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Do Produced Water Toxicity Tests Accurately Measure the Produced Water Toxicity in Marine Environments?

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ABSTRACT

U.S. Environmental Protection Agency (EPA) Region VI has issued a general permit for offshore oil and gas discharges to the Gulf of Mexico that places numerical limits on whole effluent toxicity (WET) for produced water. Recently proposed EPA general permits for other produced water discharges in Regions VI and X also include enforceable numerical limits on WET. Clearly, the industry will be conducting extensive produced water WET testing. Unfortunately, the WET test may not accurately measure the toxicity of the chemical constituents of produced water. Rather the mortality of test organisms may be attributable to (1) the high salinity of produced water, which causes salinity shock to the organisms, or (2) an ionic imbalance caused by excesses or deficiencies of one or more of seawater's essential ions in the test chambers. Both of these effects are likely to be mitigated in actual offshore discharge settings, where the receiving water will be seawater and substantial dilution will be probable. Thus, the additional salinity of produced water will be rapidly assimilated, and the proper marine ionic balance will be quickly restored. Regulatory authorities should be aware of these factors when interpreting WET test results.

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INTRODUCTION

On November 19, 1992, the U.S. Environmental Protection Agency (EPA) Region VI issued final general permit GMG2900000 for discharges to the outer continental shelf in the western Gulf of Mexico (57 FR 54642). Among other monitoring requirements, the permit places numerical limits on whole effluent toxicity (WET) for produced water, the brine that comes to the surface along with oil and gas. Two other more recently proposed EPA general permits also include numerical limits on WET for produced water. Region X proposed general permit AKG285100 on September 20, 1995, to cover discharges to Cook Inlet (60 FR 48796). Region VI proposed general permit LAG260000 on July 19, 1996, for discharges to the territorial seas of Louisiana (61 FR 37746).

It is obvious that the EPA is interested in controlling toxicity in produced water discharges and that the oil and gas industry will be conducting many WET tests in upcoming years. Produced water can be toxic to marine indicator organisms in acute and chronic toxicity tests, creating the potential for noncompliance with permit limits. In most cases, dischargers that cannot meet their WET limits will dispose of produced water through costly injection wells. These three general permits cover hundreds of dischargers, primarily in the Gulf of Mexico (1). Although the potential economic impact to these dischargers of failing to meet WET limits cannot be accurately estimated at this time, it could be many million dollars.

Given the potential large costs of noncompliance with WET limits, it is appropriate to closely examine exactly what the WET test is measuring. This paper discusses the nature of produced water toxicity and the potential impacts of recent research on the requirements for marine organisms used in the regulatory interpretation of produced water toxicity test results.

HISTORICAL BACKGROUND

The 1972 amendments to the Federal Water Pollution Control Act formed the basis of what is now known as the Clean Water Act (CWA). The CWA included as a national policy that the discharge of toxic pollutants in toxic amounts would be prohibited. The CWA established the National Pollution Discharge Elimination System (NPDES) and required that NPDES permits set limits on the basis of available technology and, where needed, on water quality standards. In the early years of the NPDES program, the greatest emphasis was placed on controlling individual chemicals; little attention was given to the composite toxicity of effluents. Subsequent CWA amendments, particularly those passed in 1987, placed a much greater emphasis on toxics. Beginning in the late 1980s, EPA headquarters encouraged permit writers in states and EPA regions to incorporate WET testing and WET limits in NPDES permits to protect against discharges of toxic pollutants in toxic amounts.

The EPA has developed and refined methodologies for evaluating toxicity of effluents to a variety of freshwater and marine organisms (2, 3). These tests were not designed to determine the actual effect on the receiving water community but rather to gauge the relative toxicity of various effluents to model or "indicator" organisms. Attention was given to organisms that were not only appropriately sensitive to potential toxicants, but also readily available and resistant to laboratory manipulation. The data from these tests were eventually used to develop permit requirements for WET. One important realization for the scientific community was that a number of effluents that were meeting water quality-based limits were toxic to indicator organisms. It was assumed that this toxicity resulted from the effects of multiple pollutants acting on the organism.

TOXICITY OF PRODUCED WATERS

Produced water is saline water brought to the surface along with oil and gas. The ratio of produced water to oil or gas increases as a well ages and can be as great as 98% of the total volume of extracted fluids (4). In offshore and many coastal areas, produced waters are typically discharged into the sea after receiving some treatment. The volume of discharged material can be enormous; nearly a billion barrels per year of produced water is discharged into the offshore Gulf of Mexico alone (1). Toxicity in produced waters has been observed by using various toxicity indicator organisms, and LC50s as low as 0.05% have been reported, although the average is typically greater than 10% (5). These data indicate that solutions containing these percentages of effluent killed half of the test organisms during the test.

The potential effects of produced waters on marine ecosystems have been debated in the literature, with much emphasis being placed on the potential impacts of hypersalinity, temperature, ammonia, hydrocarbons, and trace elements in large-volume discharges. Offshore platforms have been observed to attract high numbers of various marine species. The presence of large, healthy populations of fish and other organisms suggests that produced water discharges are not particularly toxic to aquatic life in the marine environment. A recently published risk assessment of produced water into shallow coastal waters (6) confirms this premise, concluding that ecological and health risks from radium in produced water appear to be small and that health risks from eating seafood contaminated by produced water discharges are negligible. Impacts to benthic organisms are possible within 200 feet of the discharge point, but no permanent damage to populations is expected.

Despite repeated attempts, investigators have had difficulty in determining the causative agents of toxicity in produced waters. Reference 7 presents data from a toxicity identification evaluation (TIE) on several produced waters. Observed toxicity could not be correlated with the presence of heavy metals, petroleum hydrocarbons, or BETX (benzene, toluene, xylene). Although the effluent tested in the study was hypersaline, reduction of the salinity did not eliminate toxicity. The authors concluded that the agents of toxicity could not be found.

The prevailing assumption in WET monitoring programs has been that observed toxicity always results from the presence of "toxic pollutants." Recent work, however, has shown that this is not always the case. The freshwater indicator organisms *Ceriodaphnia dubia*, a small invertebrate, and *Pimephales promelas*, the fathead minnow, can respond negatively to the presence of high quantities of dissolved solids, even when the ions present are not considered toxic per se but are, in fact, components of natural and synthetic freshwater (8). This so-called common ion toxicity or essential ion toxicity was discovered to be an important component of produced water toxicity to freshwater organisms. Although certainly the discharge of toxic effluents to receiving waters is not desirable, the nature of that toxicity is important to consider before making a determination of the potential long-term impacts of a discharge. Most current regulatory interpretations do not appear to account for essential ion toxicity.

The chemical makeup of produced water is important to consider when interpreting toxicity test results. Although produced waters from some parts of the country have salinities similar to or lower than those of seawater, most produced waters from the Gulf of Mexico are extremely high in dissolved solids, with salinities reaching 300 parts per thousand (ppt) or more (see Table 1). Toxicity testing organisms frequently used for monitoring effluent toxicity can withstand salinity up to only 50 ppt for only short periods of time. Test salinity is usually limited to 20-30 ppt. Although toxicity testing protocols offer assistance for increasing salinity of freshwater effluents slated for testing with marine organisms, no guidelines are provided for reducing salinity. If the salinity of an effluent can be raised to meet a test organism's tolerance range, it may also be appropriate to lower the salinity if it is above the organism's tolerance range.

Another important aspect of produced water is its ionic balance relative to seawater. Recent work, discussed in detail below, has demonstrated that toxicity testing organisms often have well-defined requirements and tolerances for at least some of the ions. Obviously, these "essential ions" are not pollutants in the classic sense, but they can and will cause toxicity if present in amounts differing greatly from amounts in natural seawater. Produced waters have extremely variable ionic compositions as illustrated in Table 1. Ionic balance should be considered when testing produced waters for toxicity.

EFFECTS OF SALINITY

Produced water may have a salinity as high as 300 ppt. The test organisms generally have a limited salinity tolerance range and are adversely affected if exposed to salinity outside their normal tolerance range. EPA's guidance document for conducting marine chronic toxicity tests (2) recommends culturing mysid shrimp, *Mysidopsis bahia*, at a salinity range of 30 $\pm$ 2 ppt, and at no less than 20 ppt if most tests will be conducted at a lower salinity. The EPA manual further recommends that to avoid unnecessary stress, organisms should not be subjected to changes of more than 2 ppt in salinity in any 24-hour period.

From the viewpoint of toxicity testing, the EPA has recommended two important tools. First, the salinity of effluent should be adjusted to match that of either the receiving water or the culture water for marine toxicity indicator organisms (2). Although this recommendation is relatively straightforward to implement for low salinity effluents, there is no method for salinity adjustment of hypersaline effluents that does not dilute other constituents. Second, the test organism should be acclimatized to the salinity at which the test is being conducted. To prevent salinity shock, the seawater should be adjusted by no more than 2 ppt per day. The acclimatization procedures work well at any salinity within the tolerance range of the test organism, except for hypersaline effluents.

We propose the following approach for toxicity tests in cases where the produced water salinity is greater than the tolerance range of the test organisms. If the salinity at the edge of the mixing zone falls within a range compatible with the salinity tolerance of the test organism, this concentration can be used as the highest tested concentration. Even a highly saline (300 ppt) produced water would require a dilution factor of only 10 at the edge of the mixing zone to bring the salinity into the tolerance range of the mysid shrimp. This should not be difficult to achieve for most offshore discharges. Because salinity is not, in itself, a pollutant, this strategy should be protective of the marine environment. This method will have the additional benefit of determining the potential impact of all other constituents in the discharge on the indicator organisms.

Another possible solution is to conduct tests with organisms that can withstand the high salinity. The brine shrimp, *Artemia fransisciana*, can withstand salinity as high as 300 ppt (3). This characteristic makes it a likely candidate for toxicity testing of produced waters. The organism is widely available and readily reared in the laboratory, making it an ideal toxicity testing organism. We are not aware of any researchers currently using *Artemia* in the testing of produced water toxicity.

ESSENTIAL ION BALANCE IN SEAWATER

Seawater is a complex mixture of more than 75 elements. While many marine organisms have evolved mechanisms to regulate their internal ionic chemistry, marine invertebrates simply maintain osmotic equilibrium with seawater. This makes them vulnerable to overt changes in the composition of their external environment. While this characteristic is the reason marine invertebrates are often used to monitor effluent toxicity (high sensitivity), it can also result in a toxic response to changes in the ionic balance of the seawater. Recent research has shown there are six essential ions required to support *Mysidopsis bahia*: Na, Cl, Ca, Mg, K, and Br (9). None of the other ions naturally present in seawater are required to support survival over the course of a typical toxicity test (96 hours). *Mysidopsis bahia* responds negatively to both excesses and deficiencies in these ions. In addition, the range of concentrations of each ion within which the organism survives (the tolerance range) changes as salinity changes. There may also be interactions among the ions with respect to survival of this organism. Additional researchers have also presented information regarding the determination of ion imbalance in produced waters and have developed a predictive model for the determination of ionic imbalance (10) in *M. bahia*, as well as two common fish indicator species: *Menidia beryllina* and *Cyprinodon variegatus*.

In a regulatory framework, the presence of toxicity caused by ion deficiency poses a serious interpretation problem. The regulatory guidelines are set up assuming that the presence of any compound is undesirable. This logic maintains that if the compound or element is removed, the resulting effluent quality is higher and toxicity is reduced. Although this logic is sound for the majority of pollutants, it fails to account for essential ions. Although most elements are toxic at some concentration, essential ions have two toxicity points, one of excess and one of deficiency. If one removes too many of them, the test organism dies. In a laboratory toxicity test, distilled and deionized waters are toxic, although no one would consider them pollutants.

The effects of an ion imbalance on survival of test organisms can best be visualized by example. Table 2 offers a number of case histories that illustrate ion imbalances caused by deficiency and excess. The first three examples are taken from reference 7; no attempt was made to correct an ionic imbalance. Although the presence of ion imbalance toxicity is probable, there is no way to prove that these samples would be nontoxic if they were balanced with respect to essential ions. When the last two effluents in the table, taken from reference 9, were subsequently corrected for an ionic imbalance, the observed toxicity was completely eliminated.

There are three ways to adjust a solution for ion balance, as outlined below. All three methods require analytical information on the solution being tested.

1) Deficiency: Add reagent-grade salts to bring the concentration up to the concentration found in natural seawater at test salinity.

2) Minor excess: Add reagent-grade sodium chloride to increase the salinity of the test solution. Be sure not to exceed the salinity tolerance of the test organism. Adjust the other essential ions as necessary to account for the increase in salinity.

3) Major excess: Remove excess ions with an ion exchange resin. Re-analyze the resulting solution and adjust ion deficiencies as required. Prepare and treat a "mock effluent" to confirm that a solution of essential ions of this type will be toxic and can be treated with ion balancing. This ensures that other toxins were not removed by the ion resin treatment.

These methods can all be successfully used to correct an ion imbalance in produced waters or other effluents being discharged to marine waters. However, the removal of toxicity is not sufficient to prove that ion imbalance is the sole cause of effluent toxicity. This is especially true when the third method is used, because of the potential for removal of other components of the effluent mixture. However, these methods can be used to screen effluents. If balancing the ions does not reduce toxicity, the toxicity is caused by some other component of the mixture. If balancing does reduce or eliminate toxicity, further investigative work, specifically the creation of "mock effluents," can help confirm that ionic imbalance is contributing to or causing the observed toxicity. This method has been used successfully to isolate calcium as an agent of toxicity in a petrochemical effluent (11). Methods for toxicity identification evaluations and mock effluents are provided by the EPA (12-15). In addition, the State of Florida has recently proposed guidelines for utilizing ion balancing techniques in WET testing (16).

The importance of this phenomenon is that although these ions can cause toxicity if present in large amounts, they are essential for survival in some amount and therefore cannot be considered pollutants. Certainly toxicity caused by a deficiency of essential ions cannot be considered pollution. When toxicity problems occur, permittees should check for an essential ion imbalance. If ionic imbalance appears to be responsible for the toxicity, on the basis of a TIE, regulators should be willing to review the data on a case-by-case basis. When proven, the location of the discharge, the nature of the ionic imbalance (excess or deficiency), and the amount of available dilution will need to be considered.

CONCLUSION

Produced waters will continue to require toxicity monitoring to ensure compliance with permit conditions. Certainly, some of these effluents may be toxic as a result of the presence of something other than salinity and essential ion toxicity. These effluents may require treatment or other control to ensure protection of our marine resources. However, before any compliance decisions regarding a produced water discharge are made, the toxicity information generated must be carefully evaluated to ensure that unreasonable restrictions are not placed on the dischargers. The phenomenon of essential ion toxicity will continue to be examined, and our understanding of the effects of essential ions on toxicity test results will become more refined. Until that time, the following questions need to be answered for each effluent discharge:

1) Are any of the contaminants being measured likely to produce effects outside the mixing zone?

2) Is the effluent hypersaline, and is the salinity itself the primary toxicant? Although there are methods for directly answering this question, the easiest approach is to first dilute the effluent with clean seawater to the critical dilution, then assess toxicity. Alternatively, an indicator organism known to be tolerant to hypersalinity, such as the brine shrimp, can be used.

3) Are the essential ion requirements of the organisms being met in all test solutions below the critical dilution? Dilution of a hypersaline produced water may or may not produce a tolerable ion balance. Analysis of the test solutions, followed by comparison to known tolerance ranges and adjustment as necessary, will eliminate ion imbalance toxicity.

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