Comparison of in-situ

Bioattenuation, Biostimulation, and *Bioaugmentation* and their Application to Marine Oil Spills

by Michael Bruckner

On April 20, 2010, an oil spill of catastrophic proportions occurred just off the coast of Louisiana at the *Deepwater Horizon* oil rig. The unexpected size of the spill has provoked a series of responses, some coordinated and others not. Some of the approaches used include burning of the oil and removal for ex situ filtration or even later processing of the oil. Many responses involved extensive manpower and low efficiency, and some can even be environmentally unfriendly themselves. Looking for options that are more sustainable can lead to a paradigm shift in procedure and some options suggest a more "natural" response, in which the environment around the spill is used to return itself to its prior state.

Salt marshes near Myrtle Grove, LA (Photo credit: Michael Bruckner, February 2011).

Bioremediation Technologies

In order to effectively compare these different bioremediation technologies, a brief insight into each followed by comparisons of previous case studies in past oil spills is necessary. In addition to a brief overview of these other cases, it is important to also mention the actual role bioremediation has had in the current oil spill with suggestions on how it may be implemented in future marine oil spills.

Background

Bioremediation is a growing field of research that has many different applications. Although there are a plethora of bioremediation technologies, three are discussed here: bioattenuation, biostimulation, and bioaugmentation. All of these technologies focus on biodegradation, which simply implies the environment around us is involved in the chemical breakdown of pollutants. As engineers, increased scales of simplicity and economy should grab our attention. Why reinvent the wheel? In order to use the environment around us as a tool, we must further understand its limitations and the makeup of the pollutant.

Petrochemicals, other products of petroleum and/or oil, can be described as recalcitrant materials. This means that they resist degradation in the environment, but no molecule is completely resistant to change; only that some are more so than others. The difference in time scale can be quite remarkable, as some fractions of oil may degrade within a matter of days, while others may require thousands of years. Louisiana sweet crude oil is a heterogeneous material. Therefore, blanket statements about degradation of the oil are hard to make. But once split up into generalized fractions, an easier analysis can be done. This oil is made up of paraffins, aromatics, resins, and asphaltenes with a very small amount of sulfur (hence, the name "sweet" crude), in this case, approximately 80% of the oil is comprised of paraffins. In general, both paraffins and short-chain aromatics are not deemed recalcitrant, while longer chained aromatics, resins, and asphaltenes are.

According to the "doctrine of infallibility," there is no compound known to man that cannot be degraded by microorganisms.[1] In other words, solutions to many problems related to contaminants could be found in native flora in different locations. There are different ways to manipulate and/or engineer this to our advantage.

Often remediation of an ecosystem occurs on its own without any outside intervention. This process is called bioattenuation and can be monitored by various methods to determine whether or not intervention is needed. This process is also known as intrinsic, natural, passive, and/or spontaneous bioremediation. To determine whether or not this is a viable option, there are a series of factors that are looked at to ensure that the contaminant does not advance more quickly than the native microbes can degrade it.[2] Bioattenuation requires an extensive monitoring system that must be put in place to determine the rate at which the contaminant is spreading, where it has spread to, in what quantities, and, finally, the rate of degradation.

Bioattenuation is not always sufficient alone, as oftentimes the contaminant can move faster than the flora can degrade it. Just as easily as bioremediation can be monitored, it can be manipulated as well. This "engineered" bioremediation, called biostimulation, differs in approach and implementation, but consists of a few different general areas. Also, the addition of organic or inorganic nutrient addition

Salt marshes near Myrtle Grove, LA (Photo credit: Michael Bruckner, February 2011).

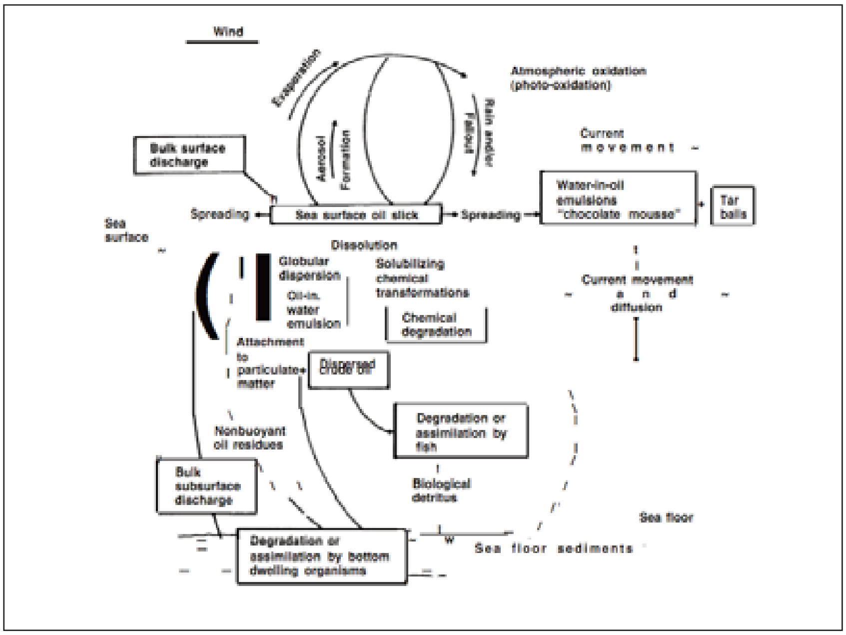

***Figure 1**. Schematic of physical, chemical, and biological processes.*

Source: National Research Council, *Oil in the Sea*; Inputs, Fates and Effects (Washington, DC: National Academy Press, 1985), p. 271. Adapted from R. Burwood and G.C. Speers, "Photo-oxidation as a Factor in the Environmental Dispersal of Crude Oil," Estuarine Coastal *Marine Science, vol. 2, 1974*, pp. 117-135.

is dictated by the types of indigenous microbes and their requirements. Approaches vary due to medium, flora, and a host of other factors. The most commonly occurring microorganisms are bacteria, although algae and fungi also play a part. Fungal bioremediation specifically is referred to as mycoremediation and has been gaining much ground lately due to advances in mycology.

An understanding of local biogeochemistry is important, as biostimulation is the addition of nutrients to aid in remediation. Nutrients most commonly used in this process are water, oxygen, nitrogen, and phosphorous.[3] Finding the limiting conditions for the indigenous organisms to carry out the desired remediation is the most important step. These limiting conditions are tied to the biogeochemistry of the region, hence the importance of knowledge of the surroundings.

These earlier, varying approaches to bioremediation all differ from bioaugmentation, which is the addition of microbes to the site of interest. Proponents of this method tend to refer to the idea that "scientists now accept that no single species of microorganisms will completely degrade any particular oil, but this involves a consortium of microorganisms."[4] It is widely accepted that no one microorganism's metabolic pathway is sufficient in degrading all the different fractions of oil. This is why there is an effort to group all of the different metabolic pathways into one "package," an effort that claims that degradation of large percentages of most oil fractions may be possible if use of recombinant DNA technology is used.[5] Although there may be future markets for bioaugmentation, to date there has been no successful application outside the laboratory setting due to competition with local flora.

Actual Impacts on Gulf

In the case of the *Deepwater Horizon* oil spill, there were two different, broad scenarios. As this was a marine oil spill, there was the impact to the surrounding marine environment and the coastal regions. The Gulf of Mexico is a dynamic environment, making it difficult to understand the movement of oil and difficult to determine the impact of bioremediation. Figure 1 may help one to better understand all the different natural processes occurring during the spill.

The Gulf is an open, dynamic marine environment. This presents challenges in understanding the effects bioremediation has on the contaminant levels, but this does not mean it is not possible to gauge reaction to increased contaminant levels. One way to measure for biodegradation is to measure the oxygen concentrations and depletions. Within a month after the spill, the oxygen was measured at a 30% depletion, which shows oil in the water column was being degraded. The sweet, light oil released is biodegraded quicker than alternative kinds, and there are ample nutrients to sustain the oil-eating flora in the Gulf. This makes for a successful environment for degradation of the light fractions of the petroleum. Also, after continued exposure to oil, the local flora shows increasing rates of degradation; it is shown that microbes previously exposed to oil can biodegrade at a rate of 10 to 400 times faster than that of microbes unfamiliar to oil.

Using dispersants has been a controversial topic in marine oil spills, but, nonetheless, a strategy that has been implemented on several occasions. Large oil slicks occurred after the *Deepwater Horizon* spill and they were negative for several reasons, including air emissions and damage to local animal and fish populations. Due to the overwhelmingly higher fraction of lighter hydrocarbons in Louisiana sweet crude oil, a majority of the oil floated to the surface and much of this over time is released into the atmosphere. Due to the high concentrations of oil in these slicks and low surface area ratios, this made for unfavorable conditions for bioremediation. Chemically dispersing the oil is hypothesized to speed up the process of biodegradation by increasing the surface area for the flora to act. Corexit 9500, the dispersant used in the largest quantity of the *Deepwater Horizon* oil spill, has been deemed to be about 54.7% effective with South Louisiana crude by the U.S. Environmental Protection Agency (EPA).[6] The dispersants can also prevent formation of "chocolate mousse," which are water-in-oil emulsions that are very resistant to degradation. Although there has been a lot of attention drawn to toxicity of dispersants, in respect to bioremediation, it makes a lot of sense for implementing dispersants.

In coastal regions, the local nutrient levels are not enough to sustain biodegradation. In this case, enhanced bioremediation in the form of biostimulation is preferable. Successful bioremediation of this nature has occurred in several spills, including some coastal areas in Alaska after the *Exxon Valdez* oil spill, and in Galicia, Spain, after the *Prestige* oil spill. In order for this to happen, tar balls that form and other thicker, recalcitrant fractions of oil must be manually removed, as these thick layers of oil will suffocate coastal plants and animals may fall ill due to ingestion and fumes released. Currently, in Plaquemines Parish, LA, the tar balls are so thick in some areas, the parish government is reporting as much as 40 feet (> 12m) of land loss directly contributed to the suffocation of the marshes by these heavier fractions of oil. The two photographs on pages 20 and 21 illustrate the conditions of the marshes; the photos were taken during a field visit to the Myrtle Grove, LA, on February 25, 2011.

Biostimulation has shown a 10–30% increase in total hydrocarbon degradation when compared to bioattenuation. An example of this took place in Galicia, Spain, after the *Prestige* oil spill, where the stimulant used was S200 (an oleophilic fertilizer).[7]

In the Louisiana salt marshes, biostimulation is important due to low natural rates of degradation of paraffins. The addition of nitrogen fertilizers has been shown to significantly increase hydrocarbon degradation over bioattenuation.[8] Again, this is important in relation to the high percentage makeup of these fractions of oil.

While bioremediation has a proven track record within certain limits, bioremediation alone cannot currently solve all of our marine oil spill problems. It must be implemented alongside other technologies. As we improve our knowledge of biodegradation of recalcitrant fractions of oil, this could all change. **em**

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