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A review of environmental impacts of salts from produced waters on aquatic resources

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ABSTRACT

Salts are frequently a major constituent of waste waters produced during oil and gas production. These produced waters or brines must be treated and/or disposed and provide a daily challenge for operators and resource managers. Some elements of salts are regulated with water quality criteria established for the protection of aquatic wildlife, e.g. chloride (Cl^-), which has an acute standard of 860 mg/L and a chronic standard of 230 mg/L. However, data for establishing such standards has only recently been studied for other components of produced water, such as bicarbonate (HCO_3^-), which has acute median lethal concentrations (LC50s) ranging from 699 to >8000 mg/L and effects on chronic toxicity from 430 to 657 mg/L. While Cl^- is an ion of considerable importance in multiple geographical regions, knowledge about the effects of hardness (calcium and magnesium) on its toxicity and about mechanisms of toxicity is not well understood. A multiple-approach design that combines studies of both individuals and populations, conducted both in the laboratory and the field, was used to study toxic effects of bicarbonate (as $NaHCO_3$). This approach allowed interpretations about mechanisms related to growth effects at the individual level that could affect populations in the wild. However, additional mechanistic data for HCO_3^-, related to the interactions of calcium (Ca^{2+}) precipitation at the microenvironment of the gill would dramatically increase the scientific knowledge base about how $NaHCO_3$ might affect aquatic life. Studies of the effects of mixtures of multiple salts present in produced waters and more chronic effect studies would give a better picture of the overall potential toxicity of these ions. Organic constituents in hydraulic fracturing fluids, flowback waters, etc. are a concern because of their carcinogenic properties and this paper is not meant to minimize the importance of maintaining vigilance with respect to potential organic contamination.

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1. Introduction

Though the organic constituents used during the hydraulic fracturing process have been the subject of much public attention, the contribution of the salt content in large volumes of produced and flowback waters must also be addressed. Scientific data related to individual salts and mixtures would characterize their ecosystem effects independent of those that are specific and unique to hydrocarbons. To summarize the current state of knowledge, this paper will provide a summary of current issues related to the effects of salts, especially the ions chloride (Cl^-) and bicarbonate (HCO_3^-), on aquatic resources.

The toxicity of salt from produced waters is not a new concept; research on its acute toxicity was investigated by Mount et al. (1997), who developed a model to define toxicity of various salts on a few aquatic species. Salt content (and related conductivity) of produced waters was the topic of a 2012 EPA workshop, and the acute and chronic toxicity of these salts is the focus of some USGS research studies (Farag and Harper, 2012). Some ionic components of produced waters are regulated with water quality criteria established for the protection of aquatic wildlife (e.g. Cl^-), but data adequate for establishing such standards has only recently been studied for other elements (e.g. HCO_3^-). Even when individual ions are regulated, additional issues arise due to total dissolved solids and salt absorption ratios (Farag et al., 2010).

Previous research determined that different ions (and salts they form) induce varying degrees of toxicity to aquatic life (Young, 1923; Rawson and Moore, 1944; Nelson, 1968; Mossier, 1971; Held and Peterka, 1974). Mount et al. (1997) completed more than a thousand acute experiments and developed a multiple regression model that described the toxicity of common ions in various combinations to zooplankton and fathead minnows (*Pimephales promelas*, FHM). One of the most pivotal findings of Mount et al. (1997) was that all major ions have a lethal concentration, and that the toxicity of a mixture of salts is generally equivalent to the additive toxicity of the individual salts.

Furthermore, data gaps exist in our understanding of the mechanisms by which salts affect individual organisms. The most prevalent theories include ionoregulatory upset with associated enzyme level changes. Understanding the mechanisms of toxicity becomes especially

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important when one attempts to interpret changes at the population level.

Multiple-approaches are needed to more completely define the potential toxicity of salt ions on aquatic life. Approaches should define the potential effects on individual organisms and populations and bridge laboratory and field studies, thereby enhancing the understanding of the potential effects of salts on aquatic resources (Fig. 1). It is the intersection of information as gathered from the individual organism with effects at the population level (moving left to right on Fig. 1), and the intersection of data gathered from the laboratory and the field (moving top to bottom on Fig. 1), that provide the ability to predict the overall effects of salts in real world conditions.

Studies that follow this multiple-approach design include: 1. Acute and chronic laboratory experiments using water that mimics field conditions and provide data to determine no-effect level (NOEL) concentrations. 2. Investigations of the mechanisms of toxicity to allow interpretations of changes that can affect growth and ultimately survival. 3. Field surveys and in situ bioassays to ground truth laboratory data and refine information about lifestage sensitivity and potential population level effects. This multiple-approach type of study design should include experiments on multiple species as suggested for the development of water quality criteria to protect aquatic life (Stephan et al., 1985).

2. Sodium chloride

Sodium chloride (NaCl) is a highly soluble naturally occurring salt commonly found with natural gas and oil reserves throughout the world. Most oil and gas deposits are the result of catagenesis and metagenesis of the residual marine-derived biogenic organic matter (Libes, 2009). Through complex geological processes, salt brines located within oil and gas producing strata can be highly concentrated, some much more concentrated than sea water (Thamke and Craigg, 1997; Iampen and Rostron, 2000; Whittemore, 2007). Most high salinity brines (>35 g/L TDS) contain chloride as their only major anion. To effectively remove oil or natural gas, water must be pumped out, or co-produced. Through the use of horizontal drilling and hydraulic fracturing, hydrocarbons can now be economically extracted in areas such as the Bakken Formation (North Dakota and Montana, northwestern USA, and Saskatchewan, western CA), the Barnett Shale (Texas, southcentral USA), and the Marcellus Shale (New York, Pennsylvania, Ohio, West Virginia and Virginia, eastern USA). However, the volume of NaCl-enriched waters produced can exceed the amount of oil or gas over the lifespan of the well (Veil et al. 2004). A general ratio of brine to oil produced is 2:1 for conventional oil wells, however, Veil et al. (2004), reported that the volume of brine to oil increases over the life span of the well and produced water approached 10:1. This estimate was made before the rapid increase in the use of horizontal drilling and hydraulic fracturing techniques which may delay or reduce water production (Veil et al., 2004), but may also increase total water production (Boysen, 2012). Regardless of the oil:water ratio, it is expected that increased oil production will require the construction of an additional 540 saltwater disposal sites before peak production in the early 2020s in North Dakota alone (KLJ Consulting, 2012).

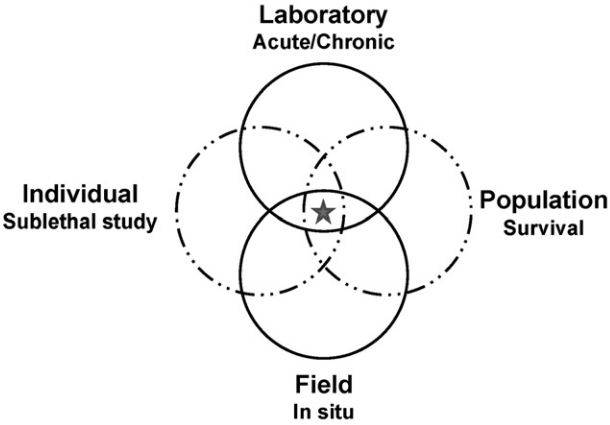

Fig. 1. A multiple- approach design needed to define the potential effects of salts at both the individual and population levels, and to move the understanding from the laboratory to the field. The star indicates where the data from the four approaches intersect to advance the state of knowledge.

While Cl^- is essential for biological function of aquatic organisms, large concentrations can disrupt ion balance. Freshwater aquatic organisms exist in a hypo-osmotic environment (internal dissolved solid concentrations are greater than the surrounding water) which requires the movement of ions to maintain ionic stasis against an osmotic gradient. This is accomplished, in part, by chloride cells, also called ionocytes or mitochondria-rich cells (Hobe et al., 1984; Perry, 1997). Chloride cells are found within membranes located in the gill or epithelium, and use energy to pump ions against an osmotic gradient (Wilson and Laurent, 2002). Chloride transfer mechanisms are also important in the movement of other ions into and out of aquatic organisms as required for biological function. When Cl^- concentrations become large enough, they can interfere with ion regulation. While not well understood, it is believed that when concentrations become large enough, the ability to move Cl^- and other ions becomes impaired, resulting in the inability to retain osmotic homeostasis and ionic balance.

Sodium chloride in produced water has been the subject of concern because of the potentially toxic effects of Cl^- on aquatic organisms, and the physical alteration of soil structure that can occur when it is exposed to Na^+. In an investigation of oil field discharge from conventional oil fields in Wyoming, Boelter et al. (1992) observed reduced survival and reproduction of *Ceriodaphnia dubia*. Major inorganic ions (Na^+, K^+, HCO_3^-, Cl^- and CO_3^{2-}) appeared to be the cause of toxicity, and trace metals and nonpolar organic compounds did not contribute to toxicity. In a study to predict the toxicity of major ions to aquatic organisms, Mount et al. (1997) found that *C. dubia* were quite sensitive to NaCl toxicity, with an acute 48 h median lethal concentration (LC50) of 1040 mg/L. Toxicity was primarily attributed to the co-occurring anion of salts containing Na^+ and Ca^{2+}. Thus, in produced waters containing predominantly NaCl, most of the toxicity was attributed to Cl^-. The USEPA water quality criterion established for the protection of aquatic life is 860 mg/L (U.S. Environmental Protection Agency, 1988) and is based on a series of experiments conducted on multiple species from various phyla.

Chronic toxicity to Cl^- can occur at much lower concentrations than acute exposures. The USEPA established a chronic water quality criterion for Cl^- of 230 mg/L in 1988 (U.S. Environmental Protection Agency, 1988). In a study of the effects of water hardness on Cl^- toxicity, Elphick et al. (2011), found that increased availability of Ca^{2+} ions can ameliorate the toxic effects of Cl^-. In this study, survival and reproduction of *C. dubia* were affected in concentrations as low as 132 and 117 mg/L Cl^- respectively, in very soft water (10 mg as $CaCO_3$). However, survival and reproduction were strongly correlated with water hardness, indicating that water quality criterion may not be protective in soft waters less than 40 mg $CaCO_3$/L, and overly conservative in hard waters exceeding 100 mg $CaCO_3$/L.

As the potentially harmful effects of Cl^- associated with oil and natural gas produced waters became better understood, disposal practices changed over time and have become more restricted and regulated. During early extraction activities, produced waters and brines were often pumped into un-lined evaporation reserve pits or simply pumped into receiving waters and drainage trenches (Gorman, 1999; Otton et al., 2005). The result of these disposal methods was often the contamination of ground and surface waters, salt scarring, erosion caused by the death of surface vegetation, and the dominance of salt tolerant organisms. Initial attempts to prevent leakage were through the use of lined evaporation reserve pits, but these were also prone to leakage. As of April 1, 2012, all waste waters associated with drilling and hydraulic fracturing activities in North Dakota must be stored in tanks.