SELECTING AND APPLYING BIOCIDES AND OXYGEN SCAVENGERS IN HIGH VOLUME, HIGH RATE HYDRAULIC FRACTURE STIMULATIONS

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ABSTRACT

Maximum production from many tight gas and shale reservoirs is obtained through high volume, high rate hydraulic fracture stimulation. The base carrier fluids for these treatments are most often shallow water wells, streams or ponds. This water is often laden with bacterial growth and saturated with dissolved oxygen requiring the fluids be treated with biocides and oxygen scavengers during the fracture stimulation to prevent accelerated corrosion of the downhole tubulars and surface separation equipment once the wells are placed on production. Unfortunately, the most commonly used biocides and oxygen scavengers either negatively react with one another or with other compounds in the fracturing fluid. This paper details the interactions and effects of various biocides and oxygen scavengers in both laboratory and field applications and presents a "best practices" for the use of these products in high volume, high rate hydraulic fracture stimulations.

BACKGROUND

The Barnett Shale gas play in the central part of North Texas is indicative of several tight gas reservoirs in the U.S. where production enhancement is gained through fracture stimulation involving large volumes of "slick water" fluid applied at a high rate. During slickwater fracture stimulations in the Barnett Shale, it has become common place during the last 4-5 years to add an oxygen scavenger, biocide and scale inhibitor directly into the blender tub "on the fly" during the stimulation process. Oxygen scavengers are necessary as the source water used during the stimulation process is usually saturated with dissolved oxygen. This saturation, if not removed, will contribute to the corrosive potential of the fluids as they are produced back and to the generation of metal solids that can adversely affect the production potential of the well. The source fluid also usually contains very large quantities of sulfate-reducing, acid producing and aerobic bacteria requiring the use of a biocide to reduce this bacteria population. Finally, the source water has been shown to have a scaling potential once exposed to minerals in the reservoir, thus requiring the use of a scale inhibitor.

Recently, concerns have been raised regarding the compatibility of the commonly used oxygen scavenger, ammonium bisulfite, and the two most common biocides used in the Barnett Shale – gluteraldehyde (glut) and tetrakis hydroxymethyl phosphonium sulfate (THPS). Information is readily available documenting the reaction between gluteraldehyde and sodium bisulfite. Sodium bisulfite is the most often recommended product for neutralizing solutions of gluteraldehyde and the normal recommendation for neutralization is 2-3 parts of sodium bisulfite per part of gluteraldehyde on a weight to weight basis. As the neutralizing chemical reaction is virtually the same between ammonium bisulfite (ABS) and gluteraldehyde and the molecular weight of ABS only differs from sodium bisulfite by 5%, the same neutralization ratio can be assumed. Based on this reaction, and the most common loading rates of 0.5 gallons per thousand gallons (gpt) (500 parts per million) for 25% gluteraldehyde and 0.12 gpt (120 ppm) for 60% ABS, there is the potential for 121 to 183 ppm of the biocide to be neutralized by the oxygen scavenger. Correspondingly, if this reaction is occurring fully, all of the oxygen scavenger is potentially being neutralized.

There is also a widespread belief that THPS (tetrakis hydroxymethyl phosphonium sulfate) should never be mixed with ABS as they, too, will neutralize one other. Again, there is literature available that states that at a 1:1 weight / weight ratio between THPS and ABS there is an interaction. At a common frac loading of 0.35 gpt (350 ppm) of 36% THPS and 0.12 gpt (120 ppm) of 60% ABS, the w/w ratio is 1.5 THPS: 1 ABS. This paper further explores the actual interaction seen between these commonly used biocides and oxygen scavengers in both laboratory and field environments.

LABORATORY ANALYSIS

The very first rudimentary test used locally available pond water and dissolved oxygen Chemets™, to measure the effect that the various products had on the dissolved oxygen content of the water. The results showed that 500 ppm of 25% gluteraldehyde had no effect on the dissolved oxygen content of the water. Adding 125 ppm of a 60% active, nickel-catalyzed, ABS reduced the dissolved oxygen level from 6 ppm to 1 ppm within 30 minutes; however, when both 500 ppm of 25% gluteraldehyde and 125 ppm of 60% ABS were added simultaneously, the dissolved oxygen content only fell 1 ppm over a 30 minute time interval. While dissolved oxygen Chemets provide a very economical and reliable method of measuring dissolved oxygen in water, a dissolved oxygen meter was utilized for much of the laboratory testing (and part of the field) so that more data points could be gathered and changes in dissolved oxygen concentration could be monitored faster. Chemets were still used periodically to insure the accuracy of the data from the dissolved oxygen meter.

Dissolved Oxygen

The first lab evaluation utilizing a dissolved oxygen meter was conducted using tap water as the base fluid. Evaluation rate for 60% ABS was 200 ppm and as can be seen in Figure 1, the ABS performed very rapidly at this rate. Little effect on dissolved oxygen concentration was noted when only 500 ppm of 25% gluteraldehyde was added. When both 500 ppm of 25% gluteraldehyde and 200 ppm of 60% ABS were added, the concentration of dissolved oxygen fell off slowly, but leveled off with less the 50% of the dissolved oxygen having been scavenged.

In the next series of tests using tap water, additional dosing levels of ABS were evaluated along with the effect of timing on product additions. As can be seen in Figure 2, 60% ABS added at 120 ppm eliminated the dissolved oxygen in the tap water, but required 11 minutes to accomplish this task. Doubling the dosing rate of ABS to 240 ppm greatly sped up the oxygen removal; however, 500 ppm of 25% gluteraldehyde was added to the tap water treated with 240 ppm ABS after two minutes and this stopped the oxygen scavenging process. When 500 ppm of 25% gluteraldehyde and 120 ppm of 60% ABS were added simultaneously, dissolved oxygen content was reduced from approximately 6.5 ppm to 5.5 ppm before stabilizing. An additional 200 ppm of 60% ABS was added to this mixture after 5 minutes and this addition resulted in elimination of the remaining dissolved oxygen. When 500 ppm of 25% gluteraldehyde and 240 ppm of 60% ABS were added at the onset, dissolved oxygen was removed completely, though approximately 18 minutes were required for this to occur.

While testing with tap water, another standard oxygen scavenger, a cobalt-catalyzed, 30% sodium meta-bisulfite (SBS) was also evaluated. This data is presented in Figure 3. At a dosing of 50 ppm, the SBS removed all of the dissolved oxygen from the tap water after only two (2) minutes. However, when either 500 ppm of 25% gluteraldehyde or 500 ppm of 22% THPS was added along with the 50 ppm of 30% SBS, dissolved oxygen levels were not reduced, an indication that both biocides are completely neutralizing the SBS. Increasing the dosage of 30% SBS to 500 ppm and then mixing with 500 ppm of each respective biocide produced interesting results – when mixed with THPS, dissolved oxygen levels were not lowered. 25% gluteraldehyde at 500 ppm and SBS at 500 ppm saw the dissolved oxygen level of the tap water slowly deplete to near zero. This is interpreted as the biocide being fully neutralized with enough available oxygen scavenger remaining to slowly scavenge the dissolved oxygen.

During this series of tests, a new, experimental biocide was added to the evaluation. This product, RBI-1, is somewhat related to the chemistry of THPS. This new chemistry was added to the evaluation based on claims of having little interaction with ABS or SBS.

In Figure 4, RBI-1 at 500 ppm has been mixed with 30% SBS at 50, 200 and 500 ppm. With 50 ppm SBS, no reduction in dissolved oxygen is noted, suggesting that some interaction may be occurring. At both 200 and 500 ppm, dissolved oxygen is removed almost as fast as when the tap water is treated with SBS alone. This demonstrates that active oxygen scavenger is still available in the mixtures, but does not answer the question of whether the biocide has been neutralized or not.

These tests and other similar tests reinforced earlier testing that indicated that the addition of glutaraldehyde or THPS did have an effect on the ability of ABS or SBS to remove oxygen from tap water. Testing then moved to actual pond water from various sources in the Barnett Shale.

In the first series of pond water tests, with all samples containing 500 ppm of 25% gluteraldehyde, every addition of 60% ABS below 1,000 ppm had little effect on the dissolved oxygen concentration of the water. The sample containing 480 ppm ABS and 500 ppm gluteraldehyde saw a very slight reduction (<10%) in dissolved oxygen. Only the sample dosed with both 1,000 ppm of ABS and 500 ppm of gluteraldehyde saw the dissolved oxygen lowered significantly and approximately 9 minutes were required to bring the dissolved oxygen concentration to zero (0) ppm. The limited ability of ABS to remove oxygen in the presence of 25% gluteraldehyde in the test above prompted us to evaluate ABS alone in this pond water at differing concentrations. During this test, 60% ABS at 120 ppm reduces the dissolved oxygen content of the pond water only one (1) ppm in ten (10) minutes and the rate of oxygen removal appeared to be slowing at the end. 240 ppm of ABS almost removed all of the dissolved oxygen in the 10 minute test period, while all dissolved oxygen was removed in the waters treated with 360 and 480 ppm of ABS. These results question the "blanket" recommendation of 100-120 ppm of 60% ABS used in many of the hydraulic fractures in the Barnett Shale.

To further evaluate the effect of the addition of biocide on the ability of ABS to remove the dissolved oxygen from pond water, various concentrations of 60% ABS were added to separate samples of the pond water and allowed to react for 3.25 minutes, at which time 500 ppm of either 25% gluteraldehyde or 22% THPS were added to the fluid. The results of this test are presented in Figure 5. The rate of reduction of dissolved oxygen is similar to the data just presented for water treated only with differing concentrations of ABS. This rate is slowed greatly for all treated samples when the 500 ppm aliquots of biocide are added. The one exception is the sample treated with 360 ppm ABS and 500 ppm of 22% THPS which continued to scavenge the dissolved oxygen after the biocide addition. This is most likely due to the relationship between THPS and ABS, in which case the 360 ppm of 60% ABS is a large enough quantity to neutralize the 22% THPS with some oxygen scavenger remaining to complete the removal of dissolved oxygen from the pond sample.

In the next set of laboratory tests on the pond water, the ability of ABS to continue to scavenge dissolved oxygen over longer periods of time in the presence of three different biocides was evaluated. In this series of tests, samples of Stagliano pond water were treated with either 120 ppm or 240 ppm of ABS. The ABS was allowed to react with the water for 3.25 minutes before the respective biocides were added. Dissolved oxygen was recorded every 30 seconds for 5 minutes. The samples were then poured into two containers, allowing the samples to overflow the containers to eliminate oxygen entry when capped. One set of samples were uncapped at 1 hour and the dissolved oxygen measured. The last set was read at 18 hours. Bacteria readings were also taken during this test and these results will be discussed later in this paper. As the results between the samples with ABS at 120 ppm were very similar to those at 240 ppm (though much slower), only the data from the test with ABS at 240 ppm is presented in Figure 6. The biggest surprise was the elimination of the dissolved oxygen in 3 of the 4 samples treated with RBI-2, a slightly different activity version of the experimental biocide discussed previously. The sample treated with 240 ppm ABS and 250 ppm RBI-2 had a dissolved oxygen level of zero (0) at 1 hour and 18 hours, while the sample treated with 120 ppm ABS / 250 ppm RBI-2 also had no dissolved oxygen at 18 hours. These results prompted us to further explore the available activity of the tested biocides to determine if they could still perform their intended function or if they were neutralized by the increased dosing of ABS.

Bacteria

While the testing to this point has revolved around 1) the reaction between ABS and the biocides, glut and THPS, and 2) the effect that this reaction has on the removal of dissolved oxygen from the frac source water, a series of laboratory tests were also carried out measuring the effect on the biocides' ability to sterilize or significantly reduce the bacteria present in the source water. For these tests, adenosine triphosphate luminescence (ATP) was used to quantify the amount of biological activity in the blank and treated samples.

In the test discussed above, the untreated pond water was measured at approximately 28,000 to 30,000 RLU's (relative light units) using a handheld luminometer. While previous data indicated that the oxygen scavenger was affected by the addition of a biocide, it appears that both 25% gluteraldehyde and 22% THPS have enough unaffected active biocidal agent to significantly reduce the biological concentration of the pond water within 1 hour (Figure 7). This reduction was seen regardless of whether the samples contained 120 or 240 ppm of ABS. The biocidal ability of the experimental product appears to be fairly slow, as the RLU's remained very high in the fluids treated for 1 hour. However, after 18 hours, the RLU's had fallen to levels equitable with that of the other biocides. As we just presented data in the previous section that showed where dissolved oxygen was completely removed in the 18 hour samples containing RBI-2 and ABS, this reduction in biological activity is very interesting and will warrant further study.

FIELD ANALYSIS

As a part of this study, samples were taken during fracture stimulations in the Barnett Shale that were utilizing 25% gluteraldehyde and 60% ABS. Dissolved oxygen and bacteria concentrations were determined on source (pond) water and on samples taken during the stimulation. Additionally, we have included a review of bacteria concentrations taken over time from both flowback and production samples from wells that have been treated with either glut or THPS, and with and without oxygen scavenger.

Frac Testing

The standard practice for the application of stimulation additives has been to apply the products directly into the blender tub "on the fly" during the frac job. For the purpose of measuring dissolved oxygen in the treated fluids, the best place to sample the fluids after the blender tub and before the high pressure environment of the frac pumps was found to be a drain line coming off of the blender. This location was used for all of the treated samples discussed below.

A Tarrant County Barnett Shale well received a multi-stage frac on October 2nd and 3rd. This frac included 25% gluteraldehyde at 500 ppm and 60% ABS at 120 ppm. At varying times, samples of source water and treated water from the blender tub drain were taken and inoculated for sulfate-reducing bacteria (SRB), acid-producing bacteria (APB) and tested for dissolved oxygen content with Chemets Vacu-vials™. Some of the samples from the blender drain were allowed to sit for periods of time and then tested again. Bacteria testing was done using serial dilution vials. In this procedure, bacteria concentrations are estimated based on the number of positive bottles after incubating the samples. The number of positive bottles relates to the amount of bacteria present (colony forming units / ml) as shown below.

# of Positive Bottles	Bacteria (CFU/ml)
1	1-10
2	10-100
3	100-1,000
4	1,000-10,000
5	10,000-100,000
6	100,000-1,000,000

During this field evaluation, dissolved oxygen measured during the frac at the blender drain were approximately 1-1 ½ ppm less than that of the source water. On samples that were allowed to sit for 12-36 hours before testing, the dissolved oxygen content fell further, but still at best was slightly over 50% less than the source water. This was still better than the scavenging rate suggested by the laboratory work presented earlier. Bacteria levels measured at various times during the frac show improvements over the source water and the sample from day 2 that had 36 hours of contact time only indicated 1 positive bottle of APB and no positive bottles of SRB.

During another frac stimulation on October 11th utilizing 25% gluteraldehyde at 500 ppm and 60% ABS at 120 ppm, dissolved oxygen removal appeared to be better with approximately 70% of the oxygen being removed in the samples that were allowed 60 minutes of contact time before being tested. Bacteria readings, on the other hand, showed little improvement from the source to the treated fluids.

Based on the frac testing presented here, dissolved oxygen removal is better than suggested by the laboratory testing, but still falls short of complete removal.

Flowback / Production Sampling

Ultimately, the purpose for adding biocides and oxygen scavenger to stimulation fluids in the Barnett Shale is to prevent corrosion in the wellbore from dissolved oxygen, prevent excessive iron solids caused through corrosion and reaction with dissolved oxygen, and prevent corrosion in the wellbore and surface equipment from bacterial activity. Towards this end, flowback returns and produced fluids are routinely monitored for solids, iron and manganese corrosion identifiers and bacterial content.

Years ago, several bacteria time kill studies performed on Barnett Shale pond water indicated that, of the two biocides most compatible with the friction reducing polymers used in slickwater fracs – glutaraldehyde and THPS, glutaraldehyde performed more efficiently in removing APB's. Both products seemed to work equally well for

SRB's. Based on these studies, 25% gluteraldehyde has been widely used, but THPS has also been used in a large number of Barnett Shale fracs.

While initially reviewing historical bacteria tests from flowbacks, some of the data does not necessarily fit original expectations. A group of 17 wells for one Operator in the same basic geographic area were analyzed for flowback profiles. Of this group, 7 wells were treated with 25% gluteraldehyde at 500 ppm and 60% ABS at 120 ppm during the frac. The remaining 10 were treated with 36% THPS at 250 ppm without the addition of ABS. Average results from this data are seen in Table 1.

While a relatively small sampling of flowbacks, this data follows our original findings that indicated THPS to be very effective against SRB's but lacking against APB's. The average iron and manganese values run contrary to what we would expect, though. To gain a more statistically relevant idea of flowback / production bacteria levels, the last 12 months of flowback and production samples from recently stimulated wells for another Operator were reviewed. This sampling involved:

71 flowback samples from wells treated with 36% THPS
15 flowback samples from wells treated with 25% gluteraldehyde and 60% ABS
4 flowback samples from wells treated with 25% gluteraldehyde w/o ABS
152 production samples from wells treated with 36% THPS
26 production samples from wells treated with 25% gluteraldehyde and 60% ABS

This data (presented in Table 2) suggests that 36% THPS without oxygen scavenger provides a better "kill" than 25% gluteraldehyde with oxygen scavenger. This could be due to the 25% gluteraldehyde being partially neutralized by the ABS; however, it should be stated that flowback samples are generally caught by the flowback monitoring crew and not production chemical personnel. These crews do not always flush manifolds properly so we generally place less weight on these samples.

Data from the production water samples (caught by production chemical personnel) indicate that 25% gluteraldehyde and ABS produce slightly better performance than 36% THPS alone.

CONCLUSIONS

- Laboratory testing demonstrates that gluteraldehyde and THPS affect the ability of ammonium bisulfite to scavenge dissolved oxygen from both tap water and frac source water.

- Tests on various pond waters suggest that the common dosage of 120 ppm of ABS (<u>without</u> the interference from a biocide) may be insufficient to completely remove the dissolved oxygen present in the water.

- Sodium meta-bisulfite (SBS) was found to perform no better than ABS when mixed with either gluteraldehyde or THPS.

- Adding the ABS upstream of the biocide allows for removal of the dissolved oxygen, but the ABS has to be in the system long enough to remove most of the dissolved oxygen as the addition of either 500 ppm of 25% gluteraldehyde or 250 ppm of 36% THPS will basically stop the reaction.

- ATP analysis of pond water indicated that sufficient biocide was still present after reaction with ABS to reduce bacteria numbers to acceptable levels. This was in pond water with a somewhat lower biological content than is expected in the Barnett Shale. Waters containing larger concentrations of bacteria may present problems with existing biocide loading rates as there is no doubt part of the biocide is rendered neutral by reaction with the ABS.

- Laboratory analysis of a new biocide chemistry, shows promise as a product that will allow complete oxygen removal while also greatly reducing bacteria numbers. It must be noted that this is based on very limited early work and a more detailed evaluation will be necessary before a field use recommendation is made.

- Actual oxygen removal during frac operations (50%-60%) appears to be better than what was seen in the laboratory testing, but is still below original beliefs / expectations.

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Table 1
Data from Flowback Returns on 17 Wells

	25% gluteraldehyde / ABS	36% THPS
SRB (avg pos bottles)	2.0	1.4
APB (avg pos bottles)	2.3	2.9
Fe (mg/l)	58.9	37.7
Mn (mg/l)	1.4	1.0

Table 2
12 Months of Flowback and Production Samples From a Barnett Shale Operator

Flowback Samples	**SRB (avg bottles)**	**APB (avg bottles)**
25% gluteraldehyde + ABS	1.8	2.7
25% gluteraldehyde w/o ABS	2.0	2.5
36% THPS w/o ABS	1.6	2.3
Production Samples		
25% gluteraldehyde + ABS	0.9	1.5
36% THPS w/o ABS	1.3	1.8

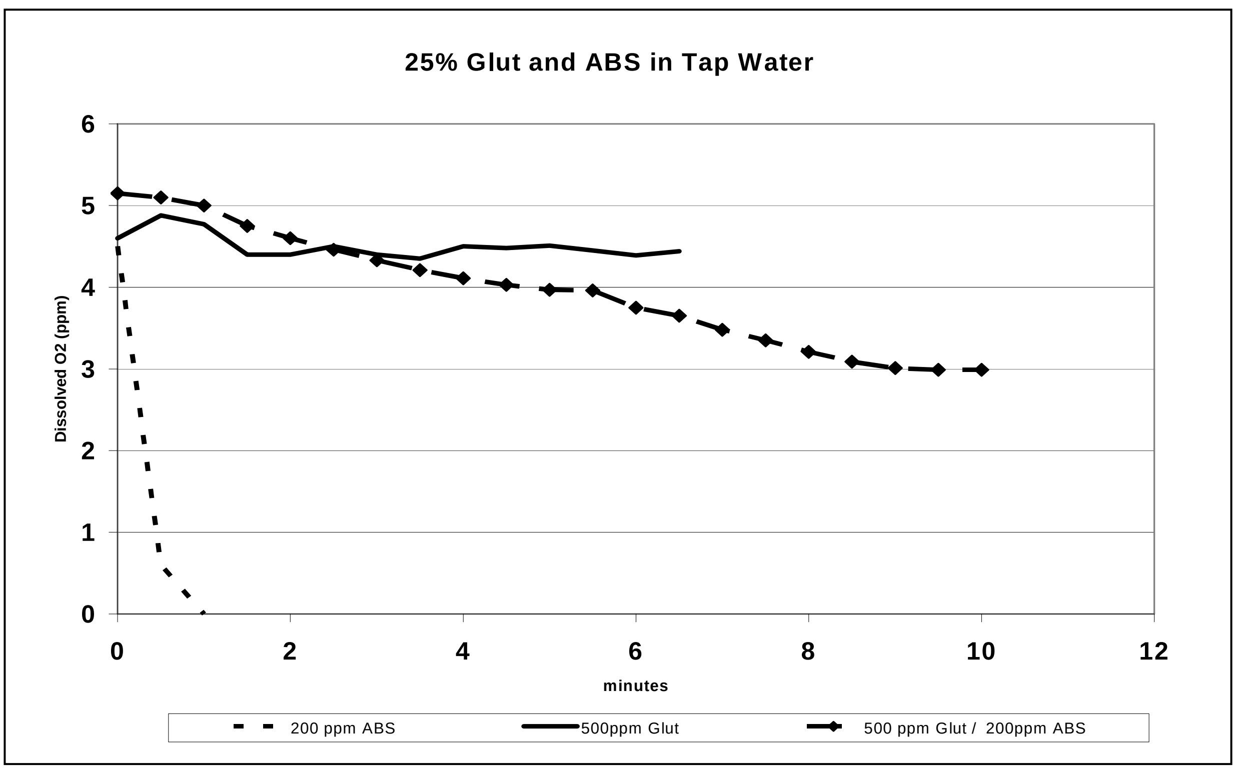

Figure 1

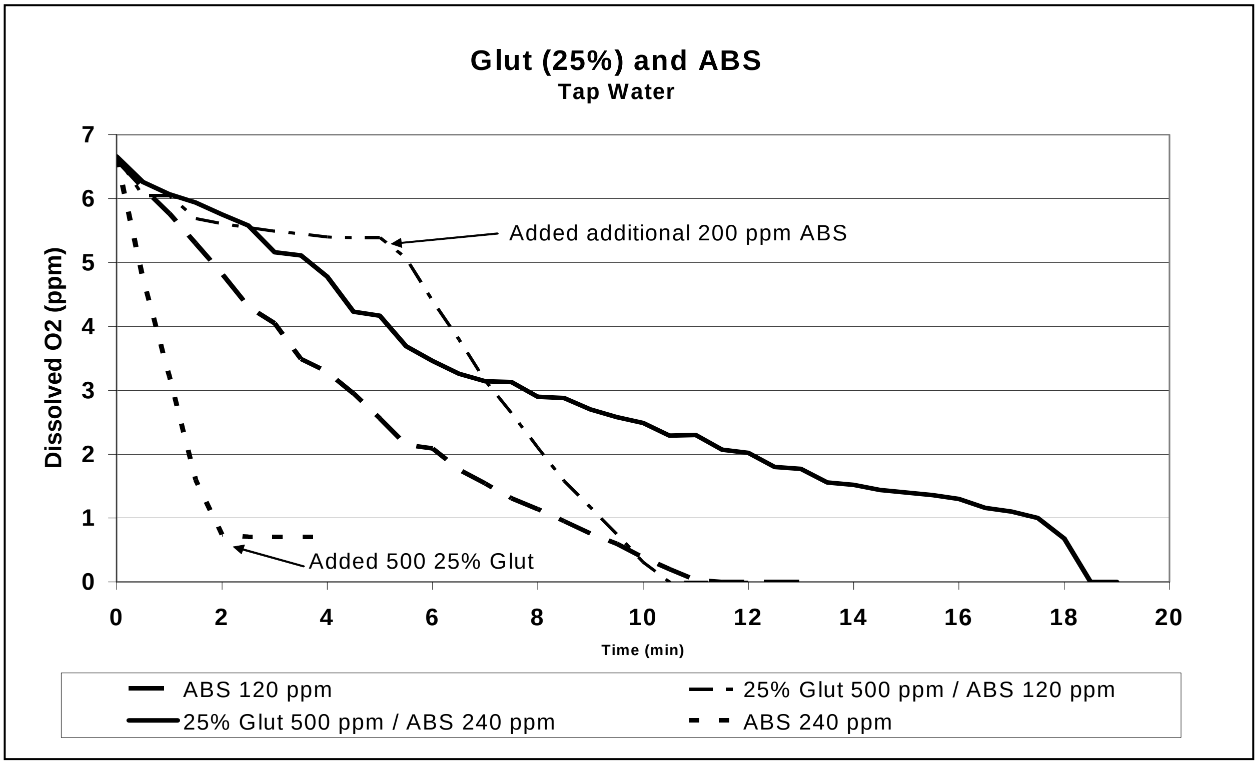

Figure 2

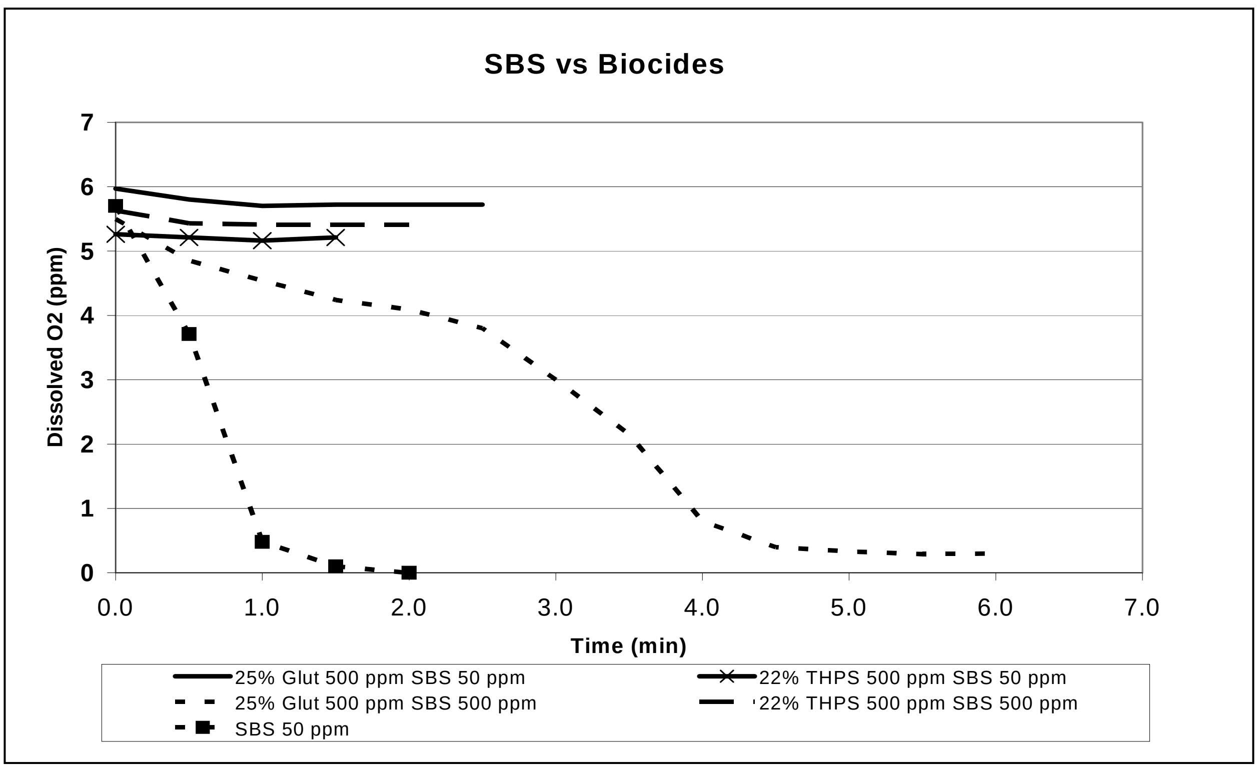

Figure 3

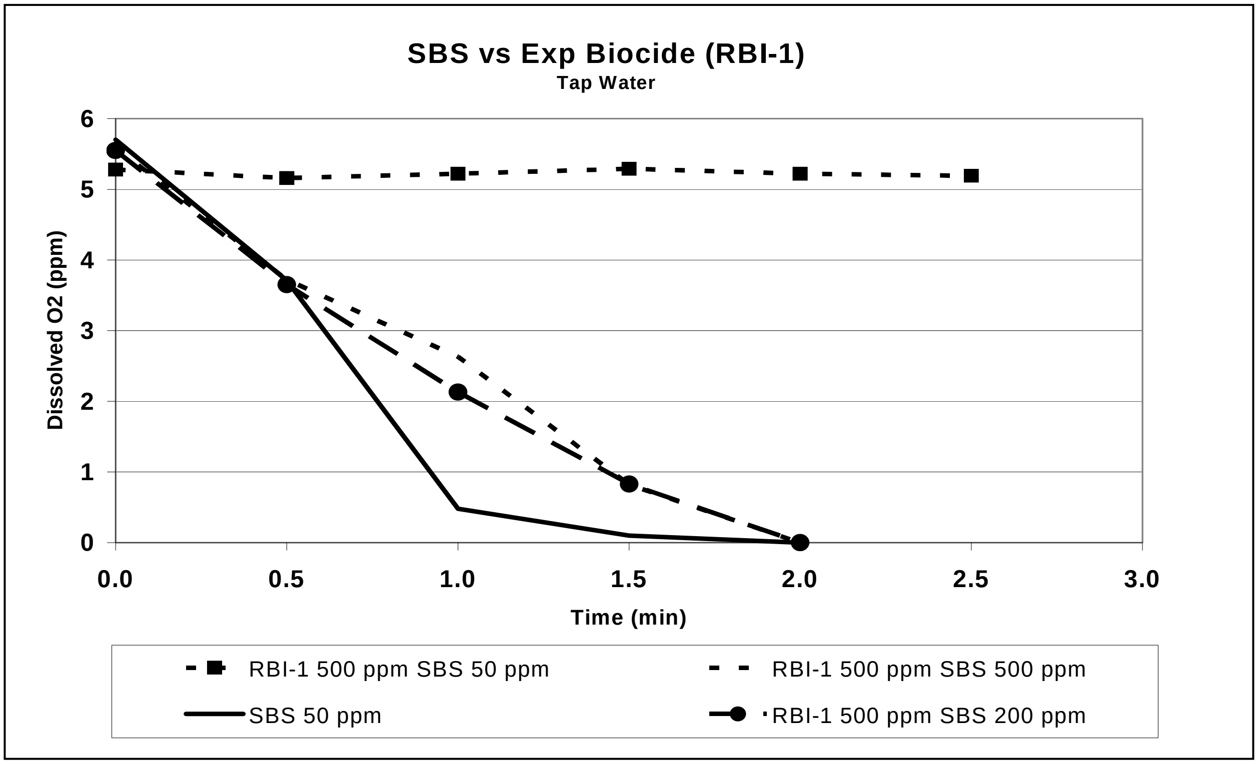

Figure 4

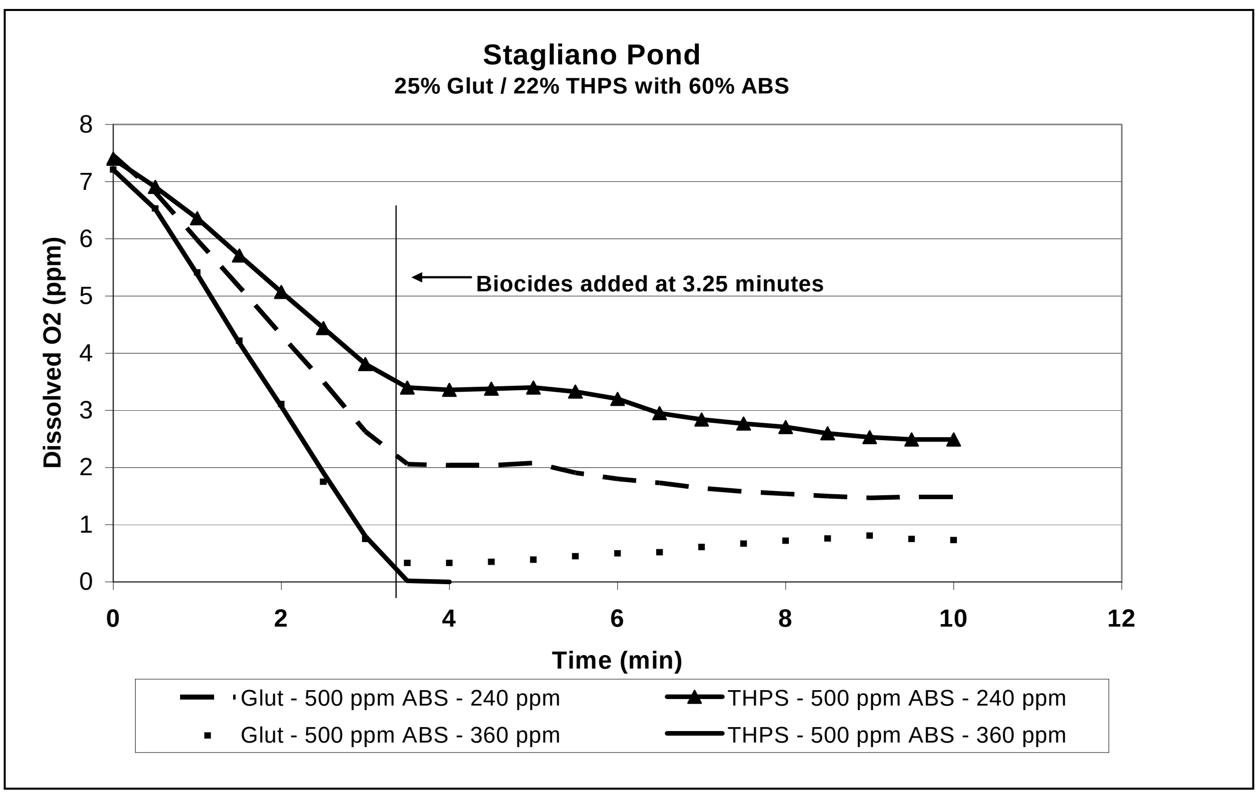

Figure 5

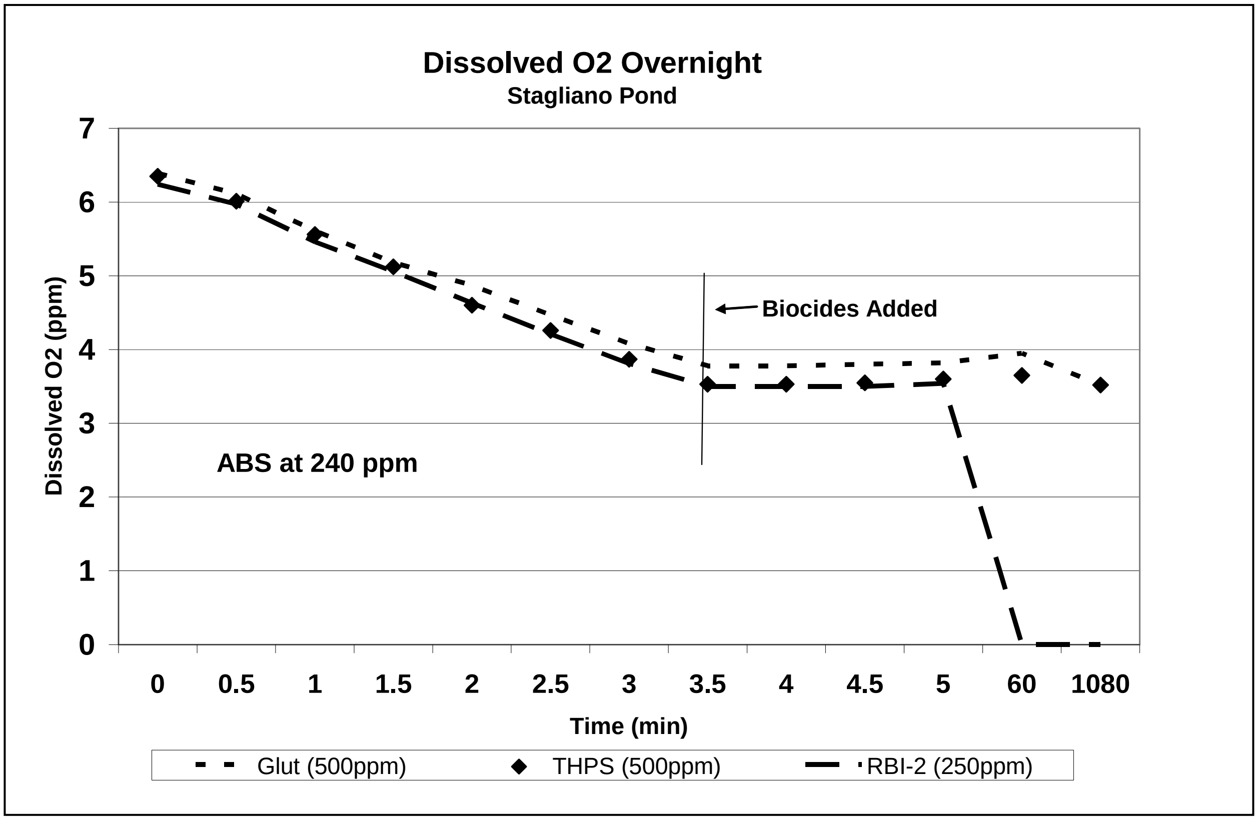

Figure 6

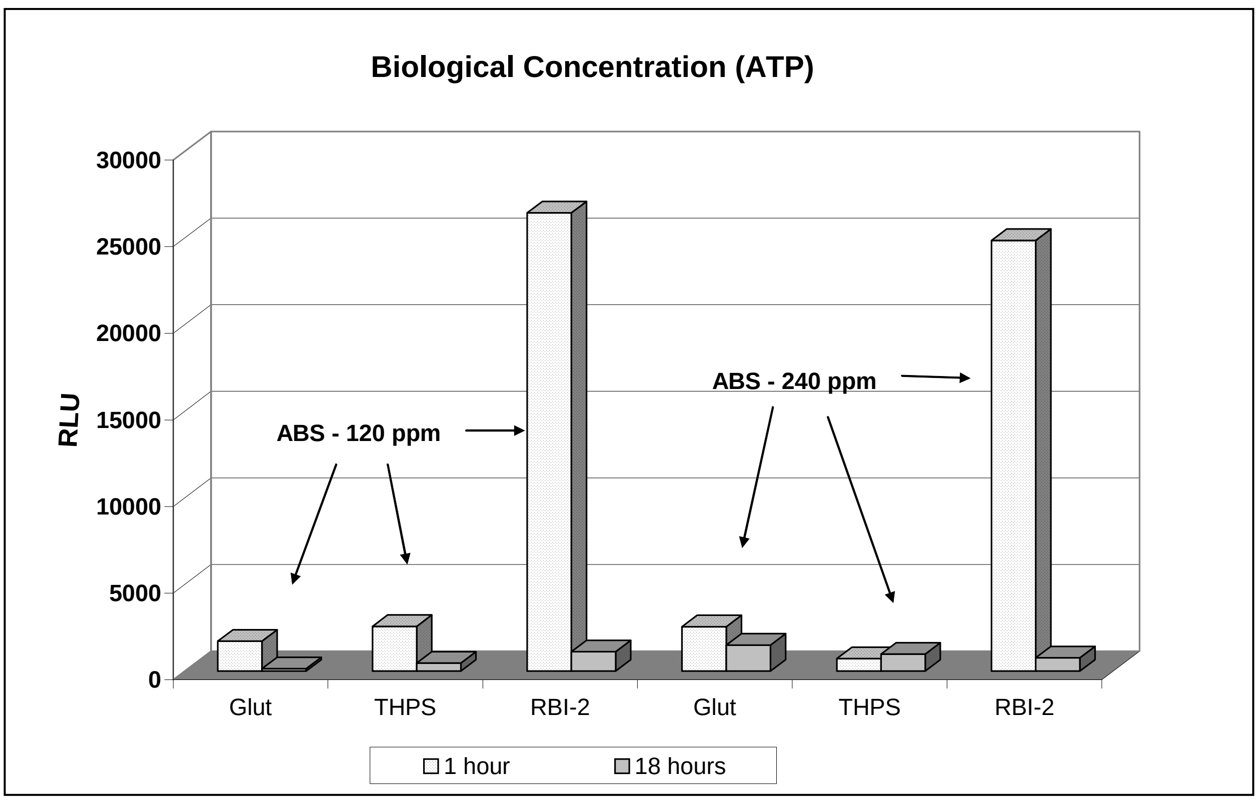

Figure 7