

## **Humic Acids and Environmental Remediation Literature Review**

One of the main active ingredients in SHAC Ponder is humic acid. Humic acids are known to have many potential agricultural and environmental benefits. This literature review focuses on industry research regarding humic acids, microbial stimulation and remediation of contaminated sites. All of the articles/research papers referenced in this document are available for review upon request.

### **Humic Acids in Ponder**

A&L Labs in Modesto, California measured the amount of humic acids in the SHAC Ponder at a concentration of 2.3%. The A&L method is qualitative and is a measurement of all humic acid derivatives. This includes both humic acid and fulvic acid. The product was also analyzed by the CDFA method with a reported concentration of 1.2%. Often the difference between the A&L method and the CDFA method is referred to as the fulvic acid fraction. Therefore, the fulvic acid fraction of SHAC Ponder is 1.1%.

### **Microbiology and Remediation Applications**

The practice of bioremediation involves using microorganisms to metabolize certain contaminants in the environment. Biostimulation of resident microbes can result in higher rates of decontamination. This biostimulation can usually be achieved by introducing specific nutrients, such as humates, into the environment. In his book, *Humic Fulvic and Microbial Balance*<sup>1</sup>, Jackson points out that several reports have demonstrated that humic acids stimulate growth and proliferation of desirable microorganisms. There has been some success in the areas of petroleum and salt contamination remediation. Salt remediation is thought to occur through the chelation of salts and humic acids to form humates. It should be noted that the adsorptive quality of humic acids alone (similar to that of activated carbon), can result in the binding of many undesirable chemicals and toxins.

In Karr's article regarding oxidized lignites in agriculture<sup>2</sup>, he points out that Bkadwaj and Guar found that humic acids had a noticeable growth stimulating effect on *Rhizobium trifolii*, and that Vallini et al found that humic acids stimulated growth of *Nitrosomonas europaea* and *Nitrobacter agilis*. The later found that nitrifying bacteria stimulation was not stimulated through providing nutrients, as is often the case, but by increasing the permeability of the cell walls allowing better utilization of nutrients. These successes in biostimulation will likely lead to greater developments in the use of humates and humic acids in bioremediation in the future.

In Mosley's paper regarding the effects of humates on remediation of contaminated soils<sup>3</sup>, he asserts that the application of humates is an inexpensive and effective alternative to standard remediation of oilfield wastes and that there are many benefits over the usage of microbes, including improvement in soil water wetability, less need for oxygen, and ease of application and cost. It is stated in the article that humic acids have

been found to alter oils into fatty acids and sugars through chemical reactions and stimulation of microbial activity. Also humic acids are thought to act as catalysts for soil enzymes in the degradation process and act as a strong chelating agent.

In a study conducted by Holman et al<sup>4</sup>. regarding the use of humic acids for PAH (polycyclic aromatic hydrocarbon) degradation, pyrene degradation experiments were conducted to determine the effectiveness of using humic acids in remediation. It was acknowledged that bioremediation of PAH-contaminated soils often experiences limited success due to the low solubility of PAH. Also, that adding synthetic surfactants to improve solubility may further inhibit microbial activity due to the toxic effect of many surfactants. The study found that pyrene degradation was enhanced and that the water insoluble pyrene was solubilized into humic acid pseudo-micelles and therefore became available for bacterial consumption. It was determined that naturally sourced humic acid treatment is a potential alternative (in unsaturated soil environments) to synthetic surfactants to accelerate the biodegradation of PAH.

A study regarding the use of aqueous humic substances for in-situ remediation of contaminated aquifers was conducted by Van Stempvoort et al<sup>5</sup>. The study involved a 5 year laboratory test in which diesel fuel within a model sand aquifer was flushed with water containing humic acid. It was found that the humic acid flushing increased the concentration of methylated naphthalenes from the diesel two to ten fold and that a corresponding increase in biodegradation of the methylated naphthalenes occurred in-situ. It was stated that as the hydrocarbons were depleted from the diesel, the contaminant plume shrank and disappeared. It was determined through numerical simulations that without the use of humic acids, complete diesel fuel dissolution would have taken six times longer. The study suggests that only a relatively low concentration of humic acids (1 g/L) is most effective in the flushing of hydrophobic contaminants and that it may be possible to use humic acids for a combination of flushing, enhancing the bio-remediation process as well as sequestering organic contaminants in aquifers.

In a study conducted by Linnik et al<sup>6</sup>. regarding the role of humic substances in the complexation and detoxification of heavy metals, a group of reservoirs was monitored specifically in regard to copper toxicity. It was found that a decrease in water toxicity correlated with a reduction in free  $\text{Cu}^{2+}$  concentration (due to complexation with humic substances) and that the greatest decrease in toxicity was observed in natural water where the complexation occurred with participation of both dissolved organic matter and added humic acid. It is stated that dissolved organic matter, and humic acids specifically, play a main role in the complexation and detoxification of many heavy metals in natural waters as free metal ions are regarded as the most toxic form. Heavy metals complexed by humic substances expose much less toxicity.

## Referenced Material

<sup>1</sup>Jackson, William R. *Humic Fulvic and Microbial Balance: Organic Soil Conditioning: An Agricultural Text and Reference Book*. Jackson Research Center, Colorado, 1993.

<sup>2</sup>Karr, Michael. *Oxidized Lignites and Extracts from Oxidized Lignites in Agriculture*, 2001.

<sup>3</sup>Mosley, Randy. *The Effects of Humates on Remediation of Hydrocarbon and Salt Contaminated Soils*. Internation Petroleum Environmental Conference, 1998.

<sup>4</sup>Holman, Hoi-Ying N., Karl Nieman, Darwin L. Sorensen, Charles D. Miller, Michael C. Martin, Thomas Borch, Wayne R. McKinney, Ronald C.Sims. *Catalysis of PAH Biodegradation by Humic Acid Shown in Synchrotron Infrared Studies*. Environmental Science and Technology, 2002.

<sup>5</sup>Van Stempvoort, D. R., Lesage, S., Molson, J. *The Use of Aqueous Humic Substances for In-Situ Remediation of Contaminated Aquifers*. The Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice, 135-154, 2005.

<sup>6</sup>Linnik, P. N., Vasilchuk, T. A. *Role of Humic Substances in the Complexation and Detoxification of Heavy Metals: Case Study of the Dnieper Reservoirs*. The Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice, 135-154, 2005.