# ANAEROBIC BIODEGRADATION OF PESTICIDES AND TNT: SITE EMERGING TECHNOLOGY DEMONSTRATION

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#### INTRODUCTION

- J. R. Simplot, Inc. is a multiconglomerate whose initial interest was in the production of potatoes in the Pacific Northwest. This has lead them into the agricultural chemical business including pesticides. Dinoseb (a carcinogenic herbicide used to kill the foliage of potato plants allowing for easer harvesting) was used by them and after its ban in the U.S., J. R. Simplot realized the only acceptable way to dispose of dinoseb contaminated soils was to incinerate them at considerable cost. Thus J.R.Simplot became interested in developing a disposal solution that would be less cost prohibitive and as effective as incineration.
- J. R. Simplot submitted a proposal and was accepted into the SITE Emerging Technology Program to optimize the anaerobic biodegradation of nitroaeromatics (dinoseb) contaminated soils with the addition of water, pH buffers, and potato waste as a source of starch. This work ultimately resulted in a good understanding of the biological and chemical process of destruction (optimum conditions of 35 and 37 degrees C, and pH of approximately 7, leads to destruction in 14 days) of both dinoseb and TNT and in several peer reviewed publications (1-7).

## **METHODOLOGY**

The process was then tested by the SITE Demonstration Program at a small field scale at much less than optimum conditions at Ellensburg, Washington in the cold summer of 1993 on soil contaminated with an average of 27.3 milligrams of dinoseb per kilogram (mg/kg) of soil. The process was also evaluated at the previously functioning Weldon Spring Ordnance Works near St. Louis in the even colder fall/winter of 1993/94 on soil contaminated with an average of 1510 mg of TNT/kg of soil.

Sixty one samples were randomly collected from the excavated one half inch screened contaminated soil and analyzed for dinoseb by HPLC using a method developed for this evaluation. The 39 cubic yards of contaminated soil was moved into a truck-trailer sized reactor while 2-5 percent of the weight was added as potato waste. Dinoseb-free water was added at a 1 L/ kg of contaminated soil ratio. The pH was buffered to about 7.1 and an inoculum of previously treated soil (5 gallon bucket) was added. Two mixers were used with the dinoseb bioreactor to keep the soils and liquids mixed but not to add oxygen. The process is initiated by allowing the aerobic organisms to consume the potato waste and thus utilize the oxygen. The anaerobic conditions that result allow the anaerobic organisms to degrade the dinoseb and any byproducts. A negative control of excavated, screened, and dinoseb-contained soil was kept at the site and analyzed before and after the testing for dinoseb. After treatment, 41 randomly generated areas of the bioreactor were sampled, and the sediments, and eluent from these samples were analyzed for dinoseb and any known byproducts along with a toxicity screen which showed the presence of other pesticides.

The TNT contaminated soils were treated in the same manner except the soils had a higher clay count and thus the mixers were ineffective. To obtain the soil/water interface, the bioreactor was therefore lanced every 7-14 days. As the ambient temperature dropped significantly at this site, heaters were added to keep the bioreactor from freezing. TNT levels were determined by EPA method 8330 at time zero, 5 months and 9 months. Toxicity tests were analyzed on time zero and at 5 months.

#### RESULTS

No dinoseb was detected in any samples after only 23 days of remediation even though the temperature was as low as 18 degrees C. The concentrations of nitroaniline, parathion, malathion, and 4.4'-DDT were also found to be decreased in this process in just 23 days.

The winter conditions in St. Louis threatened to freeze the bioreactor so heaters were added to bring the temperature up from 4 degrees C. Sampling at roughly 5 months showed a 95 percent reduction in the concentration of TNT, and significant reductions in toxicity were measured by root elongation, early seedlings, and earthworm reproduction tests. After sitting for another 4 months the TNT contamination in the soil was reduced by 99.4 (95 % C.I. is 98.3-99.9) percent.

#### CONCLUSIONS

This process has shown substantial removal of dinoseb, TNT, their known byproducts, and toxicity in general (as measured by several methods) at costs that are significantly less than soil incineration even at non-optimized conditions. Testing has also shown that nitroaniline, parathion, Malathion, and 4,4'-DDT levels can also be reduced using this technology. Although the soil is excavated and thus disrupted it is left in better condition with this process than with incineration. Thus it appears to be a viable alternative to soil incineration for these contaminants. More complete information on these demonstrations can be found in their Innovative Technology Evaluation Reports (8, 9) and Technology Evaluation Reports (10, 11).

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# IRON ENHANCED ABIOTIC DEGRADATION OF CHLORINATED HYDROCARBONS

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#### INTRODUCTION

Since the 1970s, several researchers have investigated the ability of certain zero-valent metals or alloys to enhance the degradation of halogenated organic compounds in contaminated water. Iron, zinc, aluminum, brass, copper, and stainless steel have been studied at various times with varying degrees of success. Gillham and O'Hannesin have recently made a literature review and conducted tests on 14 halogenated aliphatic compounds using zero-valent iron as an enhancing agent (1). The results showed that rapid dehalogenation occurred on all of the compounds tested except dichloromethane. Based on these test results, EnviroMetal Technologies, Inc. proposed to remediate groundwater contaminated with chlorinated organic compounds using this technology.

The EPA Superfund Innovative Technology Evaluation (SITE) program has accepted this technology for demonstration. This demonstration project will include two processes, above ground reactor and in situ permeable wall. The demonstration on the above ground reactor is being conducted at a site in Wayne, New Jersey. The main contaminants at this site are tetrachloroethene (PCE) and trichloroethene (TCE). The in situ permeable wall process will be conducted at a site in upstate New York. This site is a shallow sand aquifer containing TCE, dichloroethenes, and 1,1,1-trichloroethane.

#### **METHODOLOGY**

Before the site demonstration, laboratory experiments were conducted on the contaminated groundwater to evaluate the efficiency of the process, under simulate site conditions. The procedures of this and the two demonstration processes are described below.

Column tests were undertaken in the laboratory to simulate the dynamic conditions of groundwater. The columns were constructed of plexiglass with a length of 50 cm and an internal diameter of 6.5 cm. Seven sampling ports were positioned at distances of 2.5, 5, 10, 15, 20, 30, 40 and 50 cm from the inlet end. The columns also allowed for collection of samples from the influent and effluent solutions. A total of three column experiments were set up, one control and two reactive columns. The control column was packed with 100% silica sand. One reactive column was packed with a mixture of 50% (by weight) granular iron and 50% (by weight) silica sand, while the other reactive column was packed with 100% granular iron. The mass of iron to volume of solution ratio for the 50% iron column was 3.4 g : 1 ml and for the 100% iron column was 8 g : 1 ml.

The above ground reactor was constructed of fiberglass with a height of 9 feet and an internal diameter of 8 feet. The reactor was packed from the bottom to the top with: 6" of pea gravel, 66" of granular iron, 24" of groundwater and 12" of air. The total weight of iron was 18003 kg with a porosity of about 0.4. The pore volume was calculated to be about 3400 L. Five sampling ports were positioned at distances of 21, 36, 48, 66 and 84 inches from the inlet end (top of the water level). The influent and effluent solutions were also collected. During the demonstration, groundwater was extracted from the site by passive recovery techniques, using tiles placed in the bottom of collection trenches (about 14 ft below the ground surface).