Humate-Induced Remediation of Petroleum Contaminated Surface Soils - Annual Report

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Research Category: Bioremediation of Oil Spills

Description:

Objectives of the Research Project:

The objectives of the research project were: (1) To examine the long- term sorption-desorption kinetics of crude oil with humates; (2) to assess the extent of biodegradation of crude oil in petroleum-contaminated surface soils amended with humate by monitoring parent compound loss; and (3) to examine the efficacy of humate-induced remediation of fresh petroleum- contaminated soil versus weathered petroleum-contaminated soil.

Progress Summary/ Accomplishments:

An enduring problem confronting independent and small petroleum producers and operators is surface soil contamination by crude oil and refined petroleum products. Contamination may occur through chronic spilling of small volumes during typical operation and transfer processes, or through an accidental spill. Unlike larger spills, these smaller spills, due to the limited amount of petroleum, may not be feasible to clean up using current remediation methods. In these situations, remediation strategies such as removal and disposal, soil cleansing treatments, or advanced techniques such as pump and treat methods, or inoculation with petroleum-degrading microbes, may be too expensive, too technologically advanced, or not logistically feasible.

A real need exists for a low-cost and simple remediation method. In order to handle, in an expedient and effective manner, the numerous small, contaminated sites that may be present, the remediation method has to be technologically simple, require minimal infrastructure for implementation and operation, be easy to implement in unusual or remote sites, and require little maintenance once implemented. Moreover, it must be environmentally benign, as well as contribute to the soil quality so that vegetation can be restored to prevent erosion and so that the site can be returned to its original condition after drilling operations cease.

One such potential remediation method that meets these criteria is the application of humates to petroleum-contaminated soils. In a geologic sense, humates are highly carbonaceous rocks (e.g., weathered mudstone or coal) rich in humic and fulvic acids and originating from terrestrial, marine, or lacustrine organic matter. They are very resistant to microbial degradation.

Results of 13C NMR, TMAH thermochemolysis, stable carbon isotope, and elemental analyses unequivocally showed that humates used in our experiments originated from terrestrial plant material comprised of n- alkane fatty acids and methoxy benzene structures.

Based on preliminary petroleum sorption capacity measurements of six humates available at that time as well as their TOC contents, an Australian humate was chosen for microcosm and advanced sorption studies. After that, the ability of the selected Australian humate to enhance the remediation of petroleum-contaminated soils, either by adsorption processes, biodegradation stimulation, or both, was examined.

Initial sorption data were obtained using Rock-Eval pyrolysis and pyrolysis- GC methods. In these measurements, freeze-dried humate and humate "as is" were saturated with various amounts of crude oil followed by exhaustive Soxhlet extraction using dichloromethane. It was revealed by Rock-Eval pyrolysis method that the highest saturation of freeze-dried humate by crude oil (245 mg of petroleum hydrocarbons per one gram of freeze-dried humate) occurs when 1:1 (wt/wt) or greater ratio of crude oil to humate was used. This sorption amount of crude oil to humate is measured after the Soxhlet extraction process, thus the adsorbed crude oil is tightly bound by the humate. In case of "as is" humate, its sorption capacity was about 6 times less than that of the freeze-dried humate. This is thought to be a kinetic issue rather than a thermodynamic issue; in the "as is" humate samples, water coating the humate surface has to first be displaced by the crude oil prior to crude oil adsorption. Pyrolysis-GC results also demonstrate the extensive sorption of petroleum hydrocarbons by freeze- dried humate. Since the crude oil used contains only n-alkanes and a negligible amount of n-alkenes, while humate includes both of them, the n- alkane to n-alkene ratio serves as a measure of crude oil's n-alkanes remaining strongly sorbed to the humate after extensive solvent extraction. It was found that the ratios of n-alkanes to n-alkenes in C17-C24 range noticeably increase (21% on average) for humate contaminated with crude oil compared to uncontaminated humate.

The measurements for the second sorption experiment were performed using gravimetric methods. The total amount of sorbed oil was calculated as a difference between final loss for humate contaminated with oil and final loss for humate itself after complete dichloromethane extraction. Results of this experiment are in accordance with the results of the above- mentioned sorption experiment, also demonstrating strong sorption capacity of freeze-dried humate and less efficient sorption by "as is" humate.

Biodegradation and sorption processes were studied using microcosms. Pristine soil samples contaminated with fresh crude oil (15% by weight) represented a new petroleum

spill, while contaminated field soil samples represented soils with weathered petroleum from the same source as fresh crude, and contaminated field soil samples with additions of fresh crude oil represented soils with weathered petroleum after a recent, additional spill. Humate was added to four of total eight microcosms in amount of 10% by weight. At each sampling time (five in total during 7-month period), 16 microcosms were sacrificed, dried with sodium sulfate and Soxhlet extracted for 24 hours using a 1:1 dichloromethane-methanol mixture. To assess the extent of biodegradation, n-C17/pristane and n-C18/phytane ratios, reliable biodegradation parameters for moderately biodegraded oils, were used. Microcosm experiments demonstrated that humate significantly increases biodegradation of weathered-petroleum contaminated soil, as well as soil contaminated with fresh petroleum, or a combination of both. In weathered- petroleum contaminated soils, the presence of humates dramatically increased biodegradation rates. When fresh petroleum was added to this weathered-petroleum contaminated soil, the presence of humates increase the biodegradation rate by factors of 2 to 3 fold. The presence of humate in a pristine soil contaminated with fresh petroleum did facilitate biodegradation of n-alkanes. In this case, humate appeared to stimulate the growth of petroleum-degrading microbial consortia that was not intrinsically present (at least by 330 days) in a fresh petroleum- contaminated pristine soil without humate. Inoculating this pristine soil with a petroleum-degradating microbial culture, in the presence of humates, not only facilitates biodegradation, but also assists in the adsorptive removal of higher n-alkanes ranging from 24 to 32 carbon atoms. In the absence of humates, the microbes degrade these higher chain n-alkanes at much slower rate.

Results of sorption and microcosm experiments showed that moisture content noticeably decreased the humate's ability to adsorb petroleum hydrocarbons. However, microcosm results demonstrated that such ability was a kinetic issue rather than a thermodynamic issue. Thus, humates with moisture adsorbed petroleum hydrocarbons as extensively as dried humates, but over a time period of several weeks to months. Moreover, results from pyrolysis- GC and pyrolysis-GC-MS experiments demonstrate that the strong sorption of n-alkanes into humates increases over time. Worthy of note, however, is the observation that over a long period of time, approximately 250 days or more, humate eventually allow petroleum hydrocarbons (e.g., long chain n- alkanes) to become bioavailable. The exact mechanism by which humates facilitates biodegradation is presently unknown. Possible hypotheses are that humates provide nutrients, adsorb toxic or inhibitory compounds, or provide favorable surfaces for microbial growth.

Thus, we achieved our research goals by demonstrating that humate enhances the remediation of surface soil contaminated with crude oil through the combined processes of hydrocarbon sorption and enhanced biodegradation. The indisputable advantages of humate-induced remediation approach are based on the unique properties of humates which are: (1) a component of the natural organic carbon cycle, i.e., they are a naturally produced material; (2) environmentally benign; (3) contain additives that improve soil characteristics and encourage and foster vegetation growth; and (4) contain substances that initiate and enhance intrinsic bioremediation by stimulating indigenous microbial growth.

Economic analyses show that humate-induced bioremediation is 1.5-2.3 times cheaper compared to alternative ex-situ remediation techniques even without taking into account more expensive operating cost of the latter.

Publications/ Presentations:

1. Nanny, M.A.; Stearns, C.; Chen, L.; Andrusevich, V.E.; Philp, R.P. (2001) "Humate-Induced Remediation of Petroleum Contaminated Surface Soils" in Environmental Issues and Solutions in Petroleum Exploration, Production and Refining. Abstracts of The 8th International Petroleum Environmental Conference, Houston, TX, November 6-9, 2001, p. 122.

2. Andrus, V.E.; Nanny, M.A.; Philp, R.P. (2002) "Humate-enhanced remediation of crude oil-contaminated surface soils: Adsorption studies and microcosm results". Extended Abstracts of The 225th American Chemical Society Meeting, New Orleans, LA, March 2003 (accepted).

3. Nanny, M.A.; Andrus, V.E., and Philp, R.P. (2003) "Chemical Characterization of Humate" in progress, to be submitted to Org. Geochem.

4. Nanny, M.A.; Andrus, V.E., and Philp, R.P. (2003) "Petroleum Sorption Capacity of Humates: A Potential Organic Geomaterial for Remediation" in progress, to be submitted to Envir. Sci. Technol.

5. Nanny, M.A.; Andrus, V.E., and Philp, R.P. (2003) "Humate-enhanced Remediation of Petroleum Contaminated Surface Soils: Combined Sorption and Biodegradation Processes" in progress, to be submitted to Envir. Sci. Technol.

Future activities:

The main research goals of our second-year IPEC funding study (2003 - 2004) "A Continuation: Humate-Induced Remediation of Petroleum Contaminated Surface Soils" are: 1) to determine if hydrocarbons strongly-bound to humates are bioavailable, 2) to determine if humate-induced remediation of diesel fuel and gasoline contaminated soils is a viable and feasible remediation strategy, and 3) to transfer knowledge gained from laboratory tests to pilot-scale ex-situ experiments testing the effectiveness of humate-induced remediation for soils contaminated with crude oil, diesel fuel, and gasoline.

In that study we will address critical questions discovered to be important based upon our first-year IPEC-funded research. Biodegradation and bioavailability of hydrocarbons strongly-bound to humate must be quantitatively measured in order to determine if these strongly-bound hydrocarbons are still an environmental concern and if they can truly be biodegraded. Second, the effectiveness of humate remediation of soils contaminated with hydrocarbon products such as gasoline (including MTBE - gasoline oxygenated additive) and diesel fuel must be assessed. Finally, we will transfer knowledge gained from laboratory experiments to the field.

Supplemental Keywords:

soil, crude oil, petroleum hydrocarbons, sorption, bioavailability, bioremediation, cost benefit, environmental chemistry.