

THE EFFECTS OF HUMATES ON REMEDICATION OF HYDROCARBON AND SALT CONTAMINATED SOILS

RANDY MOSLEY, MORRIS AND MOSLEY, INC.

This paper was prepared for the 5th International Petroleum Environmental Conference to be held in Albuquerque, New Mexico, October 20th – 23rd, 1998. This conference is sponsored by:

Univ. of Tulsa Dept. of Chemical Engineering
Gas Research Institute (GRI)
Bureau of Land Management
Argonne National Laboratory
The Natural Conservancy
Okla. Independent Petroleum Assoc. (OIPA)
Sarkeys Energy Center/Univ. of Okla.
Natl. Energy-Environment Law Institute

National Petroleum Technology Office of the DOE
U.S. EPA Office of Research and Development
New Mex. Energy, Minerals and Natural Resources
Interstate Oil and Gas Compact Comm. (IOGCC)
Oklahoma Energy Resources Board (OERB)
Railroad Commission of Texas
Tx. Independent Prod. & Royalty Owners Assoc.
Great Plains/Rocky Mtn. Haz Substance Research Ctr.

Any copies or other uses of this paper should contain conspicuous acknowledgment of where and by whom the paper is presented. Publication elsewhere after publication in Sponsor's journals is usually granted upon request of the Editor of the appropriate journal provided agreement to give proper credit is made. Technology is owned by Morris and Mosley, Inc. Patents have been applied for.

Abstract

Humates are humic substances found in nature throughout the entire food chain and are the components of soil humus. They function in a wide variety of natural processes; degradation of organic matter, chelation of metals, stimulation of microbial activity, and possess many soil amending characteristics. Additionally, they contain biological and pharmacological properties once they enter the food chain.

Two elements of humate, humic acid and fulvic acid, have been examined to determine their suitability as a remediator of oil and salt contaminated soils. Humic acid has been found to alter oils into fatty acids and sugars by chemical reactions and stimulation of microbial activities. Additionally, it is thought to act as a catalyst for soil enzymes in the degradation process. Fulvic acid has been found to be an extremely strong chelating agent with the ability to strip metal ions from the salt molecule. Both materials, in the presence of an adequate supply of nitrogen, stimulate indigenous microbial activity.

The usage of humates as a remediation method has many benefits over the usage of microbes; soil water wettability, need for less oxygen, ease of application and cost.

This paper presents laboratory data along with field results showing the applications of humates as an inexpensive and effective alternative to remediation of oilfield wastes.

References and Illustrations at end of paper.

Introduction

Oil and saltwater spillage are common occurrences in field operations. The sheer volume of oil and saltwater produced daily invites contamination of the soils. Leaks occur at the well head, in flow lines and tank batteries, and at a multitude of places along the fluid flow from well bore to market/disposal. Even though saltwater spills occur more often than oil, environmentalists have given oil spills the spotlight possibly because they are more readily visible. An environmental comparison of oil or salt as hazards is not a debatable issue in this paper. How the spill is acknowledged and remedied by the operator is a responsibility of the company.

Historically, operators responded to spills in a wide variety of ways ranging from doing nothing to removal of the contaminated soil and replacing with clean soil. The economics of the remediation as well as the pressure(s) of the surface owner, community, regulatory agency and their own environmental attitudes stimulated response activities of the operators. Shoveling sand or dirt over the spill to hide it has covered many oil spills. It is almost an attitude, "If the spill cannot be seen, it possesses no risk to the environment." Salt water historically was looked at with little regard to possible damage. How much saltwater has been released on the surface to flow down drainage areas. Evidence of past events can be seen as salt scars in older oil fields.

Even today, with attitudes changing on the environment, clean up is an arbitrary issue depending on the locale, the regulatory agency or agencies and enforcement policies. The level of remediation for "clean" in one area is not the same as another area; i.e. 5,000 ppm, 1,000 ppm, 100 ppm, etc. Additionally, the amount of damage or environmental impact is relative depending on land usage. In some areas, determining which regulatory agency is responsible can be frustrating. These preceding sentences create complex problems for the operator as well as his employees and/or service contractors. The operator must make decisions as to the activity level of remediation plan and implement those steps pursuant to the regulatory jurisdiction(s) he is working under. Due to the nature of the pollutants and soils, remediation plans must address differences in clean-up techniques. This further complicated the operator's problems.

In assessing the differing clean-up techniques, it is apparent cost, simplicity and natural processes have merits over other types. The humates seem to fit the criteria in all ways. This paper will present humate usage with oil and salt-water spills and compare it's differences with bacterial and mechanical means.

DEFINITIONS

Humus. The organic components of soil containing organic compounds such as humic acid, fulvic acid, DNA/RNA fragments and humin.

Humic Acid. A brown to black polymeric constituent of soils, lignite and peat containing aromatic and heterocyclic structures, carboxyl groups and nitrogen. This material is naturally formed from the decomposition of cellular substances and acts to decompose cell walls and gluing materials (hydrocarbons) in decaying plant life. The substance enters the food chain and is soluble in alkaline solutions ⁽¹⁾. (See Figure 1 – Molecular Characteristics of Humic Acid) ⁽²⁾.

Fulvic Acid. A light orange to brown constituent of soil humus. This natural material is formed from the decomposition of cellular material and acts as a natural chelator of minerals and metals in soils. The material enters the food chain and is soluble in acid solutions.

Humin. The non-soluble portions of soil humus which breaks down slowly by soil microbial activity and affects the soil by regulating its water holding capacity, its ion exchange rates and electrical conductivity, its pH and the soil crumble.

Humate. Technically, this term refers to the salts of humic acid. Generically and commercially, this term generally refers to the combined components (humic, fulvic and humin) along with its natural carrier (peat, coal, compost, etc.) Sometimes, humates are referred to as humic substances.

OIL CLEAN UP – Microbial Stimulation

Humates naturally contain available carbon and other organic stimulants as an energy source for microbes. With the addition of nitrogen, enhancements of indigenous microbial activity occur. This increased microbial activity then causes additional hydrocarbon bioremediation ⁽³⁾. Table 1 is titled Microbial Stimulation and demonstrates the effect of humates on microbial activity when added to contaminated soil.

MICROBIAL STIMULATION

Table 1

Microbial Activity: Mg. Formazan/ 10 g/ day

Time Days	Additive to Contaminated Soil			
	Control	1% Humate	3% Humate	5% Humate
0	210	150	160	150
14	275	800	500	625
28	280	725	650	675

The above data demonstrates that small amount of humate enhances microbial activity. As humate percentages increase, there is an increased activity of the microbes over the control. It can be reasoned from looking at the data, that there are limits to the amount humates will increase activity. In the tests observed, maximum activity occurred at 1% by weight. As percentages increased, activity fell.

Knauf's experiments did not report humic acid contents of the humates. Experiments performed by the author using Dr. Knauf's procedures examined humates with varying amount of humic acid. Assuming adequate nitrogen supplies in the soil, results from these tests indicated increasing microbial activity levels as humic acid concentrations increased. When humic acid concentrations exceeded 50%, activity levels became sporadic, alternating between high and low levels. At concentrations below 50%, activity levels remained relatively constant once stimulation had occurred.

Other questions came to mind during examination of microbial activity during the remediation process. Are the microbes performing the remediation of the hydrocarbons? Are the humates simply serving as a stimulant and not actively taking part in the remediation? These are logical question, and the following experiment was performed to answer these questions. A live healthy loam was taken from the backyard and split into two samples. Each sample was placed in a glass pie pan and contaminated with 10 W 30 motor oil to a Total Petroleum Hydrocarbon (TPH) concentration of 10,000 ppm. Sample 1 was then placed in a microwave oven for 20 minutes. The radiation from the microwave was sufficient to kill any bacteria/microbes present in the sample. Humate (1% by weight) was added to each sample and blended into the soil. Both samples were then placed in a protected outdoor area for 30 days. At the end of 30 days, TPH was taken from both samples.

Table 2. Microbe vs. Humate Remediation of Hydrocarbon

	Sample 1	Sample 2
	10,000 ppm TPH	10,000 ppm TPH
	Without microbes	With microbes
30 days	5,400 ppm	950 ppm

It is apparent the humates are playing a function in the remediation over and above the stimulation of the microbes. Upon examination of the test residues, high levels

of fatty acids and sugars were found. This indicates some type of chemical reactions and/or catalytic activity is occurring which fractionates the oils ⁽⁴⁾. By observing the above data, it can be assumed the humates are responsible for about half of the total remediation. More testing of these phenomena needs to be performed in the future to further define the mechanism(s) humates are using to fractionate the oils.

One other test was performed which had significance upon the microbes' place in remediation. A hole was dug to a depth of 18 inches, using post hold diggers in a sand loam. The hole was filled with humate. Samples of soil were taken at or slightly below surface elevation every six inches along the radius of a circle surrounding the hole. Each soil sample was analyzed for a microbe count to establish a population density pattern surrounding the hole. Initial microbe density was fairly uniform around the hole out to a distance of 6 feet. After 2 weeks, soil samples were again taken and comparison of microbe density patterns made. Population density increased dramatically near the humate, and dropped out to a distance of 3 to 4 feet radius. Beyond the 3 to 4 feet radius, population densities were equivalent to initial testing. The significance of these results has application in underground contamination. It appears the microbes will migrate to the humate. The increase of microbe population causes additional remediation. Further study will delineate this matter further.

Humates have demonstrated their ability to reduce fractions of hydrocarbons from the soils by direct chemical action, microbial stimulation and catalytic action. Humates, being concentrated organic acids common to soil humus, use natural processes to fractionate hydrocarbons into lesser fractions with the final results being sugars, fatty acids and amino acids; all of which act a plant nutrient.

Humate is extremely chemically reactive with soil hydrocarbons. In nature, these organic acids perform the function of breaking down the hard cellular wall and adhesive materials. These natural compounds are formed in nature from the inner liquids of a living cell. When the cell dies and is deprived of oxygen, these inner liquids alter into organic acids (humic and fulvic acids along with many others). Humate is a concentrated form of these acids. It cannot distinguish between a hydrocarbon of oil or a cellular structure within a plant. Upon contact, these acids begin the breakdown process.

Field and Lab Tests were performed using the following typical applications:

Table 3. Typical Hydrocarbon Application

1. Assess the hydrocarbon contamination (TPH) levels.
2. Apply humates at the following rates.

<u>TPH (ppm)</u>	<u>Humate (lb. / cu. M.)</u>
Below 15,000	17
15,000 to 60,000	25
Above 60,000	50

Optional additives depending on soil conditions.

<u>Additive</u>	<u>Usage</u>	<u>Quantity</u>
Nitrogen Fertilizer	Microbe energy source	2 lbs./ cu.M.
Organic Matter	Indigenous Microbes	2 lbs./cu.M.
Lime	Adjust pH	Amounts vary
Calcium Peroxide	Oxygen source	2 lbs./cu.M.
Water	Activator	Amounts vary

Example 1. A drilling pit containing inverted oil based mud was emptied and allowed to dry for several months. The operator desired to clean the bentonite clay lining of the pit. Lab samples were taken to measure Total Petroleum Hydrocarbon (TPH) using Environmental Protection Agency (EPA) Lab Method 418.1. Samples were treated with humate at 6% by weight, nitrogen fertilizer at 2 lbs./ton of soil, potting soil at 10% by weight and sufficient lime to adjust pH to 9. All additives were well mixed and dampened with deionized/distilled water. The samples were placed in a flat glass dish and placed in a sunny location outdoors. Samples were kept moist throughout the four weeks of the experiment.

Table 4. Remediation of Inverted Oil Based Mud in Bentonite

Results ⁽⁵⁾

Elapsed Time	Sample No.	TPH	Methodology
Initial	203	161,000	EPA 418.1
1 week	204	40,300	EPA 418.1
2 week	205	24,400	EPA 418.1
3 week	206	37,500	EPA 418.1
4 week	207	14,300	EPA 418.1

Example 2. A clay bottom pit contaminated with 38 API gravity crude oil was treated with 3% by weight humate, 2 lbs. nitrogen fertilizer/ton of soil, 5 lbs./ton potting soil and sufficient lime to adjust pH to alkali. Samples were tested according to the procedure described in Example 1.

Table 5. Remediation of Crude Oil in Clay Soil

Results ⁽⁵⁾

Elapsed Time	Sample No.	TPH	Methodology
Initial	368	148,600	EPA 418.1
1 week	368A	107,000	EPA 418.1
2 week	368B	94,900	EPA 418.1
4 week	368C	78,900	EPA 418.1
5 week	368D	68,800	EPA 418.1

The remediation in Example 1 indicates a 90% clean up within a period of 30 days. The cost of clean up for this fast a response time is prohibitive. Example 2 is more realistic concerning economics. Hydrocarbons have been reduced 50% in a 5-week period. For a reduction of 90%, it is estimated the time required will be 120 days. These

two examples point out the relationship between cost and time for remediation. Lower concentrations of humate work, but time to remediate is lengthened

Example 3. An underground storage tank at an abandoned site was removed. Upon removal, the fill soil surrounding the old tank was contaminated with gasoline. Lab tests found the contamination to be between 3,500 and 5,000 ppm TPH. The soil was primarily clay with a pH of 7.9. A treatment plan consisting of one- percent humate, 2-lbs./yd. nitrogen fertilizer and 2 lbs./yd. potting soil was implemented. There were approximately 250 yards of contaminated soil. The soil was removed from the hole and stockpiled nearby. The bottom of the hole was then treated with humate, fertilizer, and potting soil. As each side of the hole was collapsed into the hole, equal amounts of treatment were tilled into the soil. After all four sides were collapsed, the stockpiled soil was replaced into the hole in 6 to 8 inch layers. Each layer was then treated with an equal portion of treatment. After all contaminated soil had been placed into the hole and treated, the site was left alone. The target for closure by the local regulatory agency was below 100 ppm TPH. Below are the lab readings from this job.

Table 6. In Situ Remediation of Underground Storage Tank Leak. ⁽¹⁵⁾

Date	TPH (ppm)	Methodology	Notes
Feb. 6	3,500	EPA 418.1	Initial
Mar.10	180	EPA 418.1	
Apr. 4	> 50	EPA 418.1	

Water Repellent Soils. ⁽¹⁶⁾

Soils contaminated with hydrocarbons exhibit a waxy appearance and resist wetting when dry. In Alberta, water repellency caused by hydrocarbon contamination is often long-lasting. One study of soil 15 years after a hydrocarbon spill found only partial restoration of its original state of wettability. This is a common characteristic of soils cleaned of hydrocarbons by microbial means, whether indigenous or commercial. Humate, by its very nature, water wets the soil. A recent article in the Carolina Greenskeeper ⁽¹⁷⁾ indicated humate was “the single most effective material to eliminate dry spot on golf greens”. In terms of remediation, this is a significant finding and a plus for humates over microbes in hydrocarbon remediation.

SALT REMEDIATION

As the United States oil industry matures and oil production declines, larger volumes of salt water are produced on a daily basis. It is inevitable ever increasing numbers of salt-water spills will occur. Salt-water spills are not new, as evidenced by salt scalds (kill areas with sterile soil) visible in older field areas. Some of the “kill” areas date back 50 to 70 years. With the number and ages of these salt scalds, it is apparent nature has limited mechanisms to remediate these spills.

Many soils in oil producing areas contain large amounts of clays, which inherently have low percolation rates. Additionally, many of these soils are generally “worn out” from farming practices, both past and present, resulting in soils containing low amounts of soil humus. Humus content affects soil crumble; hence, soil percolation rate. Soils with high humus contents are permeable allowing water to penetrate below root level. In high clay, low humus soils, the upper layer is generally broken up by root growth. Rainfall soaks into the soil to a depth determined by root growth. Below this depth, soil permeability is greatly reduced; thus water tends to pool at root depth.

No adverse occurrences are observed in a high clay soil until a saltwater spill occurs. The salt water penetrates the soil and, in areas with low humus content, pools at root depth. Needless to say, plant life is destroyed. Many leaks are not found until someone notices dead plant life. At this point nature is in a dilemma; her mechanism to rid salt pollution by drainage to below root level is blocked by tight clays. Additional rainfall may push the salt to lower topographic areas, but ultimately this pool of salt water will settle into a low area. At the final migration point a salt scald is created. Salt water is denser than fresh water; thus rainfall cannot float the salt contamination from its pooled position.

Another problem compounds nature’s dilemma. Soil microbes are vital to soil health functioning to convert organic matter and soil materials into plant nutrient. Compounds such as NaCl, CaCl, MgCl, etc., typical to salt waters are toxic to the microbes. The chief toxic agent is sodium (Na). Microbes can live, though not healthy, in many salts, but NaCl is lethal. At this point, nature has no way to remove the contaminant, nor does it have the ability to provide nutrient to any plant that can tolerate the salts present. This constitutes a double deathblow to nature for remediation.

SALT REMEDIATION THEORY

Two objectives necessary for remediation will be demonstrated by these tests: break down of salt in-situ and re-establishment of microbial populations. The salt break down will be indicated by sodium reduction. The microbial re-population will be shown by the soil’s ability to sustain plant growth after remediation.

Salt is composed of a metal ion bonded with chlorine. Depending on soil moisture, salt will occur either in solution or as a crystal within the soil. If chelation techniques can capture the metal ions, releasing the chlorine, the salt molecule will be broken. It is generally recognized organic acids common to soil humus are excellent chelating agents ⁽⁶⁾. Literary research has shown humic acid to be one of the major organic acids present in soil humus ⁽⁷⁾. Since the typical soil affected by the salt is low in soil humus, it is logical to add concentrated humic acids to the soil for chelating of the metal ions. Humate is a concentrated form of humic acid. Humate is an excellent source of carbonaceous material in a favorable state of partial decomposition. Its state of decomposition is reflected by the humic acid content; thus, the higher the humic acid content, the higher the state of decomposition. Logic would then indicate higher levels of humic acid chelate greater levels of salt. This research indicates the logic holds true, but in dealing with a natural ecosystem each part of the system effects the whole. Salt break down is the objective, but microbial activity and nutrient supply must be maintained in order to restore plant life.

Early research ⁽³⁾ indicates the humates stimulate microbial activity. Aerobic microbial activity within a soil requires an energy source for the microorganisms. Humate, in combination with molecular oxygen provides this energy. Additionally nitrogen within the humate is used to build the bodies of microbes and multiply to efficiently decompose organic wastes aerobically. Testing indicates microbial stimulation from humate for concentrations of humic acid up to 50 %. At concentrations above 50 % humic acid, microbial activity becomes sporadic cycling between high and low levels.

Once the humic acids have reduced the salt levels within the soil, microbial populations can be re-established. This is a relatively simple matter of providing the contaminated area with organic matter rich in native microbes. Organic matter such as cottonseed hull, rice hull, potting soil or thatch is rich in microbes, readily available and inexpensive in rural area. Added nitrogen from fertilizers can assist.

Example 1. Salt Clean Up ⁽⁸⁾

A historical contaminated site was selected for the test. The site was relatively flat to reduce the effects of possible drainage and/or leaching effects thereof. Samples were taken for lab testing at several points across the spill area. Each sample site was sampled from the surface, four inches of depth and 8 inches of depth. All samples sites were blended together into a composite and submitted to the lab for analysis ⁽⁹⁾.

Initially, the site was tilled with a tractor and disk to a depth of 6 inches. Humate was applied at the rate of 40 pounds per 1000 square feet of surface area. Five pounds of potting soil per 1000 square feet was spread over the site to provide organic matter to the system. The soil was then tilled with a garden tiller to a depth of approximately four inches. The site was left undisturbed for a period of eight weeks. At the end of eight weeks, the soil was then disk again. The test was terminated at the end of 16 weeks.

Additional samples, taken from marked sites initially, at eight days and at sixteen weeks. Outside air temperatures ranged from 28 to 70 degrees F., with soil temperatures ranging from 40 to 50 degrees F. Rainfall was normal for the area during the test period. Little erosion, if any, was observed from the site.

Table 7. Lab Data from Salt Test

Component	Value			Unit
	Initial	8 day	16 week	
pH	7.1	6.4	6.7	
Electrical Conductivity	62.7	54.6	43.4	Mmho./cm.
Sodium	15,570	9,472	911	ppm
Potassium	746	610	67	ppm
Calcium	8,060	5,722	5,148	ppm
Magnesium	1,983	1,383	1,132	ppm
Na Absorb. Ration (SAR)	40.2	29.1	3.0	

Analysis of the above data indicated a 94% reduction in sodium, a 91% reduction in Potassium and a drop in the sodium absorption ratio from 40.2 to 3.0. Of significant interest was the 40 % sodium drop at the eight-day test. Sodium absorption ratios of 12

or below generally indicate the ability of the soil to sustain salt tolerant grasses. A plot of sodium absorption ratio against time indicated the SAR level of 12 was reached at 10 weeks.

Example 2. Salt Remediation with Sustained Plant Growth.

The salt remediation test performed above did not perform any type of restoration of plant growth on remediated soils. Salt reduction is one matter; sustained plant growth on these soils is another matter. Historically, magnesium and calcium sulfates have been the preferred treatments. Their primary method of operation is the alternation of the electrostatic conductivity (EC) of the soil thereby increasing chemical reactivity. Many of these treatments sterilize the soil. One of the objectives in using the humates as a remediation product is its ability to stimulate plant life. Table 8 lists the pertinent benefits of humates in sustaining plant growth.

Table 8. Benefits of Humates ^{(10) (11) (12)}

Biological Benefits – Plant Stimulation

- Stimulates Plant Enzymes.
- Acts as an organic catalyst.
- Stimulates Growth and proliferation of desirable soil microorganisms, algae and yeast.
- Increases root respiration and formation.
- Increases vitamin content of plants.
- Increases germination of seed and viability.
- Stimulates plant growth by accelerating cell division.
- Increases the yield of dry matter.

Chemical Benefits – Chemically changes the fixation properties of the soil

- Increases buffering properties of soil.
- Chelates metal ions under alkaline conditions
- Rich in both organic and mineral substances essential to plant growth.
- Retains water-soluble inorganic fertilizers in the root zone and releases to plants when needed.
- Possesses extremely high ion-exchange capacity.
- Promotes the conversion of a number of elements into forms available to plants.

Physical Benefits – Modifies the soil.

- Makes soil more friable or crumbly.
- Improves soil workability.
- Increases aeration of soil.
- Increases water holding capacity.
- Improves seedbeds.
- Reduces soil erosion.

The site selected for the test was down grade from a tank battery that served as a feed for a waterflood. The waterflood had been in effect for approximately 20 years and flow lines and connections had leaked many times on the area. Although a firewall was constructed around the tanks, flow lines and manifolds outside of the firewall contributed

heavily to the contaminated soil. The site covered 10,250 square feet (approximately 0.25 acres). The area was relatively flat with no plant life. The soil was a Keeter Sandy Loam (See Figure 2 – Keeter Sandy Loam), crusted and had crystalline salt observable on the surface at a few locations.

Treatment consisted of disking the site to break up the surface crust. Humate was added at the rate of 40 lbs./1000 square feet (1 ton/acre). Additives consisted of 21-0-0 fertilizer at the rate of 175 lbs./acre and dolomitic sand at a rate of 600 lbs./acre. All material was broadcast, disk to a depth of 6 inches and left to remediate.

Table 9 -Lab Data ⁽¹⁴⁾

Item	Initial	45 Day	90 Day	Units	% Change <>=increase
pH	7.6	7.3	7.7		
Sodium	1052	1664	449	ppm	57 %
Magnesium	248	358	225	ppm	9 %
Calcium	3232	3749	3259	ppm	0 %
Potassium	107	119	141	ppm	<35 %>
Soluble Salts	1696	3097	748	ppm	56 %
Cation Exchange	24	30	21	meg/100gm	
Organic Matter	0.8	0.7	1.0	%	

Sodium levels did not drop as rapidly in this test as in the previous. Probably the lack of good topsoil affected the cation exchange rates. It should be noted during the 45-day tests the salt levels increased. Many times salts are locked up in soil clays and not recorded in leaching tests for initial amounts. When the humates are added, they affect the soil crumble and tend to break up the clays. As the clays break down they release additional salts into the system. This has been observed on a number of jobs.

In order to determine the total effectiveness of the humates as a remediation tool for salt, grass was planted on the remediated soils to determine plant health and sustainability. If the plants grow for an extended time period, then the microbe population is healthy and providing nutrient to the plants. Table 10 – Grass Test Data shows in every case the protein values on the grasses grown on the humate treated salt contaminated soil to be superior to the control. When one considers the control grasses were grown on non-contaminated soil, the results are even more impressive.

Table 10 – Grass Test Data, Salt Remediated Soils.

Grass Protein Content	Crude Protein %			Digestible Protein %		
	Control	Test	% Incr.	Control	Test	% Incr.
Indian Grass	14.8	17.6	18.9	10.4	12.2	17.3
Bermuda	13.4	15.7	17.2	9.1	12.3	35.2
Side Oats	10.6	12.7	19.8	7.4	8.5	14.9
Little Bluestem	10.1	17.8	70.3	7.1	11.9	67.9
Plains Bluestem	8.7	18.1	108.0	5.8	12.4	113.8
Switch Grass	12.7	16.9	33.9	8.8	11.9	78.4

Figure 1. Hypothetical structure of a segment of humic acid. An actual humic acid molecule should have a formula weight of more than 10,000. The formula for this segment is $C_{130}H_{140}O_{64}N_9P$, giving it a formula weight of 2,881, so it represents less than one-quarter of a typical molecule.⁽²⁾

Soil – Keeter Sandy Loam ⁽¹³⁾

This soil is deep and gently sloping on convex ridgetops, mostly in old cultivated fields. It has lost most of its surface layer as a result of erosion.

Acid	Surface Soil	Surface		
		3 inches	<u>Fine Sandy Loam</u>	Brown Neutral pH
		11 inches	<u>Sand Clay</u>	Reddish Brown Med.
	Sub Soil	18 inches	<u>Sandy Clay</u>	Yellowish Red
		38 inches	<u>Sandy Clay Loam</u>	Yellowish Red
	Underlying Material	55 inches	<u>Fractured Sandstone</u>	Pale Brown

Typical Cross Section - Keeter Sandy Loam – Figure 2
Keeter Sandy Loam

This soil is well drained. Permeability is moderately slow and the available water capacity is moderate. Runoff is rapid, and the hazards of water erosion and soil blowing are severe in unprotected areas. This soil remains relatively dry because most of the surface layer has been removed by erosion and the rapid runoff allows little moisture to enter the blocky subsoil. The root zone is moderately deep, but roots have difficulty penetrating the upper part of the subsoil. Because past erosion has reduced the fertility level and water holding capacity, it is now used mainly as unimproved rangeland

This soil is poorly suited to pasture. Seedbeds are difficult to prepare because of the eroded surface layer. After rains, a thick surface crust forms as the soil dries. This crust impedes the emergence of seedlings. During extended periods of drought, plants growing on the more severely eroded soil commonly die. Most of the soil is poorly suited to use as cropland because of eroded areas, low fertility and low levels of soil moisture. Changes in moisture content cause moderate shrinking and swelling

REFERENCES CITED

1. Stevenson, F.J., Humus Chemistry: Genesis, Composition, Reactions. New York, Wiley-Interscience, (1982).
2. Novak, Jeff, University of Georgia, and Pettit, Robert, Texas A&M University, "The Role of Humates in the Oilfield", presented at the First Panhandle Oil and Gas Show, Guymon, Oklahoma, (October 1994).
3. Knauf, T. A., "The Effect of Menefee Humate on Hydrocarbon Contaminated Soils", Menefee Mining Corporation, Dallas, Texas, (January, 1993)
4. Malcolm, R. E. and Vaughan, D., "Comparative Effects of Soil Organic Matter Fractions on Microbial Activity", *Plant Soil*, **51**: 65-72, (1979).
5. O'Donnell, Linda, "Research Project – National Oil Co. (Pemex Sample), Tucan Water Works, Norman, Oklahoma (May, 1996).
6. Chen, Y. and Stevenson, F. J., "Soil Organic Matter Interaction With Trace Elements", In Y. Avnimelech (ed.), *The Role of Organic Matter in Modern Agriculture*, Martinus Nijhoff Publ., Pg. 73-116, Dordrecht, (1986).
7. Bottomley, W. B., "The Effect of Organic Matter on the Growth of Various Plants in Culture Solutions", *Ann. Bot.*, London, **34**: 353-365, (1920).
8. Stallworth, W. R., Experiment titled "Remediation of Salt Damaged Soil" sponsored by North Texas Oil and Gas Association, Wichita Falls, Texas, (June 1995).
9. Hickey, M., Salinity Analysis Worksheet, Plains Soil, Plant and Water Testing Laboratory, Lubbock, Texas, (Dec. 1994, Jan. 1995, and May 1995).
10. Senn, T. L. and Kingman, A. R., "A Review of Humus and Humic Acids", Clemson University, Department of Horticulture, Research Series No. **145**, (March 1972).
11. Freeman, P.G., "The Use of Lignite Products as Plant Growth Stimulants", Technology and Use of Lignite, I. C. Bureau of Mines Information Circular, **8471** Pg. 150-153, 160, 162, and 164, (1969)
12. Burdick, E. M., "Commercial Humates for Agriculture and the Fertilizer Industry", *Economic Botany*, Vol. **19**, No. **2**, Pg. 152-156, (1965).
13. Soil Conservation Service, Soil Survey of Wise County, Texas, U. S. Department of Agriculture, Pg. 34-35, (May 1989).
14. Rogers, Jerry, Soil Test Report, Agricultural Division Laboratory, Samuel Roberts Nobel Foundation, Ardmore, Oklahoma, (Jan 1997).
15. McClaine, M., "TPH of Springtown Site", Talum Labs, Fort Worth, Texas (March, April and May, 1998).
16. Yeung, P., "A Method for Measuring Water Repellent Soil", Proceedings of the 27th Alberta Soil Science Workshop, Vegreville, Alberta, (Feb. 20, 1990).
17. Federal, C., "Humates – The Answer to Eliminate Isolated Dry Spots on Greens", Carolina Greenskeeper, Vol. **12**, Pg. 31-33, (Feb. 1994).