoming residents.

Geomega reviewed literature-based toxicity studies and published guidelines for each of the constituents of interest, and gathered empirical data from several Wyoming ranchers who use produced water sources for their livestock. The ecological risk assessment followed US Environmental Protection Agency guidelines (US EPA 1998).

Ranchers' experiences indicate that water containing sulfates up to 3,100 mg/L and TDS up to 5,390 mg/L do not pose adverse risk to livestock in Wyoming. The ranchers' experiences were evaluated in conjunction with published literature; as a result, the following water quality benchmarks were recommended for each constituent as an alternative to the petitioner's proposed limits:

Benchmark/Limit	Barium	Sulfate	TDS
Recommended benchmark:	13	3,010	5,600
Current effluent limit:	None	3,000	5,000
Petition proposed limit:	0.2	500	2,000

Table E-1. Summary table of recommended water quality benchmarks for barium, sulfate and TDS that are protective of livestock and wildlife receptors, compared to the current WDEQ effluent limits and the petition's proposed effluent limits. All results in mg/L.

These recommended water quality benchmarks are consistent with current WDEQ effluent limits, other published local and national established benchmarks, and ranchers' experiences. They are not, however, consistent with the proposed limits in the petition. The recommended benchmarks are protective of wildlife and livestock such that ingestion of surface water with TDS concentrations up to 5,600 mg/L, sulfate concentrations up to 3,010 mg/L, and barium concentrations up to 13 mg/L will not result in injury to the animals. Thus, reducing effluent limits of sulfate and TDS to the petitioners' proposed limits will not result in any incremental reduction in risk to wildlife or livestock.

In the larger picture, however, CBNG and conventional oil extraction industries that surface-discharge produced water have additional social and economic value to residents in

Wyoming. Reductions in exploration/development and produced water surface discharge, due to unnecessarily stringent effluent limits, could result in substantial injury to the social and economic well-being of many Wyoming residents.

Numerous landowners in the Powder River and Bighorn basins benefit from produced water surface discharges through irrigation and/or livestock watering. This statement is supported by the many letters of beneficial use, rancher interviews, and other literature sources. Produced water surface discharges also support wildlife populations that may not otherwise be viable, including wild horse populations in the Bighorn basin, and migratory and waterfowl bird species at the Loch Katrine wetland complex. In addition, produced water discharges in certain circumstances improve water quality of natural drainages, as evidenced by the increased livestock capacities cited by several ranchers in the Salt Creek area of the Powder River basin.

To analyze the social and economic impacts of produced water surface-discharge in Wyoming, Geomega gathered US Census Bureau and US Department of Agriculture information on livestock use and economic indices in the Bighorn, Powder River and Platte River basins, and reviewed use attainability analyses and economic analyses authored by Gene R. George and Associates (2005), RETEC (2004), SWWRC et al. (2002), Taylor (1999). Economic effects of reduced exploration and development include lost revenue from oil and gas extraction facilities in the form of jobs and associated earnings, and basic oil and gas export revenue. Case studies include the following:

- Elimination of the South Casper Creek field in the Platte River basin would result in annual losses of $3 million (in 2002 dollars) to the basic exports of Natrona County, with additional losses of associated jobs with annual earnings that totaled $487,142 in 2002.

- Elimination of the Hamilton Dome oil field in the Bighorn basin would result in losses of $28.7 million (in 1997 dollars) in state total annual economic output, with associated losses of 136 jobs in Hot Springs county alone with earnings totaling $4.1 million in annual labor.

- Elimination of operations in the Salt Creek area in the Powder River basin would result in losses of jobs directly and indirectly related to oil and gas production, that result in an estimated $4.6 million in annual earnings for Natrona and Johnson Counties (in 1997 dollars).

Social impacts of reduced exploration/development include loss of financial contributions that go toward the improvement of local communities. County income from these operations supports various public facilities including schools, hospitals, libraries, fire departments, environmental programs, and the county general fund. Examples include the following:

- Elimination of the South Casper Creek field would result in reduced social contributions to Natrona County such as:
  - county property tax income by 2.5%,
  - severance taxes of 0.04%,
  - sales and use taxes of 0.16%, and
  - 2.5% of federal royalties for the county (on average, between 1997 and 2002).
  - State severance taxes; in 1997, severance taxes from the Salt Creek fields were estimated at $2.4 million. 2.6% ($62,257) of the total severance tax was received by Natrona County, and 0.2% ($4,789) was received by Johnson County.
- Elimination of the Hamilton Dome oil field would reduce social contributions to Hot Springs County (in terms of fiscal contributions) totaling:
  - 29% of total property taxes
  - 9% of total general fund revenues,
  - 27% of the library system's total revenues,
  - 2% of county hospital revenues,
  - 9% of county weed and pest management program,
  - 29% of the rural fire district budget, and
  - additional funds for school districts, averaging $1.4 million annually.

- Elimination of operations in the Salt Creek area in the Powder River basin would reduce social contributions to Natrona and Johnson Counties totaling (in 1997 dollars):
    - School funding of $2 million annually;
    - County government funding of $500,000 annually;
    - Community college funding of $300,000 annually.

Even with continued industry presence, lost opportunity to surface-discharge water would have a negative impact on Wyoming landowners and ranchers in many counties in the form of lost jobs and income from livestock and farming businesses. Additional negative impacts would result for the State general fund and federal mineral revenues. The following are examples of estimated economic losses from lost opportunity to surface-discharge water:

- In the Bighorn basin:
    - 15 to 20% loss of cattle in the Cottonwood Creek area, corresponding to an estimated $2 million in lost annual livestock sales for the Bighorn basin;
    - economic losses of 1.7% ($3.3 million) of total annual economic output in Hot Springs County, plus job losses totaling $645,000 in annual labor income;
    - an 8% loss of irrigated pastureland in the Cottonwood Creek area, corresponding to a loss of 1,600 acres of irrigated cropland and 4,000 tons of annual hay production;
    - livestock losses estimated between 30 and 50% by some ranchers in the Bighorn basin, resulting in estimated losses $387,000 to $645,000 in annual livestock sales;
    - lost access to federal funding and associated employment at the Loch Katrine wetland complex, which was created from produced water sources.

- In the Powder River basin:
  - livestock losses estimated between 20 and 40% in the Salt Creek area, corresponding to estimated losses of $590,175 to $1.1 million in annual livestock sales;
- All counties affected by loss of opportunity to surface discharge produced water would face:
  - Estimated herd losses between 15% and 50%, corresponding to lost annual livestock sales between $57 million and $192 million.
  - additional costs to ranchers to develop alternative water sources such as wells, water hauling and breaking ice;
  - associated job losses related to ranching and farming; and
  - lost revenue from hunting, fishing and tourism due to declining wildlife populations.

Economic and social injury of reduced exploration/development and loss of opportunity to surface-discharge produced water would not be limited to the case studies provided in this report. State-wide, the oil and gas industry supported 2,995 employees in 2002, with a total annual payroll of $162 million (US Bureau of the Census 2002). In addition, support activities for oil and gas operations, including drilling of oil and gas wells, employed an additional 9,200 employees with earnings totaling $332.6 million in 2002. The value of shipments, sales and receipts for oil and natural gas industries in Wyoming totaled $3.9 billion (in 2002), representing ~14% of the total sales, shipments and receipts for the state. At least a portion of the jobs, earnings and state revenue is expected to be negatively impacted by unnecessarily stringent effluent limits across Wyoming. A state-wide analysis of economic and social benefits and injury upon loss of produced water surface discharge, exploration and development is recommended to evaluate the total impact of the petitioners' proposed water quality amendments.

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1 Ecological Risk Assessment of TDS, Sulfate and Barium Water Quality in Wyoming Surface Water Bodies

1.1 Introduction

The Wyoming Department of Environmental Quality (WDEQ) is reviewing a petition to change current effluent limits of total dissolved solids (TDS) and sulfate, and to add a barium limit for coal bed natural gas (CBNG) produced water. The petitioners argue that the current effluent limits are not "protective of stock and wildlife."

To analyze the adequacy of the current effluent limits and the validity of the proposed limits to protect wildlife and livestock, Geomega performed an analysis of livestock and wildlife chemical risk from TDS, sulfate and barium constituents in surface water bodies created or impacted by produced water surface discharge in Wyoming. This was accomplished by investigation along two lines of evidence. The first line included peer-reviewed scientific literature on water quality effects on animal species; the investigation sought to determine the water quality attribute (TDS, sulfate, barium) levels that are protective of animal species of interest, including livestock (heifers, steers and sheep), and wildlife (mammals and birds).

The second line of evidence included data compiled from Wyoming ranchers who use produced and natural water sources for their livestock. In-person and telephone interviews were conducted with a handful of ranchers in the Bighorn and Powder River structural basins in Wyoming to gather information on the nature and extent of produced or natural water usage and effects noted from that use. Where available, data was obtained from these ranchers to quantitatively evaluate the effects of produced water usage.

1.1.1 Ecological risk assessment procedure

A quantitative evaluation of risks to livestock and avian and mammalian wildlife from exposure to surface water in produced water bodies was undertaken to determine if the water chemistry could cause unacceptable adverse effects.

This ecological risk assessment (ERA) follows the US Environmental Protection Agency's (EPA) Guidelines for Ecological Risk Assessment (US EPA 1998), as well as other supplementary guidance documents, including:

- Guidelines for Exposure Assessment (US EPA 1992a),
- Wildlife Exposure Factors Handbook (US EPA 1993),
- Generic Assessment Endpoints for Ecological Risk Assessments (Draft) (US EPA 2002),
- other relevant federal and state regulations and guidance, and
- the general literature.

With the goal of improving the quality and consistency of its own risk assessments, the US EPA published a set of guidelines to describe the assessment process of ecological risk assessment. The guidelines incorporate the elements needed to assess the likelihood that adverse ecological effects could occur as a result of exposure to one or more stressors. As outlined in the guidance, the basic steps in an ecological risk assessment include problem formulation, analysis, and risk characterization. This report addresses each of these steps.

The problem formulation stage of this ERA includes background information on the availability and quality of water bodies in Wyoming, both from natural and produced water sources. Subsequently, wildlife and livestock uses of produced water bodies are described and an ecological conceptual model is presented that describes the relationships between the stressors (produced water bodies) and biological components. Finally, a set of endpoints is identified to ensure that the risk assessment goals are consistent with the petitioners' statements regarding WDEQ water quality regulations.

The analysis phase of the risk assessment examines the two primary components of risk: exposure and effects. The objective of the analysis phase is "to provide the ingredients necessary for determining or predicting ecological responses to stressors under exposure conditions of interest" (US EPA 1998). The products of the analysis phase are summary profiles that describe exposure and the relationship between the stressors and response. These profiles provide the basis for estimating risks.

The analysis phase was divided into three sections: exposure analysis (Section 1.3 of this report), effects analyses using literature-based studies (Section 1.4) and effects analysis using field-based data (Section 1.5). Two methods to evaluate effects were undertaken, because

during literature review and toxicity reference value (TRV) derivation (method 1), it was recognized that there are gaps between the constituent concentration clearly identified not to result in any effect, and the concentration found to result in a significant adverse effect. Concentrations in between these extremes have not yet been evaluated and hence the potential for risk is unknown. In addition, there are many differences between literature-based toxicity studies and environmental conditions of the open range in Wyoming. These differences have important impacts on animal tolerance to constituent exposure.

To reconcile the gaps in data and differences in study conditions from the Wyoming environment, a second method to evaluate effects was undertaken which involved a compilation of field-based data of water body users in Wyoming. Interviews with ranchers and other users of water bodies in Wyoming were undertaken to identify anecdotal as well as quantitative measures of effects. The field-based data served to support toxicity study results and fill in data gaps in the literature-based studies.

In the risk characterization step of the ERA, water quality concentrations were derived from the reviewed literature sources that would not result in any adverse effect on livestock or wildlife. Selected no observed adverse effects levels (NOAELs) and low observed adverse effects levels (LOAELs) were converted to water quality concentrations (WQCs). Subsequently, an uncertainty analysis was conducted and the ranges of WQCs were also compared to empirical data gathered from the Wyoming ranchers. Based on the WQCs, uncertainty analysis and empirical Wyoming studies, a recommended water quality benchmark was identified for each constituent at which risk to wildlife and livestock in Wyoming would be unlikely.

1.2 Problem Formulation

The problem formulation stage of the ERA integrates information about site characteristics, exposure opportunities, and chemical and biological information to generate a set of assessment endpoints (explicit statements of an environmental value that is to be protected) and an ecological conceptual model. Designed to establish the framework to evaluate hypotheses about what ecological effects can occur from the environmental conditions at the site, the problem formulation process is the foundation of the ecological risk assessment.

1.2.1 General description of areas containing produced water

There are more than 64,000 (WOGCC pers. Com. 2007) currently active CBNG and conventional oil and gas industry wells in Wyoming. The most active development is currently in the Wyoming portion of the Powder River structural basin, with ~25,000 currently active wells (Figure 1-1). The Bighorn and Platte River (also known as Wind River) basins also host conventional oil and gas production facilities. These basins are characterized as semiarid environments, with average annual precipitation in the Bighorn basin ranging from six to nine inches annually. To characterize produced water quality and exposure conditions, data was collected for the Powder River, Bighorn and Platte River basins. These three basins represent the majority of areas in Wyoming that receive produced water discharges from oil and gas extraction.

Some of the water produced as a result of oil and gas extraction is discharged into reservoirs or naturally occurring drainages. Drainages in these basins receiving produced water inputs include (but are not limited to) Dry Creek and Cottonwood Creek in the Bighorn basin; Powder River, Salt Creek, and tributaries in the Powder River basin; and Poison Spider Creek in the Platte River basin. Portions of all of these drainages are naturally ephemeral or intermittent creeks that have become perennial streams as a result of CBNG and conventional oil and gas industry discharges. Livestock, farmers and wildlife use the water in these drainages.

In addition, a number of reservoirs also regularly receive oil and gas produced water, including the Loch Katrine in the Bighorn basin, a playa lake enhanced and maintained by oil and gas produced water from the Oregon Basin oil field in Park County, Wyoming. Due to

its large size and rich habitat structure relative to natural water bodies in Wyoming, the Loch Katrine has become an attractive nesting and breeding ground for a number of migratory birds and other wildlife. Smaller reservoirs created by oil and gas discharge water in the various basins primarily support livestock, but are utilized by wildlife species as well.

1.2.2 Water quality of natural and produced water bodies in Wyoming

Natural background water quality is an important consideration in determining potential effects of produced water on animals, since not only will natural background give some indication of incremental risk, but animals often adapt to suboptimal environmental conditions without any long-term effect on their health. Incremental risk is defined as the added risk of exposure to a new mass of a constituent compared to the baseline risk of the natural environment.

The surface water quality of both natural and produced water bodies in Wyoming is highly variable. The Powder River basin has been extensively characterized in a recent use attainability analysis reported by RETEC (2004). Natural water quality in Salt Creek and its tributaries (measured in 2003 and 2004) is characterized as having average TDS concentrations of ~6,400 mg/L and sulfate concentrations averaging ~3,800 mg/L, with maximums as high as 22,000 mg/L TDS and 12,000 mg/L sulfate (measured in Castle Creek).

Produced water discharges into Salt Creek have the effect of lowering TDS and sulfate levels to means of ~4,000 (max 4,580) and 1,130 (max 1,680) mg/L, respectively, at discharge points. These concentrations remain approximately the same downstream; concentrations were measured at 3,880 mg/L TDS and 1,240 mg/L sulfate. TDS measured in Salt Creek and its tributaries are dominated by sodium sulfate in background waters. With the addition of produced water, the TDS composition changes to a sodium chloride type.

Total salinity in the Powder River upstream of Salt Creek ranges from 670 to 2,840 mg/L (measured in the 2003-2004 period), with a mean of 1,650 mg/L. Sulfate averaged 930 mg/L. Downstream of Salt Creek and discharge points, the corresponding TDS ranged from 900 to 3,640 mg/L, with a mean of 2,200 mg/L, and sulfate averaged 920 mg/L. There is a moderate increase in Powder River salinity due to Salt Creek. Upstream of Salt Creek, the

Powder River is characterized as a calcium and sodium sulfate type. Downstream of discharge points and flows from Salt Creek, the signature changes to more sulfate- and chloride-dominated waters.

In the Bighorn basin, Dry Creek upstream of discharge points contains a TDS concentration as high as 2,310 mg/L and sulfates up to 1,180 mg/L, as measured in a residual stream flow during summer months (M. Blakesley, personal communication). The water is characterized as a sodium sulfate type. Downstream of discharges, TDS increases to an average 4,100 mg/L with average sulfate of 2,025 mg/L, although concentrations can be as high as 5,390 mg/L TDS and 3,100 mg/L sulfate (measured between 2002 and 2006). TDS contain an increasing amount of sodium and carbonates relative to upstream samples.

In Cottonwood Creek in the Bighorn basin, TDS and sulfate average 355 mg/L and 164 mg/L, respectively, upstream of discharges, while downstream of discharges water quality averages 3,320 mg/L TDS and 1,380 mg/L sulfate (SWWRC et al. 2002). Other tributaries in the Bighorn basin downstream of produced water inputs, characterized in 1997 (Ramirez 2002), contain average TDS of 3,700 mg/L and sulfates of 1,400 mg/L. Finally, the Loch Katrine wetland complex contains 1,370 mg/L TDS and 790 mg/L sulfate (Ramirez 2002).

In the Platte River basin, natural water quality in Poison Spider Creek was reported at 3,150 mg/L TDS and 1,700 mg/L sulfates (Gene R. George & Associates et al. 2005). Downstream of discharges, TDS averages 2,630 mg/L, with 1,130 mg/L sulfates.

A summary of several produced water effluent concentrations from the Powder River, Platte and Bighorn basins are shown in Table 1-1.

Natural background concentration of barium measured in eight different watersheds ranged between 0.1 and 0.3 mg/L (WDEQ 2000). Produced water typically discharges 1 mg/L barium or less (RETEC 2004, SWWRC et al. 2002).

1.2.3 Wildlife and livestock use of produced water bodies in Wyoming

In Wyoming, livestock and a variety of wildlife species utilize both natural and produced surface water bodies for food, shelter, breeding ground and water resources. In the Powder

River basin, the Salt Creek corridor is an important habitat to both upland and riparian plant and animal species. Local topography is varied, with a number of small canyons, outcrops, cliffs and rocky hills, which provide habitat for big game, carnivores, small mammals, upland game birds, raptors, waterfowl, a variety of migratory birds, and some semiaquatic species (RETEC 2004).

In the Bighorn basin, a variety of wildlife species inhabit the Cottonwood Creek area (Table 1-2). Produced water sources in this area have created additional forage and shelter grounds for big game species including pronghorn antelope, mule deer, and white-tailed deer, and for small game birds including chukar, ring-tailed pheasants, and sage grouse; foraging grounds for a variety of large and small mammals and, subsequently, important prey resources for raptors; stopover resting and foraging grounds for migratory birds and waterfowl species; habitat for threatened and endangered species; and critical habitat for water-dependent species such as beaver and muskrat (SWWRC et al. 2002).

The Loch Katrine, also in the Bighorn basin, is a nesting and feeding ground for many species of waterfowl and shorebirds (Table 1-3), including two threatened and endangered species (peregrine falcon and bald eagle) and three candidate species (long-billed curlew, white-faced ibis and ferruginous hawk) (Ramirez 1993, T. Enright 1989). Wild horse populations also frequent the Dry Creek area (G. Flitner, personal communication), and letters of beneficial use describe wild horse dependence on produced water sources in the Bighorn basin area (Appendix B).

Finally, 97 species of birds and mammals (Table 1-4) were surveyed in the area near Poison Spider Creek (Gene R. George & Associates et al. 2005).

Agricultural uses of the creeks and reservoirs are primarily for livestock ranching. Livestock species reported by Wyoming ranchers and the US Department of Agriculture (USDA) are predominately beef cattle, and some sheep and horses. Most beef cattle in Wyoming are raised on the open range, with typically <1% feedlotted (NASS 2005). Livestock use of surface water bodies tends to be year-round, sometimes with little variation among water bodies. Wildlife, on the other hand, often use water sources on a seasonal basis. Migratory birds, for example, may use Wyoming water bodies on a transient basis between summer and

winter destinations, and mule deer and antelope migrate to different elevations depending on the time of year.

1.2.4 Conceptual model

An ecological conceptual model describes the relationship between stressors and ecological components of an environment. A conceptual model was developed based on life history characteristics of ecological receptors, environmental fate and transport properties of stressors, and ecological conditions of the Wyoming environment. The major ecological groups of wildlife in Wyoming include waterfowl, passerine birds and ruminant and nonruminant mammals (Figure 1-2). Livestock using produced water sources may include cattle, sheep and horses.

1.2.5 Endpoint selection

Assessment endpoints are explicit statements of an environmental value that is to be protected (US EPA 1998). Consistent with WDEQ water quality regulations, the assessment endpoint identified in this risk analysis is the protection of the health and well-being of populations of Wyoming livestock and wildlife species from adverse effects of consuming surface water. For this analysis, well-being is defined as the physiological condition of an animal insomuch as it impacts the social or economic welfare of the animal's owner.

From this broad assessment endpoint, more specific measurement endpoints can be identified. Measurement endpoints are defined as measurable environmental characteristics that are related to the values (i.e., assessment endpoints) that are to be protected (US EPA 1992b). Measurement endpoints to protect animal health in this analysis include developmental, behavioral, reproductive and longevity effects. Growth effects are usually considered less desirable in risk assessments for evaluation of health endpoints, because growth effects can be short-term or reversed, depending on the exposure program, and the relationship between growth and other adverse effects is uncertain. However, for livestock species, measurement endpoints that include growth rate or weight gain were considered in this risk analysis because these parameters relate to the well-being of the animal, as defined above. Feed or water intake rates and digestibility were not considered adequate endpoints in themselves to evaluate the well-being of livestock species, because research has shown that

there is considerable individual variation in feed intake above and below that expected or predicted on the basis of size and growth. Individuals of the same body weight often require widely different amounts of feed for the same level of production (NRC 2000). Thus, in the risk analysis, only those studies that measured growth rates in addition to intake rates or other performance parameters such as digestibility were considered for water concentration derivation.

1.3 Exposure Analysis

In the exposure analysis, general fate and transport properties of constituents of interest in the aquatic environment and in biological organisms are described, and exposure profiles for indicator species are identified.

The fate and transport of constituents of interest in the environment play a significant role in determining toxicity to receptors. In general, constituents in water are available from solution as free ions for uptake into organisms, or are sometimes transported over biological membranes as inorganic complexes. The chemical composition of the water, e.g., pH, hardness, dissolved organic carbon content, etc., strongly influences the speciation of constituents and the degree of uptake by biological organisms. Specific fate and transport properties of barium, sulfate and TDS are described below.

1.3.1 Barium

In water, barium will form compounds in the +2 oxidation state. Barium compounds such as barium nitrate and barium chloride are soluble in water (ASTDR 2001). However, the solubility of barium is often limited by the presence of sulfate and carbonate, which bind the barium in sparingly soluble forms, including barium sulfate and barium carbonate compounds (McCauley and Washington 1983). These forms of barium are relatively nonbioavailable. Bioavailability is defined in this document as that fraction of the constituent that is available for absorption into biological receptors. Barium does not bioconcentrate through food chains (Moore 1991, Hope et al. 1996), for example, soil-to-mammal bioaccumulation factors are <0.05 (Sample et al. 1997). In biological organisms, barium competes with and replaces calcium in processes normally mediated by calcium, particularly those relating to the release of adrenal catecholamines and neurotransmitters, such as acetylcholine and noradrenaline (US EPA 2005).

1.3.2 Sulfate

Sulfate (SO_4^{-2}) is an inorganic, ionic form of aqueous sulfur that has a -2 valence. Aqueous sulfate reacts with and forms chemical complexes with nearly all constituents, from metals to salts to organic matter. In animals, inorganic sulfur is converted into organic sulfur, an essential component of proteins and numerous other organic compounds (NRC 1980, Henry

1995). Thus, sulfur is considered by many to be an essential nutrient. Most sulfur compounds are synthesized in animals in vivo from methionine and cystine, two amino acids. Monogastrics cannot manufacture organic sulfur compounds in vivo, and therefore must obtain the amino acids from outside sources. Methionine and cystine are routinely supplemented in poultry diets, for example. Although ruminants contain gut bacteria capable of synthesizing sulfur-containing amino acids and vitamins from inorganic sulfur sources, nutritional supplements for sulfate are sometimes recommended for these species as well.

1.3.3 TDS

Total dissolved solids (TDS) is a measure of all constituents dissolved in water. In natural and produced water bodies, the most abundant of these constituents are typically chlorides, carbonates, bicarbonates, sulfates (collectively referred to as 'anions'), and calcium, magnesium, potassium, and sodium (collectively referred to as 'cations'). Iron and manganese may also be present sporadically at minor to moderate concentrations in Wyoming water bodies. Thus, the components of TDS in natural and produced water bodies are variable.

Most compounds must be solubilized in water to be absorbed from the digestive tract. Solubility will affect the mass absorbed and rate of absorption (Church 1979). Solubility is also affected by the relative ratios of different constituents; availability of magnesium, for example, is ~60% when consumed on its own, but it can be reduced by high potassium intake. Sodium is almost completely absorbed as is chloride.

1.3.4 Receptor identification

In ecological risk assessments, the quantitative evaluation of point-of-contact-type stressor response requires that specific numerical information about the livestock or wildlife be measured, such as food and water intake rates and body weights. Because not all individual trophic components of an ecological system can be evaluated for risk, several representative indicator species were chosen in association with the assessment endpoints. Selection of the indicator species used in this analysis was based on consideration of various functional groups, their potential for exposure and regulatory concerns.

The receptors chosen for the risk analysis included a developing ruminant (growing heifer), a nonruminant small mammal (rodent), and waterfowl (mallard duck). These receptors are representative of the types of livestock and wildlife species in Wyoming that are exposed to surface water bodies, including locations where produced water effluent might be deposited. The growing heifer and small mammal represent two particularly sensitive animal types, since small body size and young, developing animals are generally at a greater risk for adverse effects at lower doses than are larger, adult animals. As an example, a sulfate water quality concentration was derived for an adult steer to compare with the concentration derived for a growing heifer (Section 1.6.2). It was assumed that the receptors are exposed year-round to the same water body, thus maximizing potential water ingestion rates.

Sheep were also considered in the initial risk analysis, however the tolerance of sheep for these constituents is much higher than cattle (as described in the analyses below), and hence specific water quality ranges were not derived for this species. Little information is available on horses, and therefore this receptor was not specifically evaluated; however, effects on other ruminants and mammals were selected to represent this species.

Water ingestion rates of wildlife receptors were calculated using empirically based ingestion models from Nagy (1987) or Calder and Braun (1983). Representative body weights of each receptor were obtained from either standard EPA information on laboratory animals or from the general literature. For the livestock receptor, average body weights and ingestion rates were obtained from NRC (2000). Exposure parameters for each indicator receptor are summarized in Table 1-5.

1.4 Effects Analysis I: Literature-Based Analysis

In this section, general toxicity characteristics of each constituent of interest are described and a quantitative evaluation of effects is undertaken using two different methods. The first method consists of a review and synthesis of published toxicity studies, from which no-effects and low-effects concentrations were derived in the risk characterization section. A description of the toxicity reference value (TRV) derivation process is included, followed by general effect profiles of each constituent. Discussion of toxicity studies selected for final TRV derivation is provided in the risk characterization step (Section 1.6).

1.4.1 Methods used to derive TRVs

TRVs are estimates of exposure levels below which unacceptable adverse effects are not expected to occur. TRVs were derived for each individual receptor and chemical combination, and are used as ecotoxicity screening values against which receptor-specific exposure estimates are compared.

To derive TRVs based on phylogenically similar species exposed via similar routes of exposure (i.e., through the diet) and that measured toxicological endpoints comparable to the assessment endpoints, several steps were taken:

Step 1. Assemble toxicological databases. Literature databases were assembled that contained all available chronic and subchronic studies on livestock, birds and mammals. Acute studies were excluded from the database since these studies do not assess long-term effects on animals and therefore do not accurately represent potential adverse risks associated with growth, reproduction and development of species. TRV information was obtained by review of several secondary sources, including NRC 1980, Sample et al. 1996, Eisler 2000, the Cal/EPA toxicity database, EPA IRIS, TerreTox/EcoTox databases, and the general literature.

Step 2. Select appropriate studies from the databases. As the databases show, the availability of toxicity studies varies widely by constituent and by species. Therefore, selection of the appropriate studies from these databases necessarily involves a detailed

assessment of the differences from one study to the next, with an objective selection process required to make decisions.

Selection of appropriate studies was based primarily on five principal decision factors, including:

- biological effects,
- technical quality of study,
- method of administration,
- duration of study / identification of a toxicological endpoint, and
- biological parameters.

Biological effects describe the effects that were measured in each study. They can be broadly classified into effects on reproduction, growth, development, or mortality. Effects on reproduction include eggshell thinning, low birth weights, reduced litter sizes or number of offspring, and decreased hatchability. Reproductive effects are considered one of the most sensitive measurement endpoints of species, and therefore a key response in assessing long-term chronic impacts on animals. Growth effects include weight loss or gain, and physiological impairment.

Feed or water intake rates and digestibility were not considered adequate endpoints in themselves to evaluate the well-being of livestock species, because research has shown that there is considerable individual animal variation in feed intake above and below that expected or predicted on the basis of size and growth. Individuals of the same body weight often require widely different amounts of feed for the same level of production (NRC 2000). Thus, in the risk analysis, only those studies that measured growth rates in addition to intake rates or other performance parameters such as digestibility were considered for water concentration derivation.

Developmental effects include decreased feed consumption and other individual responses such as biochemical effects, histopathological changes and behavioral effects. Developmental effects are sometimes not obvious and are difficult to quantify at times.

Mortality is not a preferred endpoint for study selection because its effects are final and usually is the cumulative result of other sublethal effects that are also detected at lower exposures, however in some instances mortality was the only endpoint identified in the study.

Technical quality of study includes assessment of critical parameters such as whether the chemical is isolated or in combination with other chemicals, and whether a normal nutritional level was maintained during the exposure period. It is important in this assessment to derive TRVs from studies involving exposure to isolated chemicals because many effects of one chemical can be masked by the addition of another chemical. Further, while it is recognized that exposure to a combination of constituents may sometimes reflect conditions in the field, the long term additive effects of multiple constituents are not known.

Normal nutritional levels are a second critical parameter for each study selected because malnourishment can interfere with chemical assimilation and metabolic functions, which can result in exacerbated or subdued effects from exposure (Newman 1998). Finally, the number of test organisms is an important consideration in the selection of studies because individual effects of chemicals can vary; statistically significant numbers of test individuals are important in order to assess population-level effects of constituents on receptors.

Method of Administration describes the route of exposure. Because wildlife populations are assumed to be exposed to chemicals in the environment primarily through their diets, studies that administered chemicals orally in the diet were considered more desirable than administration by capsule or gavage. Injection of chemicals directly was not considered acceptable because the route of exposure is significantly different.

Duration of Study and Identification of a Toxicological Endpoint identifies the exposure time of the test group to the constituent, and whether a no effects level or low effects level was identified in the study. Chronic exposure is defined for mammals as more than one year, and/or over a critical life stage, and greater than 10 weeks for birds (Sample et al. 1996). Acute studies were not considered appropriate for TRV derivation.

Biological Parameters are receptor-specific and consider the similarity in phylogeny between the test organism (ROC_t) and the wildlife receptor (ROC_w). Although it was considered most

desirable to match the test species to the wildlife receptor, toxicological studies are typically limited to a few species. If the test organism had the same phylogenic characteristics of the wildlife receptor, this aspect of the study was preferred over a study for which the test organism had only a similar diet or physical traits as the wildlife receptor.

Step 3. Derivation of NOAELs and LOAELs. Once appropriate studies were selected, study NOAELs and LOAELs were derived. NOAELs and LOAELs are expressed as mg constituent/kg body weight per day.

If not provided in the report, ingestion rates were calculated using empirically based ingestion models from US EPA (1988), Nagy (1987) or Calder and Braun (1983) (Table 1-6). Other missing information needed to calculate NOAELs and LOAELs, such as body weights, was either obtained from standard EPA information on laboratory animals or from a paired study published separately. For the livestock receptor, average body weights and ingestion rates were obtained from NRC (2000).

Step 4. Apply uncertainty factors. Once study NOAELs and LOAELs were calculated, uncertainty factors were applied if warranted to extrapolate the study NOAELs and LOAELs to TRV_{NOAEL}s and TRV_{LOAEL}s. In general, application of uncertainty factors is not supported by science (Chapman et al. 1998), however in some cases where there were large gaps in understanding of effects, uncertainty factors based on US EPA (1995) methods were employed.

1.4.2 Review of the toxic effects of barium

Barium affects the nervous system of vertebrates; at low doses it is a muscle stimulant, but at high doses barium can lead to hypertension, vomiting, muscular tremors, diarrhea, gastrointestinal hemorrhage, and eventually paralysis and cardiac arrest (Sample et al. 1997). Subchronic toxicity in rats includes increased arterial pressure and decreased weight gains (US EPA 1984); in birds, ingestion of toxic amounts of barium salts results in growth suppression (Mehring et al. 1960, Taucins et al. 1969). Barium poisoning can be treated by ingesting a solution of sodium or magnesium sulfate, which forms insoluble barium sulfate.

Relevant studies on ruminant species are lacking, and the few published studies address only lethal dose limits of barium salts (NRC 1980) or changes on a cellular level (e.g., Almudena et al. 1996, Aromolaran and Large 1999), the significance of which to the health or well-being of the animal is unclear. NRC (1980) recommended a maximum tolerable dose of 20 parts per million (ppm) barium (as highly bioavailable salts) for livestock, however this recommendation was based on two types of studies: (1) lethal dose studies of barium, none of which addressed effects on cattle; and (2) an in vitro study on the effects of rumen microorganisms. It is unclear how a 20 ppm threshold dose was derived from the acute studies, which show for a variety of animals, only a range in lethal doses between 50 and 733 mg/L Ba as $BaCl_2$ or $BaCO_3$. NRC (1980) stated that the in-vitro study on rumen microorganisms by Martinez and Church (1970) showed that depressed cellulose digestion above 30 ppm $BaCl_2$ occurred, but it is uncertain what the clinical significance of this effect was on the livestock in the study. Thus, the 20 ppm recommendation is not supported by the cited literature. In 2005, NRC (2005) revised its recommendation to 100 ppm barium for horses, poultry and swine based on the same acute studies cited in the 1980 publication. The US EPA does not recommend barium water quality criteria for livestock.

Geomega found no other US-published resources that had evaluated livestock risk to barium in surface water, however Canada's recommended water quality guidelines for livestock ranged between 5 and 300 mg/L, based on US-published studies (CCREM 1987).

1.4.3 Review of the toxic effects of sulfate

Because sulfate is a component of numerous biologically important compounds and metabolic processes (Murray et al. 2000), it has been suggested that sulfate is an essential nutrient, although other sources (e.g., NRC 2005) refute this claim. Nevertheless, daily requirements of sulfur for livestock and poultry are recommended between 10% and 45% of total water intake (NRC 1974). For nonruminants, dietary recommendations are between 0.28% and 0.69 % (NRC 1980). Sulfur derived from sulfate is retained in tissues throughout the body of ruminants, as part of sulfur-containing amino acids synthesized by rumen microorganisms. Nonruminants must obtain sulfate sources from the environment, and are limited to using sulfate for formation of sulfate esters that are required for various metabolic processes.

Sulfate is one of the least toxic forms of sulfur, but the ability of animals to tolerate exposure to elevated sulfur levels depends on the rate of exposure (Mudd et al. 1967). Acute levels administered to livestock produced muscular twitching, colic, dyspnea, blindness, coma and death (Coghlin 1944, White 1964). Subchronic effects of toxic quantities of sulfate (usually administered as sodium sulfate in water) on livestock include reduced weight gain, presumably as a result of reduced feed or water intake. The toxicity of sulfur is reduced in the presence of some sodium compounds such as sodium fluoride (Dziewiatowski 1954).

Relative to barium, research on inorganic sulfate impacts to livestock is more extensive, but other animal test studies are not as developed. Ruminant studies indicate that sheep are far more tolerant of high levels of sulfate in drinking water than cattle (NRC 1980). Sulfate levels up to 5,000 ppm were not found to be detrimental to sheep (Pierce 1960). Cattle, however, appear to be less tolerant of sulfate in drinking water. It has been reported that excessive sulfate consumption can produce a laxative effect in various livestock species, as well as inhibiting rumen fermentation (Hubbert et al. 1958). Despite this, however, total tract digestion of feed consumed by various livestock species does not appear to be adversely affected by excessive sulfate intake, as shown by Zinn et al. (1997) and Qi et al. (1993), and reviewed by NRC (2005).

High sulfate intake in ruminants has been associated with reduced copper absorption (Suttle 1974) and thiamine deficiency (Gould 1998). It has been suggested that thiamine deficiency in cattle is a leading cause of polioencephalomalacia (PEM), although results have been inconsistent (Gould 1998). For ruminants, NRC (2005) recommended a general range of 600 to 2,500 ppm SO_4 for cattle (the most sensitive ruminant receptor), based on reported increases in the incidence of PEM; however, this recommendation contrasts that of other studies, including Loneragan et al. (1998), Patterson et al. (2002), and Patterson et al. (2003), which found no increased incidence of PEM below 3,500 ppm. Other sources of water quality guidelines for livestock (US EPA 1972, NRC 1974) have no specific recommendations for sulfate. NRC (2005) recommends up to 2,500 mg/L sulfate, but this is applicable only to feedlotted cattle. Canada's livestock guidelines range between 1,000 and 3,000 mg/L sulfate.

1.4.4 Review of the toxic effects of TDS

Several common components of TDS are required nutrients in animals. Calcium, magnesium, sodium, and chloride are involved in acid-base balance, muscle contraction, nerve signal transmission, nutrient transport and other functions (Murray et al. 2000). There are no recommended nutritional requirements for TDS; however, daily requirements of salt (as sodium chloride, NaCl) for livestock and poultry range between 6% and 40% of total water intake (NRC 1974).

Acute effects of excessive TDS intake in livestock include excess salivation, vomiting, diarrhea, ataxia, disorientation, blindness, seizures and paralysis (NRC 1980). Subchronic effects in mammals include reduced feed and/or water intake, and subsequent reduction in weight gains. In birds, effects include reduced reproductive rates and weight loss associated with prolonged reductions in food and water intake.

The toxicity of TDS to organisms will depend in part on the individual components. Sufficient research data is lacking on the toxic thresholds of individual TDS components for animals; however, the relative toxicity of TDS components is generally well understood. Embry et al. (1959), in a subchronic study on rats experimented with several different mixtures of TDS – sodium chloride, sodium sulfate, magnesium chloride, magnesium sulfate, or calcium chloride – and found that tolerance to sodium chloride was highest. Other salts affected growth rates at lower doses, with magnesium chloride and magnesium sulfate affecting growth at the lowest dose levels. Similar results were found by Weeth and Hunter (1971) and Rodenburg (1989) in their studies on cattle. The US EPA (1976) advised that "livestock and poultry can survive on saline waters up to 15,000 mg/L salts of sodium and calcium combined with bicarbonates, chlorides and sulfates. But only 10,000 mg/L of corresponding salts of potassium and magnesium could be tolerated. The approximate limit for highly alkaline waters containing sodium and calcium carbonates is 5,000 mg/L." NRC (1974) suggested that an upper limit of 5,000 mg/L TDS should be used as a benchmark for livestock (dairy and beef cattle, sheep, swine, and horses), based on a similar literature review.

According to the literature published to date, livestock species most susceptible to elevated TDS concentrations are growing cattle. Studies on sheep (Peirce 1957, 1959, 1962, 1963) indicate that sodium chloride levels up to 13,000 mg/L do not adversely affect sheep health, weight gain or wool production. Effects on sheep from other types of TDS (e.g., calcium chloride, bicarbonates, magnesium chloride) were typically evaluated in conjunction with sodium chloride. Peirce (1959) showed that combinations of sodium/magnesium chlorides (up to 11,800/1,000 mg/L) did not affect sheep health or performance; Peirce (1962) also demonstrated that calcium plus sodium chloride levels of 12,900 mg/L did not affect weight gain or wool production. In swine, Anderson and Stothers (1978) showed that 6,000 mg/L sodium chloride did not affect weight gain in pigs.

1.5 Effects Analysis II: Wyoming Field-Based Data Analysis

One limitation of a literature-based toxicity study review is that in most cases, the conditions employed in the studies are not representative of field conditions in Wyoming. Almost all livestock studies on TDS and sulfate toxicity involve feedlot environments, where test animals are given limited water and/or feed, and typically only short-term responses to sudden changes in the diet are measured. Differences between feedlot and field environments have been shown to result in large differences in response to TDS and sulfate toxicity in particular. Johnson and Patterson (2004) showed that cattle confined to feedlot environments and provided with natural water sources from South Dakota (with 3,000 mg/L sulfate) generally exhibited adverse effects, while cattle grazing on the open range did not exhibit adverse effects at water concentrations as high as 4,600 mg/L. The differences in tolerance thresholds were attributed to forage quality differences and more stressful conditions (higher temperatures, lack of shade, etc.) in feedlot environments.

Additionally, animals are known to adapt to higher levels of sulfate and TDS without long-term adverse effects (NRC 1974). In field populations, adaptation refers to the adjustment of an organism to its environment. Adaptation can produce large differences in the threshold of low-adverse effects levels. For example, in a review of laboratory toxicity trials, the consensus from NRC (1974) was that cattle (heifers) that were fed 7,000 mg/L or less of sodium chloride or sodium sulfate on a chronic basis did not experience adverse effects. In the field, however, tolerances were reported to be higher: Spafford (1941) and Ballantyne (1957) observed that cattle owned by various landowners could tolerate water containing up to 14,250 mg/L total salts (11,400 mg/L sodium chloride) with no reported adverse effects. In these cases, adverse effects were noted at 18,500 mg/L or higher of total salts. The omission of adaptive factors in many laboratory-based tests creates (perhaps an unnecessary degree of) conservatism inherent in extrapolating the results of laboratory-based toxicity tests to natural conditions.

Finally, it was revealed in the literature review that there is a large data gap between NOAELs and LOAELs; effects to receptors between these two extremes are unknown. Therefore, a field-based investigation was undertaken to gather effects data specific to users of water bodies in Wyoming. USDA and related livestock data for Wyoming and the US

were obtained, interviews with a handful of ranchers in the Bighorn and Powder River basins were conducted, and further information was gleaned from letters written by users of produced water sources (Appendix B).

Overall, the ranchers indicated that water containing sulfates up to 3,100 mg/L and TDS up to 5,390 mg/L did not result in adverse risk to livestock in Wyoming's Bighorn and Powder River basins. Weaning rates, body condition, breeding percentage and mortality rates were no different between pastures associated with natural water sources and those with produced water, which typically contain higher concentrations of sulfates and TDS. Adverse effects were apparent in livestock exposed to evapoconcentrated surface water that originally contained more than 4,000 mg/L sulfate and 7,000 mg/L TDS. Analyses of effects of these concentrations on wildlife were less conclusive; however, it appears that no adverse risk to wildlife occurred from exposure to water at Loch Katrine, which contains relatively elevated sulfates and TDS compared to background. Individual interview statements are summarized below. Full interview statements are provided in Appendix A.

The Flitners

The Flitners ranch all their cows (~1,000 head in 2005) in the spring and fall on BLM lands adjacent to Dry Creek near the Cody Highway. In this area, Dry Creek has average sulfate and TDS concentrations of 2,720 mg/L and 5,080 mg/L, respectively. Produced water sources account for 100% of water availability on these lands, because drought has eliminated other natural reservoirs. The Flitners have additional, private lands in the Bighorn basin and on Heart Mountain, and the cattle typically graze there during the summer months. Water resources in these areas originate from natural sources, with estimated concentrations of 1,180 mg/L and 2,310 mg/L sulfate and TDS, respectively, based on average background concentrations measured upstream of discharges (M. Blakesley, personal communication).

Weaning rates were recorded for calves that started out the spring in various produced water and natural-water-associated pastures (Appendix A, Table A-1). These records demonstrate that no adverse effect on weaning rates occurred on calves that drank the produced water, which contains elevated sulfate (2,720 mg/L) and TDS (5,080 mg/L) relative to natural

sources. The Flitners noted no other variation in cattle quality between those grazed on lands containing produced water versus land with natural water sources.

Mr. McCarty

Mr. Mike McCarty owns several ranches in the Bighorn basin. He utilizes four pastures (totaling 1,600 acres) on BLM lands that contain exclusively produced water sources originating from the Oregon Basin oil field. The herd sizes on these lands are between 650 and 700 head, all cattle. The pastures include Avon, South/North Oil Wells, Lake and Highway pastures. Surface water concentrations near these pastures average 4,830 mg/L TDS and 2,300 mg/L sulfate, with maximums as high as 5,390 mg/L TDS and 3,100 mg/L sulfate (measured between 2002 and 2006). Lake pasture has one well in addition to the produced water sources. Mr. McCarty owns another ranch near Cody, WY, which has natural water sources associated with the pasture. Surface water concentrations at the ranch are not precisely known, but assumed to be in the range of natural background concentrations for the Bighorn basin area, i.e., between 1,180 mg/L sulfate and 2,310 mg/L TDS.

The cows utilize the pastures associated with produced water sources between November and May. Two out of four pastures are used per year (allowing a 2-year fallow period). The cattle are allowed to forage on the open range, and are provided a mineral supplement package. The supplement contains a chelated copper form, recommended by Mr. Patterson (pasture manager for Mr. McCarty) for areas with higher sulfate concentrations associated with water or forage.

Mr. McCarty noted that there were no adverse effects on the livestock that use the pastures with produced water, which contains elevated sulfate (3,100 mg/L) and TDS (5,390 mg/L), compared to his other pastures at which there are natural water sources. He related the following measurement comparisons:

Measure:	Produced water	Natural water
1) Body condition	5	same
2) Breeding percentage	96%	same
3) Death rate	</= 2%, all cows < 10-11 yrs	same
4) Calf weaning rate	94-95%	same

Additionally, Mr. Patterson related that the cattle in this area perform very well, above industry standards and production numbers.

Mr. Patterson

Mr. Trey Patterson manages the Padlock ranch, located in northern Wyoming in the Powder River basin. Cattle graze year-round in the area. The ranch lands receive produced water from a CBNG facility near Decker, MT. The produced water is discharged to a fenced-off reservoir, and into stock tanks.

Water quality samples are taken periodically by Mr. Patterson. Concentrations generally reported are between 1 and <500 mg/L sulfate and up to ~3,600 mg/L TDS (as measured in 2001 and 2002). Sodium makes up a large proportion of the total TDS. Natural water in the area contains between 1,500 and 2,000 mg/L sulfate and up to 3,700 mg/L TDS. Weaning weights recorded over several years do not indicate any difference between cows raised on land with produced water compared to land with other water sources. No negative effects of consuming produced water have been seen or noted in cattle. Generally, Mr. Patterson notes that the increase in available water has resulted in an increase in cattle performance and forage quality.

Mr. Patterson also related his experience with a cattle ranch in North Dakota. Natural water sources at the ranch, containing about 4,000 mg/L sulfates, resulted in incidences of polio in the cattle that consumed this water. A supplemental mineral program was instituted there to help mitigate the effects of the high sulfates, and although some cattle continued to be affected, the ranch continued to use the water source because it was the only water available in the area. Despite this, the ranch was able to make a profit.

Mr. Shepperson

Mr. Shepperson recounted his experiences with cattle drinking from various locations in Salt Creek. He noted that in the summertime, evapoconcentration of the water upstream of produced water outfalls, with concentrations originally as much as 4,000 mg/L sulfate (average 1,200 mg/L) and ~15,000 mg/L TDS (average 2,000) (RETEC 2004), resulted in cattle disorientation and symptoms similar to PEM. Downstream of produced water outfalls, sulfate concentrations of ~1,100 mg/L and TDS concentrations averaging 4,300 mg/L did not

produce any adverse effects. His observations are supported by a use attainability analysis for Salt Creek (RETEC 2004).

Mr. Shepperson also noted that wildlife appeared to be using the water downstream of the outfalls, where population densities appear greater than upstream of the outfalls. Mr. Shepperson speculates that this phenomenon is a result of changes in water quantity as well as quality.

Mr. Schlaf and Mr. Meike

Interviews given by Mr. Schlaf and Mr. Meike relate experiences similar to the above examples, citing that the use of produced water sources in the Bighorn and Powder River basins did not result in any measurable adverse effect on their livestock herds.

Beneficial Use Letters

Beneficial use letters written to industry, BLM and state DEQ offices cite long-term dependence on produced water sources for cattle, sheep and horses without adverse effects. Concentrations were noted as high as 5,000 mg/L TDS, and 3,000 mg/L sulfates, in accordance with NPDES permits (e.g., J. Barquin et al. 2002, J. Fike 2002, J. Turnell 2002, E. Ledder 1988, M. Pitz and L. Meisinger 1988, M. Zinn 1988, D. Grabbert 1988).

Loch Katrine

Oil field discharges have created a number of wetland and riparian habitats in Wyoming, which attract a variety of wildlife. In particular, Loch Katrine, a playa lake maintained and enhanced by produced water in the Oregon Basin oil field in Park County, WY, provides breeding habitat for a variety of aquatic migratory birds (Ramirez 1993). A Fish and Wildlife Service analysis of avian risk in Loch Katrine (Ramirez 1993, 2002) and letters sent regarding wildlife use of the Loch Katrine wetland complex (Appendix B) indicate that chemical constituent concentrations in the water are not impacting avian populations or other types of wildlife that use this area. In addition, the area typically produces an estimated 100 to 150 broods of waterfowl and 50 to 100 broods of shorebirds, and is considered to have an above-average reproductive success rate (Audubon Wyoming 2006). Sulfate and TDS levels measured in the wetland in 1997 were 797 and 1,372 mg/L, respectively (Ramirez 2002). Produced water discharges with TDS concentrations up to 5,000 mg/L, and sulfate

concentrations up to 2,050 mg/L, contributed to the Loch Katrine without noticeable impacts on wildlife (Ramirez 2002).

1.6 Risk Characterization

This section contains reviews of specific studies in which water quality concentrations (WQCs) were derived. The WQCs were then used to identify a single recommended water quality benchmark for each constituent of interest.

A range of WQCs (mg/L) is presented for each constituent-receptor combination. The lower extreme of the range is based on the no observed adverse effect level (NOAEL) TRV. The NOAEL selected represents the highest dose reported not to have an adverse effect on the receptor. The upper extreme of the range is based on the low observed adverse effects level (LOAEL) TRV. The LOAEL selected represents the lowest dose reported to have a significant, sublethal adverse effect on the receptor. Selected TRV-NOAELs and TRV-LOAELs were converted to WQCs by the equation:

$$\text{WQC} = \frac{\text{N/LOAEL (mg constituent/kg body weight/day) x water ingestion rate (L/day)}}{\text{body weight (kg)}}$$

As part of every risk assessment, an uncertainty analysis should be conducted to identify data gaps and the magnitude of uncertainties associated with characterizing risk (US EPA 1998). Therefore an uncertainty analysis was conducted on the derived WQCs, and ranges were compared to the empirical data gathered from Wyoming ranchers. Based on the WQCs, uncertainty analysis and field-based data, a recommended water quality benchmark was identified for each constituent at which risk to wildlife and livestock in Wyoming would be unlikely.

1.6.1 Determination of water quality concentrations and benchmark for barium

There are few toxicity studies available for barium. Perry et al. (1983) and Deitz et al. (1992) showed a range of reported NOAELs for nonruminant mammals. These NOAELs are consistent with the LOAEL identified in Deitz et al. (1992). There were no ruminant-specific studies that addressed sublethal effects that could clearly be interpreted for the health or well-being of these receptors, and hence the Perry et al. (1983) and Deitz et al. (1992) studies were used as a basis for both ruminant and nonruminant receptor TRVs. For birds, there were also limited studies from which to draw upon; Johnson et al. (1960) identified a subchronic

NOAEL and LOAEL in chicks, and hence these concentrations were used to derive WQCs for birds. Subchronic is defined the duration of toxicity test of less than 1 year for mammals, or less than 6 weeks for birds.

A summary of all studies reviewed, and final studies selected to derive WQCs for barium, are shown in Table 1-7. Because a ruminant-specific study addressing chronic health or well-being effects was not identified, studies on other mammals were used, and an uncertainty factor of 10 applied to these results consistent with US EPA (1995) methodology. The final WQCs for barium for which there will be no risk to receptors include:

Nonruminant mammal (rodent)	100 - <915
Ruminant (growing heifer)	13 - <120
Passerine bird (mallard)	360 - <735
Petition proposed limit:	**0.2**
Recommended benchmark:	**13**

Table 1-8. Barium water quality range from no adverse effects to low adverse effects, compared to the proposed surface water effluent limit for Wyoming. Water quality concentrations between the extremes will not likely result in risk to receptors. All results in mg/L.

The degree of uncertainty associated with the recommended benchmarks is moderate to high, because there is a general lack of toxicity studies on ruminants and birds. Although uncertainty factors were employed in the derivation of water quality benchmarks for ruminants, the technical basis for the use of a 10-factor is weak (Chapman et al. 1998). Nevertheless, even the lowest barium water quality benchmark derived (13 mg/L for ruminants) was over an order of magnitude higher than the proposed limit. Similarly, Canada's lowest recommended water quality criteria for livestock at 5 mg/L is also over an order of magnitude higher than the proposed limit. Finally, NRC (2005) recommends 100 ppm barium for horses, poultry and swine.

Due to the high level of uncertainty, **the recommended water quality benchmark for livestock and wildlife protection is 13 mg/L,** which is not only the lowest derived WQC, but is also consistent with published water quality criteria for livestock.

The recommended water quality benchmark for barium, however, is not consistent with the proposed limit. Reported support in the petition for the 0.2 mg/L barium limit is based on a Utah Extension Service publication (Bagley et al. 1997), which lists a US EPA water quality recommendation for livestock of 0.2 mg/L. The US EPA citation in Bagley et al. (1997) is presumably the 1972 water quality criteria publication referenced in the document; however, there is no recommendation for barium in this literature source. No other studies supporting a 0.2 mg/L barium limit were found, including Colorado State University's extension service bulletin which revised its guidelines to exclude any limit for barium.

1.6.2 Determination of water quality concentrations and benchmark for sulfate

In the review and selection of toxicity studies for indicator species, special emphasis was placed on matching the form of sulfur that will be found in surface water bodies (SO_4) to the form of sulfur administered in the study, because animal tolerance and metabolism of sulfur will vary depending on its chemical form.

Upon review of rodent studies, Brown and Gamatero (1970) found a subchronic NOAEL of 18.1 mg/kg/d in rats; however, a LOAEL was not identified in the study. Weeth and Hunter (1971) later reported a subchronic NOAEL of 668 mg/kg/d for rats. No LOAEL could be identified from a literature review. Although Cohen et al. (1958) and Daniel and Waisman (1969) identified subchronic LOAELs in the range of 410 - 515 mg/kg/d, the form of sulfate in these studies was organic, administered as DL-methionine in the diet, and hence these studies were not considered adequate to derive a LOAEL for inorganic sulfate.

In birds, no adverse effects were found at doses of >1,000 mg/kg/d reported by Krista et al. (1961); however, Harter and Baker (1978) reported reduced growth rates at 288 mg/kg/d. Both studies administered sodium sulfate in water to chickens over a subchronic duration period. In another study with laying hens, Adams et al. (1975) identified a NOAEL of 101 mg/kg/d, finding no effects on egg production, feed intake rates or mortality.

Of the subchronic toxicity studies evaluated for growing cattle (no chronic studies exist), NOAELs were typically identified in the studies at 604 mg/kg/d or less (Embry et al. 1959). Fewer LOAELs were adequately identified in the available studies; Embry et al. (1959) identified a LOAEL at 699 mg/kg/d, noting decreased weight gains and feed intake rates. Although Grout et al. (2006) reported a LOAEL at 170 mg/kg/d, this LOAEL was lower than the reported NOAEL (270 mg/kg/d) from the same study. Weeth and Hunter (1971) found that at 337 mg/kg/d, significant effects on weight gain were seen in growing cattle. However, this study (as well as many others) was performed in a feedlot environment; Johnson and Patterson (2004) demonstrated that the conditions in feedlots are more stressful to the animal, resulting in reduced sulfate toxicity thresholds to growing cattle compared to conditions in open rangeland environments. Patterson et al. (2003) and Johnson and Patterson (2004) reported a feedlot-associated LOAEL of 251 mg/kg/d, but a NOAEL from the open rangeland tests at 360 mg/kg/d (Johnson and Patterson 2004), noting that although declines were seen in water intake rates, no effect on weight gain was found.

The open rangeland-associated NOAEL from Johnson and Patterson (2004) is not only more consistent with most other studies, but is also consistent with the Wyoming field-based empirical data, which shows that at concentrations up to 3,100 mg/L sulfate (~259 mg/kg/d), no adverse effects are seen in livestock. Hence, the NOAEL identified for water quality derivation in this risk analysis is 360 mg/kg/d (from Johnson and Patterson 2004), and the LOAEL identified is 699 mg/kg/d (from Embry et al. 1959).

Effects on growing cattle were noted at lower concentrations in these studies than for adult cows and steers. Weeth and Caps (1972) noted no effects on intake rates, feed efficiency or growth rates in adult cattle fed 122 mg/kg/d sodium sulfate. The lowest LOAEL at which effects on adult cattle were noted were reported by Patterson et al. (2004) at 327 mg/kg/d, noting significant declines in growth rates of adult cows, though no effects were noted on cow reproduction or calf weight gain (calf-cow pairs were evaluated in the study). Results of Ward and Patterson (2004) and Patterson et al. (2002) were consistent with Patterson et al. (2004), reporting LOAELs of 352 and 381 mg/kg/d, respectively.

A summary of all studies reviewed, and final studies selected to derive WQCs for sulfate, are shown in Table 1-9. To show the relative differences in the sensitivity of developing ruminants versus adult ruminants, sulfate WQCs were derived for an adult steer to compare with the concentration derived for a growing heifer. From these results, it is apparent that the upper end of acceptable WQCs is much lower for the growing heifer than the adult steer.

The final WQCs for sulfate for which there will be no risk to receptors include:

Nonruminant mammal (rodent)	5,070
Ruminant (growing heifer)	3,660 – <7,100
Ruminant (adult steer)	2,800 – <7,500
Passerine bird (mallard)	1,780 – <5,080
Current effluent limit:	**3,000**
Petition proposed limit:	**500**
Recommended benchmark:	**3,010**

Table 1-10. Sulfate water quality range from no adverse effects to low adverse effects, compared to the current and proposed surface water effluent limits for Wyoming. Water quality concentrations between the two extremes will not likely result in risk to receptors. All results in mg/L.

There is a considerable range of lower-end WQCs for the various receptors, from 1,780 to 5,070 mg/L. Studies on growing cattle and adult steers are the most abundant for sulfate, and associated uncertainties with the range of water quality is low. However, very few NOAELs were reported for adult steers, and doses administered to adults were less than those of studies with growing heifers. Hence, the NOAEL derived in the table above is actually lower for adults (2,800 mg/L) than for growing heifers (3,660 mg/L) despite the reported higher sensitivity of growing heifers compared to adults. All of the adult steer studies were conducted in feedlot environments, which probably contributed to the lower reported NOAELs.

Additionally, there is a large gap between the lower-end 2,800 mg/L) and the upper-end (<7,500 mg/L) extremes for adult steers, due to fewer toxicity studies on adults rather than growing heifers. These differences in data availability are not surprising, since the most commonly reported adverse effect from sublethal sulfate intake is reduced growth rates, hence growing organisms are typically used to evaluate toxicity.

Uncertainties associated with bird and nonruminant receptors were moderate. The relative paucity of data for these types of species contributed to lower-end WQCs derived for birds and mammals being lower than for livestock, with a large difference between lower- and upper-end concentrations.

The ranges of WQCs were used to derive a single recommended water quality benchmark for sulfate. Only NOAELs were reported for rodent receptors, indicating that concentrations up to 5,070 mg/L would still be protective of these types of mammals. For remaining receptors, the geometric mean of the low- and high-end concentrations was taken to obtain an estimated concentration at which risk to these receptors would be unlikely (methods based on EPA guidance for ecological risk assessments, e.g., US EPA 2003). Geometric means of the water quality benchmarks are 5,100, 3,010 and 4,590 mg/L for growing and adult cattle and birds, respectively. Therefore, **the recommended water quality benchmark for sulfate is 3,010 mg/L** because this number is the lowest of the geometric means for cattle and birds, it is within the range of NOAEL-based WQCs for rodents, and it is consistent with the field-based data from Wyoming water users. This benchmark also takes into account the effects on both growing and adult cattle.

This recommended water quality benchmark is consistent with the current regulatory effluent limits for sulfate. In contrast, the petitioners' proposed limit (500 mg/L) is not supported by this risk analysis. The proposed amendment to sulfate water quality was based on a recommended limit of 500 mg/L for calves. Support for this recommendation is lacking, however, and cannot be found in the literature. The support referenced in the petition is the Utah State University Extension service bulletin. This bulletin references Kober (1993) in support of its sulfate guideline for livestock. However, the Kober (1993) paper, recommends that 3,500 ppm is unfit for sows, and "[w]ater with levels above 4,500 ppm should not be

used." "Slight" effects on livestock were cited in the paper for 1,500 ppm and above, although those effects were not elaborated upon beyond the possibility of temporary diarrhea. The other reference provided is from the Wyoming Department of Agriculture Analytical Service. This web publication does not reference any support for its recommendation of ≤ 1000 mg/L sulfate as "suitable" for livestock. Furthermore, the web publication does not define "suitable," referencing only that the criteria are for classification purposes only.

1.6.3 Determination of water quality concentrations and benchmark for TDS

Because variation in TDS makeup will affect toxicity thresholds, and much of produced water effluent is dominated by sodium chloride, this review focused on compiling studies which addressed toxicity to sodium chloride. Other types of TDS constituent studies were also reviewed, although far fewer exist. Studies involving sulfate-dominated TDS waters were not considered for TDS analyses, since sulfate toxicity is addressed elsewhere.

Review of chronic or subchronic toxicity studies on growing cattle shows a wide range in NOAEL and LOAEL thresholds for NaCl-type waters. Growth effects in growing cattle have been reported in the range of 800 mg/kg/d to >2,100 mg/kg/d (Weeth and Haverland 1961). This wide range in toxic thresholds appears to depend on the season in which the cattle are exposed, as well as other factors, such as diet and timing of watering and feeding (Ray 1989). Interestingly, significant growth effects were seen at a lower dose (800 mg/kg/d) during winter months than in summer months (900 mg/kg/d) The lower LOAEL, in winter, reported by Weeth and Haverland (1961) could be attributed to reported differences in drinking rates and body weights between experimental groups.

NOAELs reported by Spafford (1941), Weeth and Hunter (1971), Weeth (1962) and Embry et al. (1959) are consistent with the LOAEL reported in Weeth and Haverland (1961); only Weeth et al. (1960) found that a dose of over 1,600 mg/kg/d TDS (as NaCl) did not result in any adverse effects on growth. Other studies evaluated effects only on food/water intake and aspects of digestibility, including Lassiter and Cook (1963), Ray (1989) and Johnson et al. (1959). Although growth was not measured in these studies, NOAELs and LOAELs reported are still consistent with Weeth and Hunter (1971) and Weeth and Haverland (1961). A summary of all evaluated studies on growing cattle are shown in Table 1-11.

Fewer studies have focused on evaluating effects in adult cattle, but the effects of TDS (as NaCl) on milk production in dairy cows has been widely studied. Significant declines in milk production have been reported between 380 and 600 mg/kg/d (Challis et al. 1987 and Jaster et al. 1978, respectively) but Bahman et al. (1993) did not see any effect on milk production at 610 mg/kg/d, and no effects were reported by Frens (1946) at over 900 mg/kg/d. Experiment durations and seasonal differences varied among studies, as did the source of water. Jaster et al. (1978) added NaCl to tap water, the sources of water in the Challis et al. (1987) and Bahman et al. (1993) studies were natural well waters. Only Challis et al. (1987) reported all individual constituent concentrations, which showed the water to be a calcium sulfate type, while data from the Bahman et al. (1993) study suggest that water contained primarily sodium and magnesium, which is more consistent with the makeup of produced water in Wyoming.

Studies on nonlivestock species are primarily limited to rat studies. The most comprehensive and quantitative study was initiated by Embry et al. (1959), who demonstrated a range of effects on rats that were administered different types of TDS components. Effects were seen at lower concentrations for water containing MgCl and $MgSO_4$ (790 mg/kg/d) compared to NaCl waters (>1,540 mg/kg/d). Calcium chloride resulted in reduced water consumption and growth rates at the lowest level (365 mg/kg/d). These results appear roughly consistent with Heller (1932, 1933) and Heller and Larwood (1930), as reported by NRC (1974).

Toxicity studies for birds were conflicting. Only one study, by Krista et al. (1961), tested the effects of NaCl on mallard duckling growth and intake rates. The NOAEL and LOAEL from this study were 269 and 385 mg/kg/d, respectively. A related series of studies on hens, measuring eggshell defects, demonstrated LOAELs as low as 104 mg/kg/d (Belnave and Yolowitz 1987, Belnave et al. 1989, Yolowitz et al. 1990) but all other studies on poultry demonstrated LOAELs at 350 mg/kg/d or higher (Heller 1933, Scrivner 1946, Krista et al. 1961). NOAELs demonstrated for these other studies were not lower than ~115 mg/kg/d (Heller 1933, Scrivner 1946). Particular details regarding the environmental conditions of the hens and feed/water diet are lacking in the Belnave and Yolowitz study series, which created unacceptable uncertainties associated with the study selection process.

Studies selected for ruminant and birds receptors were restricted to NaCl-dominated water only, as few (if any) studies were published on other types of TDS. Findings published by Weeth and Haverland (1961) and Weeth and Hunter (1971) were found to be most representative of the range of concentrations for which risk is not likely in growing cattle. Embry et al. (1959) was selected as the representative study on rats, and two NOAELs were identified as representative of the range of study effects: a low NOAEL based on MgCl exposure, and a higher NOAEL based on NaCl exposure. The range of study effects selected for the passerine bird included the NOAEL and LOAEL from Krista et al. (1961), as this study addressed effects specifically on mallard ducks.

The final WQCs for TDS for which there will be no risk to receptors include:

Nonruminant mammal (rodent)	4,750 – <11,700
Ruminant (growing heifer)	7,380 – <8,200
Passerine bird (mallard)	4,750 – <6,790
Current effluent limit:	**5,000**
Petition proposed limit:	**2,000**
Recommended benchmark:	**5,600**

Table 1-12. TDS water quality range from no adverse effects to low adverse effects, compared to the current and proposed surface water effluent limits for Wyoming. Water quality concentrations between the two extremes will not likely result in risk to receptors. All results in mg/L.

Uncertainty associated with the range of WQCs derived for growing cattle is low. When compared to barium and sulfate, a larger dataset was available for growing cattle; toxicity thresholds were largely consistent among studies but N/LOAELs varied widely between studies. The wide diversity in NOAELs is the result of lack of data at higher exposures rather than differences in cattle response. Most studies identified NOAELs but not LOAELs, hence uncertainties were slightly greater for the upper-extreme ranges of WQCs. However, almost all studies conducted experiments in feedlot-type environments that are not representative of conditions in Wyoming associated with higher TDS concentrations due to

produced water outputs. The Johnson and Patterson (2004) study suggests that general toxicity thresholds in feedlot environments will be lower than in open range environments due to harsher environmental conditions in the feedlots. Hence, the studies used to derive WQCs for growing cattle are conservatively based.

The literature-based toxicity review primarily looked at effects of sodium chloride-dominated TDS water, which is consistent with much of produced water discharges. In some locations, discharges have significant components of carbonates as well. Literature review on general effects (Section 1.4) indicates that carbonate-dominated TDS waters result in toxicity to nonruminant mammals at slightly lower concentrations. However, literature-based toxicity thresholds for TDS in growing cattle are consistent with the field-based data gathered from Wyoming ranchers at locations with variable TDS makeup, including those with carbonate-dominated waters. Data from these interviews indicate that concentrations up to 5,390 mg/L do not result in adverse effects on growing or adult cattle.

Uncertainties associated with WQCs for nonruminant mammals and birds are moderate to high. There were very few available studies for rodents, although results were relatively consistent between studies. Toxicity studies on birds were conflicting; most studies such as Krista et al. (1961) were adequately designed, and confidence using these studies to derive WQCs is high, but particular details regarding the environmental conditions of the hens and feed/water diet are lacking in other studies (i.e., the Belnave and Yolowitz series), which showed lower toxicity thresholds.

To derive a single recommended water quality benchmark for TDS, the geometric mean of the low- and high-end concentrations was taken to obtain an estimated concentration at which risk to these receptors would be unlikely. Geometric means of the water quality benchmarks are 7,460, 7,800, and 5,680 mg/L for rodents, growing cattle and birds, respectively. Therefore, **the recommended water quality benchmark for TDS is 5,600 mg/L,** because this number is the lowest of the geometric means for cattle and birds (rounded down), it is within the range of NOAEL-based water quality criteria for other types of livestock (i.e., dairy cows), and it is consistent with field-based data from Wyoming water users.

The recommended water quality benchmark for TDS derived in this paper is consistent with the current regulatory effluent limits, as well as other published benchmarks for livestock from extension services around the country (e.g., Bagley et al. 1997, Faries et al. 1998, Looper and Waldner 2002). In contrast, the petitioners' proposed TDS limit of 2,000 mg/L does not represent the maximum tolerable level in livestock or wildlife. The citation provided as support lacks consistency with Wyoming produced water. Whereas Wyoming produced water typically has a sodium-bicarbonate or sodium-chloride signature, the reference, a South Dakota extension bulletin (Lardy and Stoltenow 1988) recommends ≤3,000 mg/L for *sulfate*-dominated TDS water for conditions in South Dakota. Thus, this recommendation more accurately describes toxicity thresholds for sulfate. It is important to note that all of the references cited in the petition are non-peer reviewed recommendations based on a review of either scientific literature or other extension publication bulletins.

1.7 Summary and Conclusions

To analyze the adequacy of the current effluent limits and the validity of the petitioners' proposed limits to protect wildlife and livestock, a risk analysis was done of livestock and wildlife chemical risk from TDS, sulfate and barium levels in surface water bodies created or impacted by produced water in Wyoming. This was accomplished by investigation along two lines of evidence. The first line included peer-reviewed scientific literature on water quality effects on animal species; the investigation sought to determine the water quality attribute (TDS, sulfate, barium) levels that are protective of animal species of interest, including livestock (cattle and sheep) and wildlife (mammals and birds). The second line of evidence included data compiled from ranchers and others in Wyoming who use produced and natural water sources for their livestock or farming use.

The analysis followed the US EPA's Guidelines for Ecological Risk Assessment (US EPA 1998), which outlines three basic steps for ERAs: problem formulation, analysis, and risk characterization.

1.7.1 Problem Formulation Summary

In the problem formulation stage, background information on the availability and quality of water bodies in Wyoming (both from natural and produced water sources) was reviewed, and animal use of those water bodies was described. There are more than 64,000 currently active CBNG and conventional oil and gas industry wells in Wyoming. Some of the water produced as a result of oil and gas extraction is discharged into reservoirs or naturally occurring drainages. Livestock and a variety of wildlife species utilize both natural and enhanced (from produced waters) surface water bodies for food, shelter, breeding ground and water resources. Examples of the water quality from active produced water discharges across Wyoming compared to the petition proposed standards are shown in Table 1-1. Much of this water could not be discharged if the petition-proposed water quality effluent limits were adopted by the WDEQ.

An ecological conceptual model was presented to describe the relationships between the stressors (produced water bodies) and biological components. Finally, a set of endpoints was identified to ensure that the risk assessment goals are consistent with the petitioners'

statements and goals regarding WDEQ water quality regulations. The assessment endpoint identified in this risk analysis is the protection of the health and well-being of populations of Wyoming livestock and wildlife species from any adverse effects due of consuming surface water.

1.7.2 Exposure Analysis Summary

The analysis phase of the risk assessment examined the two primary components of risk: exposure and effects. In the exposure analysis, the exposure profiles for barium, sulfate and TDS were reviewed and exposure profiles for indicator species were identified. The fate and transport of constituents of interest in the environment play a significant role in determining toxicity to receptors. The chemical composition of the water, e.g., pH, hardness, dissolved organic carbon content, etc., strongly influences the speciation of constituents and the degree of uptake by biological organisms.

Barium compounds such as barium nitrate and barium chloride are soluble in water. However, the solubility of barium is often limited by the presence of sulfate and carbonate which bind the barium in sparingly soluble forms including barium sulfate and barium carbonate compounds. These forms of barium are relatively nonbioavailable.

Aqueous sulfate reacts with nearly all constituents, from metals to salts to organic matter, to form chemical complexes. In animals, inorganic sulfur is converted into organic sulfur, an essential component of proteins and other organic compounds.

Total dissolved solids (TDS) is a measure of all constituents dissolved in water. In natural and produced water, the most abundant of these constituents are typically chlorides, carbonates, bicarbonates and sulfates (collectively referred to as 'anions'), and calcium, magnesium, potassium, and sodium (collectively referred to as 'cations'). Most compounds must be dissolved in water to be absorbed from the digestive tract.

The receptors chosen for the risk analysis included a developing ruminant (growing heifer), a nonruminant small mammal (rodent), and waterfowl (mallard duck). These receptors are representative of the types of livestock and wildlife species in Wyoming that are exposed to surface water bodies, including locations where produced water effluent might be deposited.

1.7.3 Effects Analyses Summary

The effects analysis was divided into two parts. In the first part, existing toxicity studies and published guidelines were reviewed for each of the constituents of interest, and the methods used to derive TRVs were described. During the literature review, it was recognized that there were gaps between the constituent concentration clearly identified not to result in any effect, and the concentration found to result in a significant adverse effect. Concentrations in between these extremes (NOAEL, LOAEL) have not yet been evaluated and hence the potential for risk is unknown. We conservatively based the water quality benchmarks on the lowest of geometric means between the NOAEL and LOAEL. In addition, there are many differences in the environmental conditions between literature-based toxicity studies and environmental conditions in Wyoming. These differences have important impacts on animal tolerance to constituent exposure.

To reconcile the gaps in data and differences in study conditions from the Wyoming environment, a second method of effects evaluation was undertaken that involved a compilation of field-based data of water body users in Wyoming. Interviews with ranchers and other users of water bodies in Wyoming were undertaken to identify anecdotal as well as quantitative measures of effects. The field-based data served to support toxicity study results and fill in data gaps in the literature-based studies.

Overall, the ranchers indicated that water containing sulfates up to 3,100 mg/L and TDS up to 5,390 mg/L did not result in adverse risk to livestock in Wyoming's Bighorn and Powder River basins. Weaning rates, weaning weights, body condition, breeding percentage and death rates were no different between pastures associated with natural water sources, and those with produced water, which typically contain higher concentrations of sulfates and TDS. Adverse effects were apparent in livestock exposed to evapoconcentrated surface water that originally contained more than 4,000 mg/L sulfate and 7,000 mg/L TDS. Analyses of effects of these concentrations on wildlife were less conclusive; however, it appears that no adverse risk to wildlife occurred from exposure to water at Loch Katrine, which contains elevated sulfates and TDS relative to background.

1.7.4 Risk Characterization Summary

In the risk characterization step, ranges of WQCs were derived for each receptor-constituent combination from the reviewed literature sources. The WQCs were then used to derive a single recommended water quality benchmark for each constituent.

There were relatively few toxicity studies available for barium. Hence, additional uncertainty factors were employed to derive WQCs for livestock. The final WQCs for barium ranged from 13 to <915 mg/L. Although the degree of uncertainty associated with these benchmarks was high, even the lowest barium water quality benchmark derived (13 mg/L for ruminants) was over an order of magnitude higher than the proposed limit. Similarly, Canada's lowest recommended water quality criteria for livestock at 5 mg/L is also over an order of magnitude higher than the proposed limit.

Sulfate toxicity thresholds for birds and nonruminant mammals were consistent between studies. NOAELs for growing cattle were typically identified in the studies at 604 mg/kg/d or less, though one or two studies identified LOAELs at lower concentrations. Most studies were performed in a feedlot environment. Johnson and Patterson (2004) demonstrated that the conditions in feedlots are more stressful to the animal, resulting in reduced toxicity thresholds to growing cattle compared to conditions in open rangeland environments. The reported NOAEL from the open rangeland tests was 360 mg/kg/d (Johnson and Patterson 2004).

The final WQCs for sulfate ranged from 1,780 mg/L (lowest NOAEL) to <7,500 mg/L (highest LOAEL). These WQCs were consistent with the concentrations identified in the field-based studies, which found that concentrations up to 3,100 mg/L do not result in adverse risk to either wildlife or livestock.

The toxicity of TDS depends in part on its dominant constituents. The literature review focused on sodium-chloride-dominated TDS waters. The WQCs for TDS ranged from 4,750 to <11,700 mg/L. Uncertainty associated with the range of WQCs derived for growing cattle is low. Relative to barium and sulfate, a larger dataset was available for growing cattle; toxicity thresholds were largely consistent among studies, but N/LOAELs varied widely between studies. However, due to the feedlot conditions in most toxicity studies, these

WQCs for livestock are conservative. Moreover, literature-based toxicity thresholds for TDS in growing cattle are consistent with the field-based data gathered from Wyoming ranchers, who indicate that concentrations up to 5,390 mg/L do not result in adverse effects on growing or adult cattle.

The results of the risk analysis yielded the following recommended water quality benchmarks for barium, sulfate and TDS:

Benchmark/Limit	Barium	Sulfate	TDS
Recommended benchmark:	13	3,010	5,600
Current effluent limit:	None	3,000	5,000
Petition proposed limit:	0.2	500	2,000

Table 1-13. Summary table of recommended water quality benchmarks for barium, sulfate and TDS that are protective of livestock and wildlife receptors, compared to the current WDEQ effluent limits and the petition's proposed effluent limits. All results in mg/L.

The recommended benchmarks derived in this analysis are consistent with the current WDEQ effluent limits for sulfate and TDS. Furthermore, this ERA shows that there would be no incremental reduction in the injury to the health and well-being of animals and wildlife if water quality effluent limits were reduced to the petitioners' requested limits. The petitioners' proposed limits for barium, TDS and sulfate are not supported either by this analysis or by the literature cited in the petition.