

Accelerating Bioremediation Using A Particular Surfactant

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ABSTRACT

This paper describes the use of a particular type of surfactant which is non toxic and biodegradable to speed up bioremediation of soils and sludge. Most contamination of soils and sludge are organic compounds, which makes bioremediation one of the most cost effective means of cleanup. One of the draw-backs of bioremediation is the relatively long time it takes to achieve acceptable criteria. Another difficulty that can occur is air pollution if the contaminate is a volatile organic compound (VOC). This is especially true if the remediation is ex-situ.

A surfactant accelerates the bioremediation and minimizes air pollution by:

- Increasing the speed of carbon substrate exposure to the micro-organisms and the dispersion of enzymes;
- Desorbs the contaminate into water phase which is a more acceptable environment for micro-organisms;
- Encapsulates VOC's in water to prevent volatilization.

University laboratory control test results will be discussed which show the surfactants can:

- Increased the rate of CO₂ production by micro-organisms 2 1/2 to 10 times compared to the control;
- Can be used in a marine environment;
- Can be used on either refined products or crude oil;
- Enabled CO₂ production in situations where the control couldn't;
- Controlled VOC volatilization.

Also, the results of the following full-scale commercial projects using a surfactant will be discussed:

- Two in-situ soil bioremediation cases;
- One in-situ soil washing case.

1. INTRODUCTION - PROBLEM OF IMMOBILIZED NAPL's IN SOIL

Soil can have non-aqueous phase liquid (NAPL) contaminate spilled onto or into it. When this happens the NAPL's tend to migrate down as a separate liquid phase and disperse into the soil matrix until they become trapped in the soil as immobile droplets or ganglia. NAPL's tend to follow high permeability pathways and spread along low permeability layers (Melrose, J. C et al). The disposition of NAPL's in the soil matrix can be in one or all of the following forms:

- evaporate and stay in the vapor phase;
- adsorb onto solid surfaces;
- dissolved into the soil moisture. (Wunderlich, R. W. et al).

In the case of a water table being in the migration route of the NAPL the path is determined by NAPL's specific gravity (SG):

- Dense non aqueous-phase liquids (DNAPL's) have a SG greater than the groundwater and therefore continue on a downward migration and will spread out at the bottom of the aquifer.
- Light non aqueous-phase liquids (LNAPL's) have a SG less than the groundwater and will spread out on top of the groundwater.
- In both cases the NAPL will disperse into the soil matrix until some of contaminate becomes immobile droplets or ganglia. (Hunt, J. R. et al).

Usually NAPL's have a low solubility in water (i.e. 5 ug/liter to 1000 mg/liter). However, regulations can require considerably lower concentrations thus requiring remediation. The slow release of the contaminate has often limited the effectiveness of many of the conventional soil treatment systems such as pump and treat, vacuum extraction and in-situ bioremediation. This is because the remediation process takes too long to achieve the desired limits.

2. POSSIBLE SOLUTION -USE SURFACTANTS

One of the techniques used to overcome the problem of the slow release of immobilized NAPL's is to solublize them with surfactants (Edwards, D. A. et al). Surfactants are capable of emulsifying LNAPL to facilitate increased mobility and recovery efficiency (Chevalier *et al.*, 1997; Abdul *et al.*, 1990). In many cases this technique can then enhance bioremediation if the surfactant is not toxic to the NAPL degrading microorganisms. In most cases it has been found that surfactants do enhance bioremediation.

Surfactants are essential to the bioremediation process. This is borne out by the fact that microorganisms produce surfactants in order to solublize hydrophobic organic compounds (Lange, S. and Wagner, F). Whether the surfactant is produced by microorganisms or manufactured they both act to solublize the target compound. Surfactants can act in two ways: (1) increase solubility (solubilization) and (2) lower the interfacial tension (mobilization).

The lowering of the interfacial tension increases the mobility of the NAPL by reducing the capillary forces that immobilized it. Solubilization moves the NAPL from being adsorbed on the soil to the water phase as an emulsion. When solubilized the NAPL is then available to be metabolized by mico-organisms. Surfactant field studies, primarily conducted at Hill Air Force Base in Utah, have attained up to a 99% source removal rate.

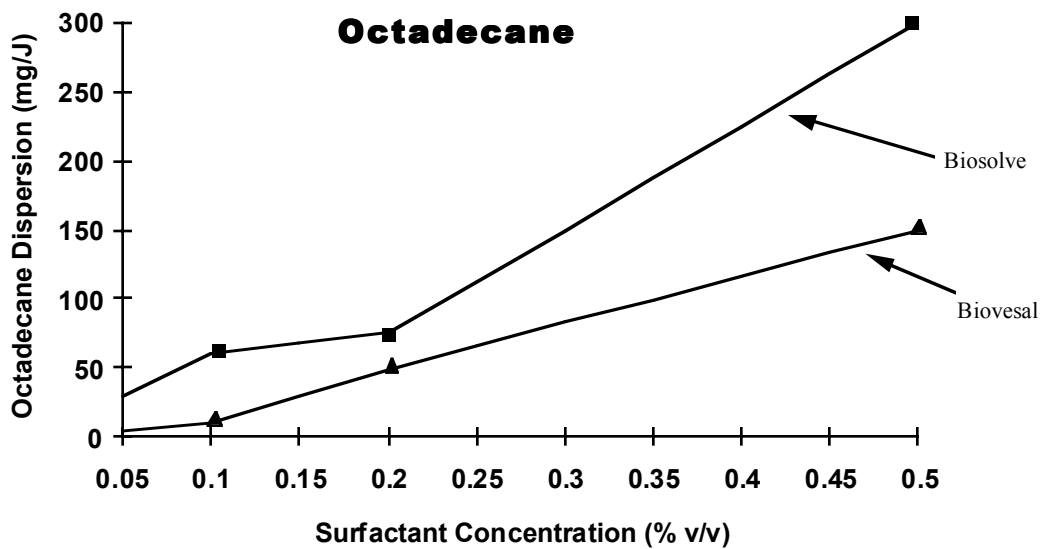
Toxicity and biodegradability of surfactants are also factors in bioremediation because they affect the efficiency of the bioremediation system. There are a number of low toxicity and highly biodegradable surfactants. One such compound that we have had experience with is a patented product (BioSolve™) that is also used as a fire suppressant. This product acts as a surfactant in that it encapsulates (solubilizes) the compound in water so that it cannot vaporize. That is how it acts as a fire suppressant. It has both UL and ULC approval through testing which proved its capability to suppress the vapors of volatile organic compounds (VOC's).

After the compound is encapsulated there is an indication that BioSolve tends to disperse the compound more than most surfactants by making extremely small micelles in the aqueous phase. This dispersing action makes more of the compound available to the microorganisms. Some studies show the slowest step in biodegradation is accessing the carbon substrate (Churchill, S. A. et al). Thus the more the compound is dispersed in water the more it is available to the microorganisms. The main reason for adding a compatible manufactured surfactant to a bioremediation system is to

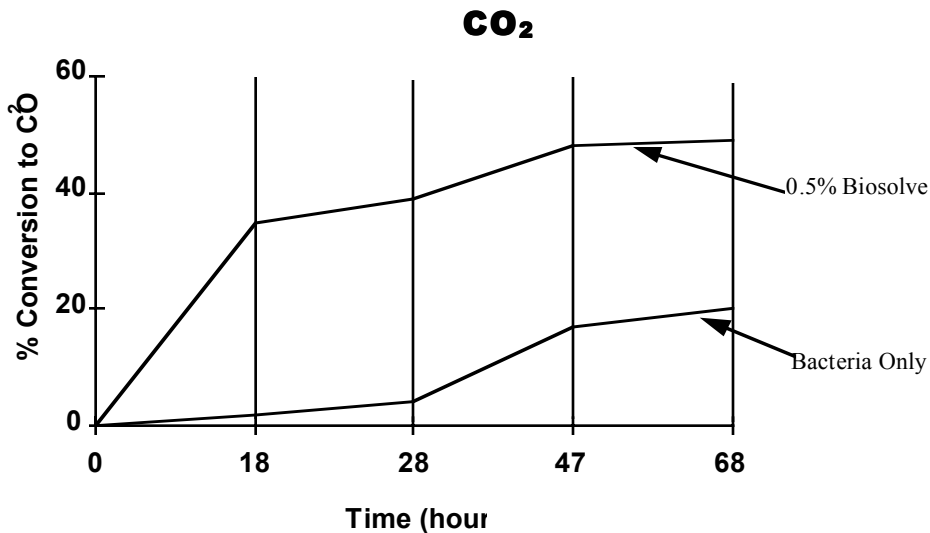
speed up the process. It takes considerable time for micro-organisms to create enough surfactants accelerating the process. In some cases micro-organisms cannot produce enough surfactant to start biodegradation.

3. AQUEOUS DISPERSION OF OCTADACANE AND CO₂ CONVERSION USING TWO DIFFERENT SURFACTANTS

Tests of octadecane solubilization and carbon to CO₂ conversion tests at the University of Alabama using two commercially available surfactants showed: (1) BioSolve dispersed the octadecane 50% to 100% more at concentrations of 0.1 % to 0.5% than another popular surfactant and (see Graph #1); (2) After 68 hours BioSolve had a 48% conversion rate to CO₂ compared to 19% for bacteria only (see Graph #2). These tests indicate some of the effects of using surfactants for remediation of hydrocarbons and especially for BioSolve.



GRAPH #1



GRAPH #2

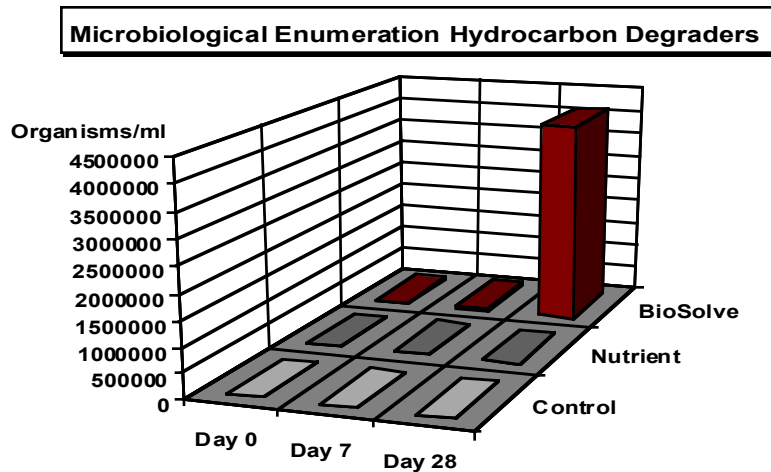
4. EFFECT OF A SURFACTANT ON HYDROCARBON DEGRADER MICROBIAL POPULATION AND ALKALINE DEGRADATION

Tests on BioSolve by the National Environmental Technology Applications Center (NETAC) at the University of Pittsburgh included a series of runs comparing the microbiological enumeration of hydrocarbon degraders for the following samples:

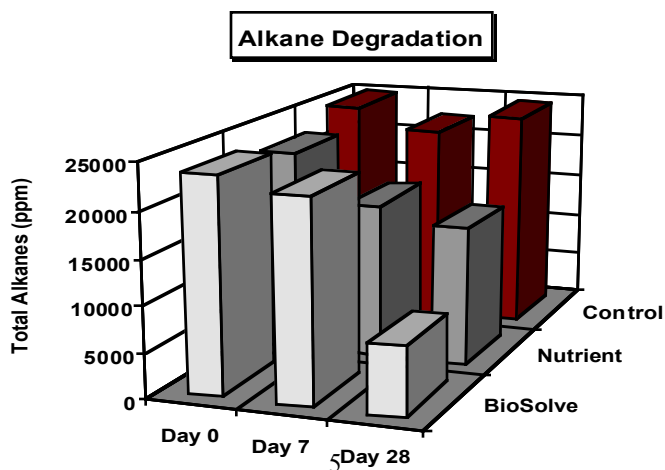
- Control
- Control plus nutrient
- Control plus nutrient and BioSolve

These tests showed: (1) After 28 days the BioSolve test had 4,500,000 organisms/ml where as the control and the control plus nutrient samples had less than 100,000 microorganisms/m (see Graph #3); (2) After 28 days the control still had 25,000 ppm hydrocarbon whereas the nutrient only sample had 17,500 ppm and the BioSolve sample had 7,500 ppm (see Graph #4).

The runs show that the surfactant accelerates the microbial population and hydrocarbon degradation. It should be noted that the most common hydrocarbon degrader micro-organisms are aerobic (need oxygen and produce CO₂ and water).



GRAPH #3

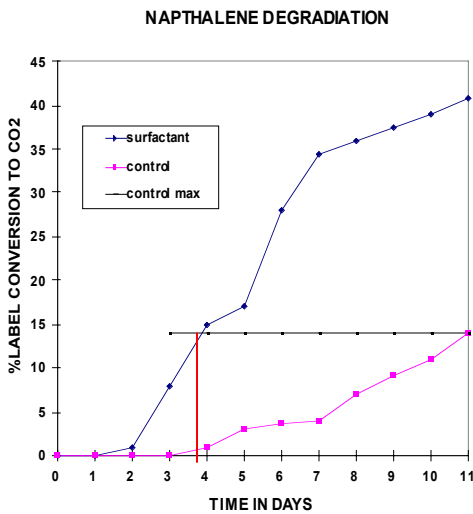


5. CO₂ PRODUCTION CONTROL TESTS WHEN USING A SURFACTANT

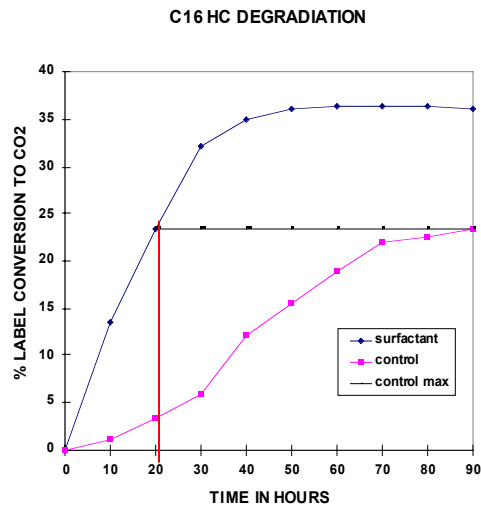
An indirect way of assessing aerobic biological activity is to measure CO₂ production. The following five CO₂ production tests were conducted at the University of Alabama. A summary of the protocol used is as follows:

- For each test a quantity of thoroughly mixed soil or beach sand was divided into two equal parts.
- Each part had an equal amount of radioactive carbon marked contaminant mixed into it.
- Each part had an equal amount of water mixed in, one part with only water and one part with water and surfactant.
- Each part was enclosed and the CO₂ production was measured.
- Each of the five tests had a different type of contaminant and/or different levels of contamination.

The results of the tests are summarized on the following graphs:



TEST #1



TEST #2

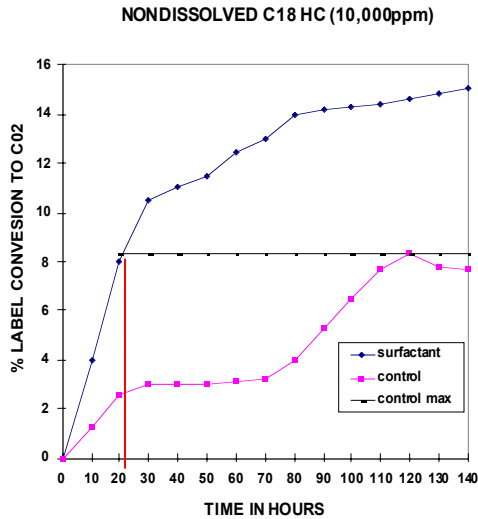
Test # 1 shows a control test in which the contaminant was a relatively light refined hydrocarbon. After 11 days the maximum CO₂ % of the control is approximately 14.75 %. The surfactant reached the same % in 3.85 days. This implies the surfactant speeded up the bioremediation process by close to a factor of 2.88.

Test # 2 used crude oil as the contaminant. The control part of the test reached 23.5% CO₂ production after 90 hours whereas the surfactant part reached the same level in about 17 hours. This implies the surfactant speeded up the process by over a factor of 5.

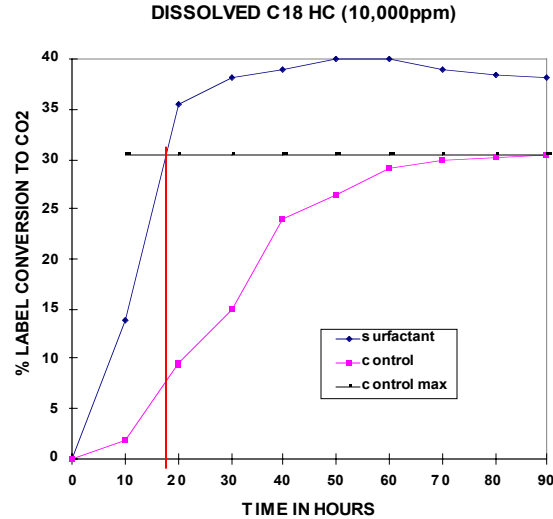
It should be kept in mind, that easily bioremediated contaminants will eventually degrade to non-detectable limits whether or not surfactants are used. All the surfactant does is speed up the

process. This is not necessarily true for all situations where the contaminate is difficult to biodegrade. An example of this will be discussed in Test # 5 and Test # 6.

Tests # 3 and # 4 are with crude oil. The difference in these tests is how the oil contaminated the soil. Test # 3 simulates a dry land situation *i.e.* pipeline break. The oil was poured on the soil and mixed then followed by the addition of water or water and surfactant, then mixed again. This tends to create more oil wetted soil surfaces than when the soil is already water wetted. The control reached a CO₂ production of 8.33% after 120 hours, while the surfactant reached it in about 21.2 hours or a factor of approximately 6 times faster.



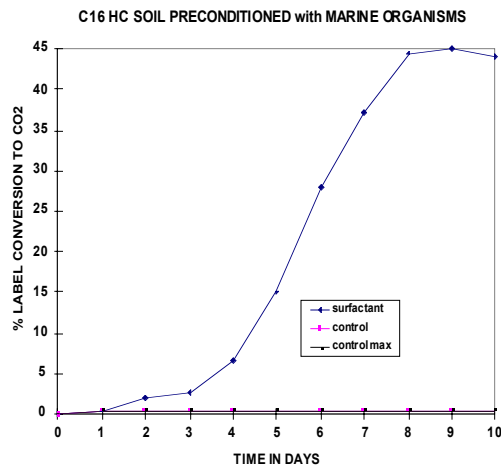
TEST # 3



TEST # 4

Test # 4 was conducted to simulate a fresh water spill *i.e.* on a river. The soil was wetted with water and then oil was mixed with water before being put on the soil. The control reached a CO₂ % production of 30.5% in 90 hours. The surfactant reached the same % in 17 hours or a factor of over 5 times faster. It should be noted that Test # 3 has a lower % over the same period of time as in Test #4. This may be accounted for by the fact that more oil is adhering to the dry oil wetted soil, which marked it more difficult to solubilize the oil.

Test # 5 simulates a spill onto a salt-water beach. The soil has been preconditioned with marine micro-organisms for seven days. In this case the control indicated very little remedial action. The surfactant showed significant CO₂ % production indicating that the surfactant can start remediation that would not start on its own.



TEST # 5

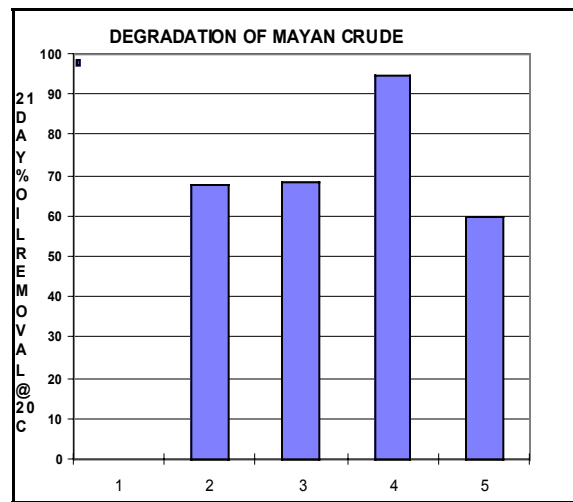


FIGURE # 6

6. COMPARISON OF A SURFACTANT/DISPERSANT COMBINATION WITH A COMMONLY USED DISPERSANT

The results shown in Figure # 6 was part of a program to remediate sites of old crude oil spills where it appears the natural bioremediation had virtually stopped. Figure # 6 summarizes a series of tests conducted on contaminate that was a 5 year old heavy crude oil that had been weathered in a tropical environment. The tests consisted of four bioreactors set up with a specially developed culture of microorganisms, nutrients and aerated (reactors #2, # 3, # 4 and # 5) plus one reactor (reactor # 1 the control) was setup without microorganisms, nutrients and aeration. The protocol was:

- Reactor # 1 had only the contaminated soil.
- Reactor #2 had only microorganisms, nutrients and aeration.
- Reactor #3 had microorganisms, nutrients, aeration and 0.5% surfactant.
- Reactor #4 had microorganisms, nutrients and aeration and 5.0% surfactant/dispersant.
- Reactor #5 had microorganisms, nutrients and aeration and a commonly used dispersant.

Figure # 6 shows that in:

- Reactor # 1 bioremediation of this crude had virtually ceased.
- Reactor # 2 bioremediation can take place by augmenting with microorganisms, nutrients and aeration.
- Reactor # 3 low concentration of the surfactant produced little or no additional effect.
- Reactor # 4 with the 5.0% surfactant combination solubilized the high molecular weight hydrocarbon and sped up the bioremediation leaving only 5% of the original contamination after 21 days, where as the other tests had 6 times more contaminate left.
- Reactor # 5 the commonly used dispersant actually slowed the bio-remediation process slightly. There have been cases were some dispersants significantly slow down bioremediation (Falatko, D. M., et al.).

7. 28 DAYS CO₂ PRODUCTION COMPARING CLEAN & CONTAMINATED SOIL WITH AND WITHOUT A SURFACTANT

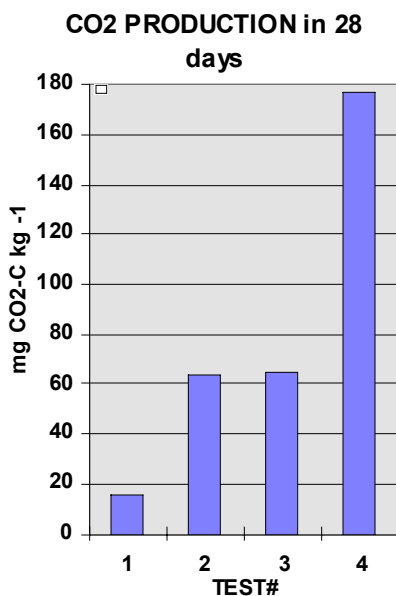
Figure # 7 summarizes the results of a control test conducted at the University of California - Berkeley. The test used an autoclave sterilized gravel and fill soil matrices. A summary of the protocol is as follows:

- Test # 1 was the control which consisted of sterile gravel and filled with w
- Test # 2 was the same as Test # 1 except it had 3% BioSolve added to the water.
- Test # 3 was the same as Test # 1 except it had Hydrocarbon added.
- Test # 4 was the same as Tests # 3 except the water had 3% BioSolve.

These tests show the following:

- That the soil matrix contained enough carbon for the micro-organism to produce 15 mg CO₂.
- That BioSolve is biodegradable and to produced 60 mg CO₂ (Test # 2).
- That the hydrocarbon was used as a supplemental food source by the micro-organisms and produced 60 mg CO₂ (Test # 3).
- BioSolve made more of the hydrocarbon available as a supplementary food source by producing 175 mg CO₂ (Test # 4).

FIGURE #7



8. A CASE STUDY OF IN-SITU BIOREMEDIATION USING A SURFACTANT

The site on which this in-situ bioremediation took place was in Bakersfield, California for an agricultural manufacturer. Two 2270-liter leaking underground gasoline and diesel storage tanks caused the contamination. The contamination went to a depth of 13.7 m. The plot plan area of the contamination was 10 m by 10 m. Thirteen monitoring/inoculation wells were drilled, nine on an outside circumference of the plume and four in the plume. These were used to measure the VOC levels and inoculate the surfactant combination (BioSolve), nutrients, air (by vacuum) and microorganisms. Three sample spots on the periphery of the plume and two sample spots in the center of the plume were used to sample the soil. The following is a summary of events, dates, high, low and average VOC readings that occurred in the remediating this site:

Figure # 8 summarizes the high, low and average VOC readings from the wells on this project. An interesting occurrence that was observed in the results was the increase of the high VOC values 12 days after the remediation process had began. This was caused by immobilizing more of the trapped hydrocarbon, which could not be detected.

Unfortunately in this situation a control could not be used. However this was an old spill and the initial levels give an indication of what a control would look like. This protocol was used because it was estimated to be 38%-45% less expensive than thermal treatment and more acceptable to the public. Other benefits of this process are: (1) The bioremediation continues on after the site closing which can result in the ultimate destruction of the hydrocarbons; (2) The surfactant/dispersant combination minimizes the VOC's from migrating from the ground.

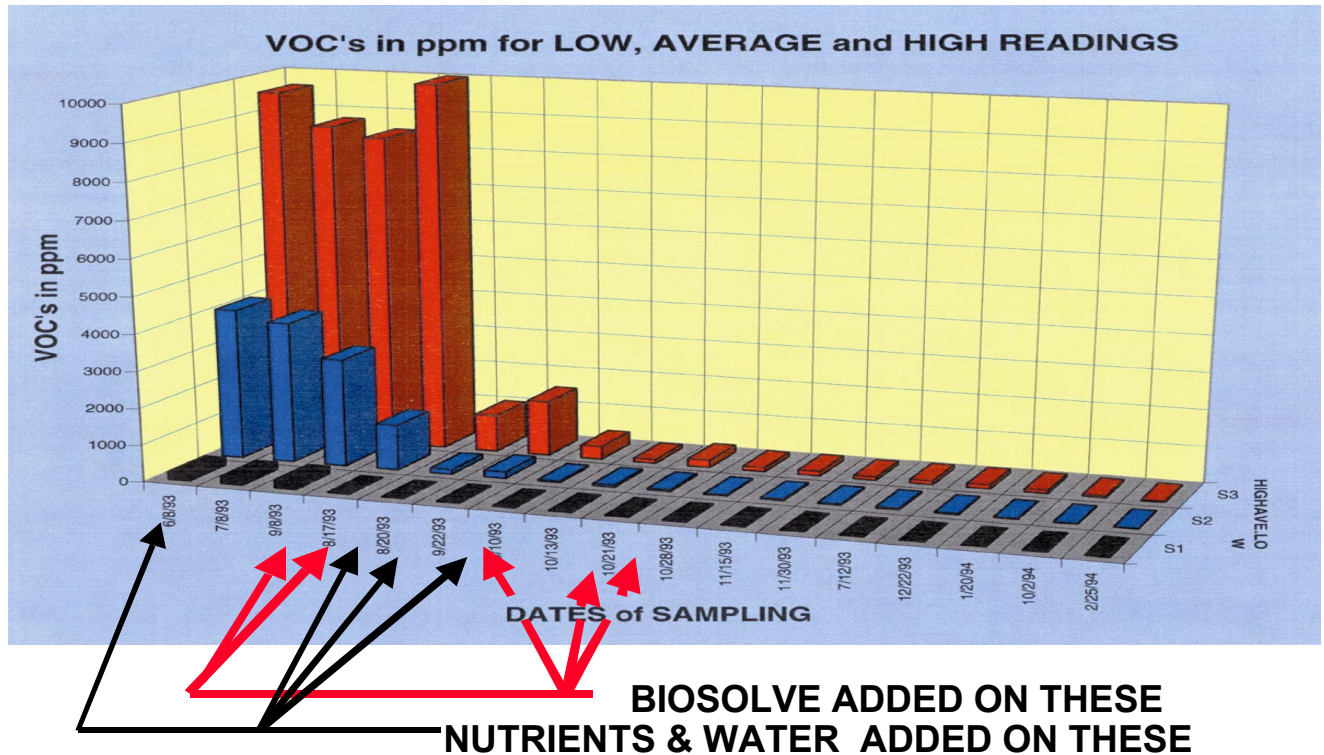


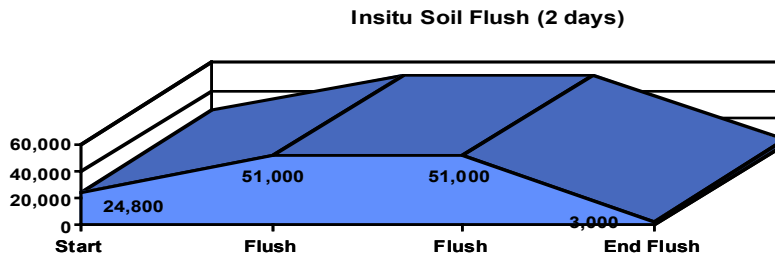
FIGURE # 8

9. A CASE STUDY USING A SURFACTANT TO FLUSH HYDROCARBONS FROM THE SOIL

This case study shows the ability of a surfactant to mobilize a hydrocarbon in soil. In this situation an underground storage tank leaked diesel fuel next to and underneath a building. The surface above the contaminated soil next to the building was flushed three times with a 250 gallon 2% BioSolve solution. On the opposite side of the building a trench was dug to collect the flushes. Figure #9 summarizes the soil testing results. The reason for the rise in the ppm of TPH is the mobilization of the diesel. Once the diesel was flushed out the soil showed a significant decrease in diesel. The BioSolve that remained in the soil speeds up the biodegradation of the remaining soil.

Although this does not directly show acceleration of biodegradation it shows the mobilizing capabilities of a surfactant, which is necessary in many in-situ bioremediation projects. Sometimes there is too much contaminate in the soil to allow for relatively fast bioremediation and this can cause a toxic situation or just too much food. So soil flushing can get the contaminate concentration down to acceptable levels and accelerate the bioremediation of the soil and the flush water.

FIGURE #9



10. CONCLUSION

From the bench and field scale tests, it appears that the bioremediation process can be sped up through the use of surfactants/dispersant combination. Secondly, there are some cases where bioremediation can only occur through the application of surfactants. This was demonstrated in the control CO₂ production tests on beach sand (see Test # 5). The field test showed that surfactant application could be used in in-situ situations. Caution should be used in in-situ situations because the contaminant can be mobilized and if not controlled the contaminate can move and contaminate more soil.

In-situ mobilizations of NAPL's through the use of surfactants is becoming better documented (Fountain, J. C and C. Waddell-Sheets), (Fountain J. C, Wayt, H. J. and D. J. Wilson), (Vigon, B. W. and A. J. Rubin). Also, there has been considerable technology done on removing crude oil from various oil producing formations by the oil extraction industry that can be applied to contaminated soils. Further field tests with in-situ controls need to be conducted to better determine the degree to which surfactants can enhance and speed up bioremediation. Most in-situ remediation projects do not use controls.

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