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# A Comparison of Clays Used in Formulated Sediments and Their Effects on Toxicity in the Sediment Toxicity Test

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## Abstract

The development of the sediment toxicity test using *Leptocheirus plumulosus* was in response to an Environmental Protection Agency (EPA) and oilfield industry initiative to monitor the use and discharge of synthetic base muds (SBM). Since 1998, an industry-led work group has worked diligently with testing laboratories and academia to develop reliable methods for the culturing and testing of *Leptocheirus plumulosus*. An important part of this work has been to reduce variability of the test by developing a formulated sediment to be used during testing. The components used to create this sediment are a mixture of a number of organic and inorganic components. Inherent to this is locating suitable, reliable, and consistent sources of materials to use in the formulated sediment. This paper evaluates several different sources of clay for their suitability as a component in a formulated sediment. Sediment toxicity tests have been conducted to determine if the clay source, structure, etc. affect sediment toxicity results.

## Introduction

In 1998, the Oil and Gas Industry formed the Synthetic Based Muds Research Program to address questions and concerns that the Environmental Protection Agency had concerning the use and discharge of SBM. Within this program, the Sediment Toxicity Workgroup was formed to develop a test to effectively assess the effects of SBMs on the sea floor. The group has worked to identify and resolve issues that affect the variability of the test and ultimately has developed a standard method that appears to be, in general, quite successful.

Initially, sediment toxicity tests were conducted using natural sediment as a test medium. The sediment was collected from a site that had been deemed “clean” based on chemical analysis and the successfulness of culturing *L. plumulosus*. This worked satisfactorily but there was concern that due to the sheer volume of samples to be tested, the environment could be adversely affected by removing large volumes of sediment on a frequent basis. It was also believed that by creating a formulated sediment (FS), the variability of the test could be reduced. Research was done to create a FS that would support survival and growth of *L. plumulosus* using inorganic and organic components that could be readily obtained. The authors are aware of two successful FSs currently being used by commercial testing laboratories. It has been determined that some of the vendors of the FS components may not have the quality control or product specifications needed to maintain a high quality FS. In these cases, an alternate supply of a component may be needed to ensure a high quality FS, one that will not negatively impact the results of sediment toxicity tests. This study evaluates three different bentonite clay sources to determine their effect on sediment toxicity tests when used as a substitute for the current bentonite clay material.

## Study Plan

Three clays were included in this study: Bentonite B (BB), Panther Creek 150 (PC), and Southern Bentonite (SB). A fourth clay, Polar White (PW), was initially considered but its particle size and surface area were significantly different than the other three clays. The mineralogy and percent composition of all four clays are listed in Table 1. BB is the clay source used in existing FS.

Formulated Sediment 17.1 was prepared with each clay source: BB Clay, PC clay, and SB clay. Three rounds of nine *L. plumulosus* Sediment Toxicity Tests were completed. Each test round included a standard 9.0, ppg reference SBM and two SBMs. The properties of the SBMs are shown in Table 2. Each mud sample was tested in each FS a total of three times.

## Scope and Application

*L. plumulosus* Sediment Toxicity Tests were completed in accordance with the Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-aqueous Fluids or Synthetic Based Drilling Muds. The *L. plumulosus* Sediment Toxicity test method is used to evaluate survival of *Leptocheirus plumulosus* exposed to natural marine sediments (NS) or FS spiked with various synthetic-base fluids (SBF) or SBMs. The test method is included in Appendix A of the Final NPDES General Permit for New and Existing Sources and New Discharges in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico, GMG290000, US EPA, October 7, 2004. This toxicity test method is required for demonstrating compliance with the toxicity limitations established for cuttings with adhered SBMs and pre-certification of synthetic-base fluids (SBF) as per the Effluent Limitation Guidelines and New Source Performance Standards for the Oil and Gas Extraction Point Source Category, US EPA, January 22, 2001. This toxicity test method is also applicable to research and development (R&D) with field and laboratory prepared SBMs. When used as a tool in R&D, it is important to establish discriminatory power (DP) or ranking of toxicities. DP enables one to distinguish between materials that are toxic and non-toxic by spreading out the absolute toxicity values.

## Materials and Methods

*L. plumulosus* amphipods were cultured and maintained at Environmental Enterprises USA (EE USA) in natural sediment at 20±1 parts per thousand (ppt) salinity and 23±2°C. Synthetic seawater (SSW) for use with cultures and tests was prepared using hw-MARINEMIX + Bio-Elements and Crystal Sea Marinemix Bioassay Laboratory Formula sea salts (80:20) and deionized water and adjusted to 20 ppt salinity. *L. plumulosus* were acclimated to 20±1°C prior to test initiation. *L. plumulosus* cultures were fed a mixture of TetraMin, Wheat Grass, Alfalfa, and Neo-Novum (48:24:24:4) three times per week. Test organisms were randomly selected from a group that passed through a 900-um sieve but were retained on a 710-um sieve, and were not fed after the tests were initiated.

For this study, each round of tests included the BB Clay, PC Clay, and SB Clay FS. For each FS, 14.2 kg dry materials were wetted with 13.2 kg 20 ppt SSW and thoroughly homogenized on the day prior to being spiked with SBM. Characterization data (total organic carbon, percent sand, silt, clay, and volatile solids) for each FS are presented in Table 3. Additional characterization data (wet-to-dry ratio, etc.) and calculations for preparing each treatment or concentration of each test are presented in Table 4. For each test, six treatments were prepared with FS, five SBM concentrations and a negative control. Test concentrations were 15, 30, 60, 120, and 240 ml SBM per kg of dry FS for the first round of tests and 7.5, 15, 30, 60, and 120 ml SBM per kg of dry FS for the second and third rounds of tests. Eight hundred milliliters of each treatment in each test were prepared. Each treatment was mixed for ten minutes with a KitchenAid Model KHM6 or similar hand-held mixer.

One hundred *L. plumulosus* (five replicates of 20) were each exposed to FS spiked with SBM at five different ml/kg concentrations and negative controls. A total of six-hundred *L. plumulosus* were used in each test. Each replicate contained approximately 150 ml FS and 600 ml 20 ppt overlying SSW. All treatments were prepared and dispensed 18 to 24 hours prior to initiating the test. Treatments were kept in a dedicated environmental chamber with 14 hours light and 10 hours dark at 20±1°C. At 24-hour intervals, temperature, DO, pH, and salinity were measured in each treatment. After 96 hours, all five replicates of each treatment were terminated and the number of surviving organisms recorded. All tests were aerated for the duration of the test. Initial 0-hr and 96-hr dry weights and 0-hr lengths of representative test organisms are presented in Table 5. The 96-hr weight data are from surviving concurrent control organisms. The 96-hour survival data were used to calculate a 96-hr LC50 for each test.

## Results

The LC50 results for all 27 tests are presented in Table 6. The 96-hour LC50s for the reference sample tested in the standard FS, FS 17.1 with BB clay, were 31 ml/kg, 10 ml/kg, and 24 ml/kg. The first and third results, 31 ml/kg and 24 ml/kg, fell within established +/- 2 sd control chart limits for this reference sample and FS combination. These reference sample results were routine but a little on the low side of expectations. The 2nd result, 10 ml/kg, fell just within - 3 sd on the same control chart. The reference sample LC50s were higher in the PC clay FS and lower in the SB clay FS but the variability as measured by percent coefficient of variation (%CV) was approximately twice as high in these two clay FSs as compared to variability in the BB clay FS.

The N465A SBM sample had been contaminated with chemicals picked up during drilling operations that have been known to cause toxicity problems. This sample performed poorly in all three FSs. The %CV for the LC50 results for this sample were similar in the BB clay FS and the SB clay FS and slightly lower in the PC clay FS.

The N465B sample was very similar to a routine field-type SBM and had the highest LC50s in all three clay FSs. The LC50 results for this sample were very high in the BB clay FS. The LC50 results were >240 ml/kg, >120 ml/kg, and >120 ml/kg. These results were taken as 240 ml/kg, 120 ml/kg, and 120 ml/kg in order to calculate summary statistics. Therefore, the standard deviation and %CV are overstated in Table 5. The N465B LC50s in PC clay FS were much lower and more variable. The N465B LC50s in SB clay FS were the lowest and the least variable but this also made it more difficult to distinguish between the SBM samples since all of the LC50s, including the reference sample, were low.

When comparing "good" (non-toxic) and "bad" (toxic) SBMs to a reference sample, the DP becomes very important. The BB clay FS demonstrated the highest DP with the N465B sample consistently yielding LC50s of >240, >120, and >120 mg/kg and the N465A sample consistently yielding results of 10, 5, and 11 ml/kg. This shows very significant differences in the toxicities of these samples.

## Conclusions

Review of the results in Table 5 supports several conclusions. Obviously, N465A and N465B are very different. The N465B sample was much less toxic than the

N465A sample. Even though the samples were similar in their overall mud properties, the N465A sample contained contaminants that have been shown to cause toxicity. Of the three clay FSs included in this study, the BB clay FS has the best DP. The BB clay FS also had the most consistent variability (37-49%) across all three samples tested. Results from this study show that FS formulations and the clay component do affect the toxicity results of L. plumulosus Sediment Toxicity Tests.

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## Nomenclature

*LPC = Laboratory Performance Control*

*LC50 =concentration expected to result in 50% mortality of the test organism exposed for a specific duration*

*mg/kg = milligram per kilogram*

*ml/kg = milliliter per kilogram*

*%CV = Percent coefficient of variation*

*ppm = parts per million, milligram per liter*

*ppt = parts per thousand*

*Reference SBMs = field SBMs must be tested concurrently with one reference SBM (selected based on weight of the field SBM). Three reference SBMs are specified in GMG290000, with different weights to cover the range of mud weights encountered in the field, and their physical properties are specified in the Effluent Guidelines. The reference SBM result is used to calculate the Pass/Fail or Compliance Ratio for SBM test sample(s).*

*Replicate = separate exposure chambers containing equal portions of the same treatment solution, equal numbers of randomly chosen test organisms of the same species, source, and age (or size), that are treated in exactly the same way.*

*Sample Container = air-dried, HCl and deionized water rinsed plastic container or precleaned glass container.*

*Treatment = specific concentrations of SBF or SBM prepared by spiking NS or FS on a mg per kg or ml per kg dry sediment basis, respectively, or the LPC.*

## References

1. ASTM, 1999. Standard Guide for Conducting 10-day Static Sediment Toxicity Tests with Marine and Estuarine Amphipods. E 1367-99.
2. EE USA. April 2007. Standard Operating Procedures. EE USA, Slidell, LA 70461.
3. Tidepool Scientific Software. Toxcalc Version 5.0. 1996.
4. U.S. Environmental Protection Agency, 1994. Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine Amphipods. EPA/600/R-94/025, Section 11. U.S. EPA Office of Research and Development. Washington, DC 20460.
5. U.S. Environmental Protection Agency Region VI, Effective: October 1, 2007. Final NPDES General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000). Appendix A, METHOD FOR CONDUCTING A SEDIMENT TOXICITY TEST WITH *Leptocheirus plumulosus* AND NON-AQUEOUS FLUIDS OR SYNTHETIC BASED DRILLING MUDS. FR Volume 72, No. 109: 31575, June 6, 2007.

**Table 1**
**Clay Mineralogy, % Composition**

| Sample ID | PC | PW | BB | SB |
|---|---|---|---|---|
| Ca-Montmorillonite | 92 | 91 | 89 | 92 |
| Quartz | 4 | 3 | 8 | 4 |
| Cristoballite | 2 | 3 | 2 | 1 |
| Clinoptilolite | Trace | 1 | - | Trace |
| Muscovite | Trace | - | - | Trace |
| Calcite | - | 1 | - | Trace |
| Plagioclase Feldspar | - | 1 | 1 | Trace |
| Hematite | - | - | - | 2 |
| | | | | |
| CEC, meq of methylene blue/100g clay | 61 | 30 | 58 | 44 |
| Specific Surface Area, $m^2/g$ | 0.199 | 0.386 | 0.215 | 0.185 |
| Particle Size Distribution - $D_{50}$, μ | 35.25 | 11.58 | 34.94 | 39.61 |

**Table 2**
**SBM Properties**

| Mud Properties Rheology @150ºF | N465A | N465B |
|---|---|---|
| Density, lb/gal | **10.0** | **10.0** |
| Plastic Viscosity, cps | **28** | **16** |
| Yield Point, lb/100 ft² | **10** | **6** |
| Initial Gel Strength, lb/100 ft² | **4** | **4** |
| 10 min. Gel Strength, lb/100 ft² | **11** | **4** |
| | | |
| AgNO3, ml/1cc mud | **3.4** | **6.2** |
| EDTA, ml/1cc mud | **3.3** | **2.9** |
| Volume Precent Oil, % | **62.5** | **57** |
| Volume Precent Water, % | **24.0** | **25** |
| Volume Precent Solids, % | **13.5** | **18** |
| Electric Stability Meter (23D),Volts | **346** | **879** |
| Pom, ml/1cc mud | **0.0** | **0.0** |
| Drilled Solids S. G., gm/cc | **2.6** | **--** |
| Weight Material S. G., gm/cc | **4.2** | **--** |
| Base Oil Density, lb/gal | **6.59** | **--** |
| | | **--** |
| Total Lime, lbm/bbl | **0.0** | **0.0** |
| CaCl2, ppb | **18.7** | **34.07** |
| CaCl2, % by weight | **18.2** | **28.02** |
| CaCl2, ppm | **181948** | **280244** |
| Brine S. G., gm/cc | **1.16** | **1.26** |
| Brine volume, % | **25.3** | **27.61** |
| Corrected Solids volume, % | **12.2** | **15.39** |
| Oil Water Ratio (Oil/Water) | **72.3/27.7** | **69.5/30.5** |
| Brine Water Ratio (Oil/Water) | **71.2/28.8** | **67.4/32.6** |
| Average Solids S. G., gm/cc | **3.29** | **2.76** |
| Weight Material volume, % | **5.2** | **1.54** |
| Weight Material, lbm/bbl | **76.5** | **22.64** |
| Low Gravity Solids volume, % | **6.95** | **13.85** |
| Low Gravity Solids, lb/bbl | **63.3** | **126.05** |
| | | |
| Rheology 600 RPM | **66** | **38** |
| Rheology 300 RPM | **38** | **22** |
| Rheology 200 RPM | **26** | **15** |
| Rheology 100 RPM | **15** | **10** |
| Rheology 6 RPM | **3** | **3** |
| Rheology 3 RPM | **2** | **2** |

**Table 3**
**Sediment Characteristics**

| | FS17.1 W BB | FS17.1 W PC | FS17.1 W SB |
|---|---|---|---|
| % Sand (Medium) | 0.3 | 0.2 | 0.3 |
| % Sand (Fine) | 2.6 | 3.7 | 4.2 |
| % Silt | 56.2 | 64.2 | 64.1 |
| % Clay | 40.9 | 31.9 | 31.4 |
| % Volatile Solids | 6.34 | 5.98 | 6.69 |
| Total Organic Carbon | 2.53 | 3.02 | 2.71 |

**Table 4**
**Sediment Characteristics and Spiking Calculations**

| | DATE | BB | PC | SB |
|---|---|---|---|---|
| Wet to Dry Ratio (W2DR) | 02/02/08 | 2.03 | 1.99 | 1.99 |
| | 02/07/08 | 2.07 | 2.03 | 2.03 |
| | 02/08/08 | 2.07 | 2.03 | 2.03 |
| Wet FS Density (WFSD) (g/ml) | 02/02/08 | 1.39 | 1.44 | 1.43 |
| | 02/07/08 | 1.44 | 1.42 | 1.40 |
| | 02/08/08 | 1.40 | 1.42 | 1.43 |
| FS Water Content (%) | 02/02/08 | 50.7 | 49.7 | 49.7 |
| | 02/07/08 | 51.7 | 50.7 | 50.7 |
| | 02/08/08 | 51.7 | 50.7 | 50.7 |
| Wet FS Needed (g) | 02/02/08 | 1112.0 | 1152.0 | 1144.0 |
| | 02/07/08 | 1152.0 | 1136.0 | 1120.0 |
| | 02/08/08 | 1120.0 | 1136.0 | 1144.0 |
| Dry FS Needed (kg) | 02/02/08 | 0.5478 | 0.5789 | 0.5749 |
| | 02/07/08 | 0.5565 | 0.5596 | 0.5517 |
| | 02/08/08 | 0.5411 | 0.5596 | 0.5635 |
| **Desired Concentration in ml/kg X Dry weight FS in kg X Density g/ml of SBM = SBM (g)** | | | | |

**Table 5**
**Initial and Final Organism Weights**

| Initiation Date | Sample ID | Sediment Type | Initial Weight | Final Weight |
|---|---|---|---|---|
| 2/2/2008 | Reference | BB | 0.349 | 0.361 |
| | N465A | | 0.294 | 0.346 |
| | N465B | | 0.285 | 0.302 |
| | Reference | PC | 0.249 | 0.274 |
| | N465A | | 0.317 | 0.329 |
| | N465B | | 0.307 | 0.354 |
| | Reference | SB | 0.276 | 0.362 |
| | N465A | | 0.226 | 0.312 |
| | N465B | | 0.232 | 0.293 |
| | | **Average** | 0.282 | 0.326 |
| | | **Standard Deviation** | 0.041 | 0.032 |
| | | **%CV** | 14.45 | 9.87 |
| 2/7/2008 | Reference | BB | 0.283 | 0.302 |
| | N465A | | 0.275 | 0.344 |
| | N465B | | 0.336 | 0.402 |
| | Reference | PC | 0.297 | 0.317 |
| | N465A | | 0.266 | 0.336 |
| | N465B | | 0.300 | 0.369 |
| | Reference | SB | 0.253 | 0.352 |
| | N465A | | 0.299 | 0.346 |
| | N465B | | 0.292 | 0.349 |
| | | **Average** | 0.289 | 0.346 |
| | | **Standard Deviation** | 0.024 | 0.029 |
| | | **%CV** | 8.26 | 8.29 |
| 2/8/2008 | Reference | BB | 0.265 | 0.310 |
| | N465A | | 0.252 | 0.334 |
| | N465B | | 0.299 | 0.324 |
| | Reference | PC | 0.350 | 0.374 |
| | N465A | | 0.315 | 0.364 |
| | N465B | | 0.299 | 0.344 |
| | Reference | SB | 0.285 | 0.305 |
| | N465A | | 0.275 | 0.338 |
| | N465B | | 0.273 | 0.250 |
| | | **Average** | 0.290 | 0.327 |
| | | **Standard Deviation** | 0.030 | 0.037 |
| | | **%CV** | 10.184 | 11.209 |
| **Overall Average** | | | 0.287 | 0.333 |
| **Overall Standard Deviation** | | | 0.031 | 0.033 |
| **Overall %CV** | | | 10.85 | 9.85 |

**Table 6**
**LC50 Results**

| | 6-Feb | 11-Feb | 12-Feb | Mean | STD | %CV |
|---|---|---|---|---|---|---|
| **BB Clay** | | | | | | |
| Newpark | 31 | 10 | 24 | 22 | 10.7 | 49.4 |
| N465A | 10 | 5 | 11 | 9 | 3.2 | 37.1 |
| N465B | 240 | 120 | 120 | 160 | 69.3 | 43.3 |
| **PC Clay** | | | | | | |
| Newpark | 75 | 19 | 18 | 37 | 32.6 | 87.4 |
| N465A | 9 | 7 | 12 | 9 | 2.5 | 27 |
| N465B | 100 | 48 | 102 | 83 | 30.6 | 36.7 |
| **SB Clay** | | | | | | |
| Newpark | 9 | 3 | 21 | 11 | 9.2 | 83.3 |
| N465A | 12 | 5 | 8 | 8 | 3.5 | 42.1 |
| N465B | 31 | 23 | 40 | 31 | 8.5 | 27.1 |