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FIELD DEMONSTRATION OF A SURFACTANT-ENHANCED SOIL SLURRY BIOREACTOR TECHNOLOGY FOR THE REMEDIATION OF EXPLOSIVES-CONTAMINATED SOIL

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Introduction

Biological treatment of explosives-contaminated soil is currently of interest to the U.S. Department of Defense. Composting is a fully implemented technology capable of removing explosives from soil cost-effectively. The biological and chemical reactions occurring during composting remove 2,4,6-trinitrotoluene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), leaving no intermediates. Over the past several years, various groups have examined the use of soil slurry reactors to degrade explosives in soil. Several years of laboratory study have culminated in a pilot demonstration at the Joliet Army Ammunition Plant (JAAP), Joliet, Illinois. Laboratory and field studies (Manning et al., 1995) have demonstrated that TNT, HMX, and RDX can be biologically degraded with molasses as a cosubstrate. Waterways Experiment Station has conducted experiments examining the impact of surfactants on enhancing the degradation of explosives in a slurry reactor. These studies have been encouraging in batch reactor situations. The laboratory studies examined many different surfactants and determined that polysorbate 80 (Tween 80) is the most cost-effective. In addition, Tween 80 can be purchased commercially as a food-grade compound, eliminating regulatory concerns. The laboratory studies also investigated the different concentrations of surfactant in the reactor. The operating conditions were periods of aerobic conditions (with measurable dissolved oxygen), followed by periods of anoxic conditions (with no measurable dissolved oxygen but significant concentrations of nitrate, nitrite, and sulfate). The laboratory studies led to the development of a pilot-scale system to investigate the performance of soil slurry reactors with surfactant enhancement under field conditions. The pilot study at JAAP ran for almost six months. (This was an extension of a previous pilot study conducted at JAAP.) For this work, soil containing TNT, HMX, and RDX in varying concentrations was removed from an area at JAAP designated as Group 61.

System Design

The pilot system is shown in Figure 1. Soil was excavated from Group 61 in areas of TNT contamination. The excavated soil had TNT concentrations of 1,000-7,500 mg/kg, HMX concentrations of 0-300 mg/kg, and RDX concentrations of 0-100 mg/kg. In addition, small amounts of 2,4- and 2,6-dinitrotoluene were in several of the excavated soil samples. The soil was sieved through a 1/4-in. screen to remove rocks, plant roots, and other objects. The material passing through the sieve was used to create a soil slurry (15% or 25% weight/weight in water) that was pumped into 350-gallon stainless steel reactors. The contents were mixed with a 1-hp variable-speed motor with blade-type impellers. Molasses (0.15% on a volume basis; feedlot grade) was added twice weekly in reactors that had molasses added, Tween 80 (3% on a volume basis; food grade) was added once per week in the reactors that had Tween added, and commercial-grade NaOH was added as necessary to maintain pH > 6 but less than 7.

Four reactors were operated. The first was a 25% slurry with a 20% (volume/volume) replacement soil per week, with molasses. The second reactor received 25% slurry with a 20% (volume/volume) replacement soil per week and molasses and 3% Tween 80. The third reactor

was a 15% slurry with a 10% replacement per week; 3% Tween was added to this reactor as the sole cosubstrate and surfactant. The fourth reactor was a 15% slurry with a 10% replacement per week, with molasses and Tween 80. Soil removed from the reactors during replacements was tested for explosives and then subjected to several dewatering schemes. Water removed in dewatering was reused in slurry preparation. This recycled water could be used at least three times before it was discarded after polishing with granular activated carbon.

Analytical Methods

Explosives were analyzed in the soil and water phases by using EPA method 8330. In addition, at the end of the reactor study, small subsamples were removed from the reactors and subjected to a laboratory metabolic study in which the radiolabel carbon-14 was added. Various fractions were identified, including labeled carbon dioxide and other microbial products.

Results

Figure 2 reveals certain trends in the data for the 20% (volume/volume) replacement without surfactants. As indicated in the figure, the adaptation of the microbial system is immediate for TNT. The TNT was removed, and 2-amino-4,6-dinitrotoluene (2A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4A-2,6-DNT) were generated. As Figure 2 shows, approximately two months were required to achieve TNT concentrations below 20 mg/kg. The 4A-2,6-DNT concentrations were initially around 300-400 mg/kg and decreased to less than 100 mg/kg over the course of the study. The system operated with a high level of consistency, removing TNT to a level of less than 20 mg/kg and also decreasing the concentrations of 2A-4,6-DNT and 4A-2,6-DNT to less than 100 mg/kg.

Figure 3 demonstrates the results from the 20% volume/volume replacement reactor with surfactant as a cosubstrate. Figure 3 demonstrates that the reactor with Tween 80 initially appeared to have slightly improved performance with regard to the degradation of the 4A-2,6-DNT. This reactor did not demonstrate the variation in either TNT removal or 4A-2,6-DNT, as did the molasses-only reactor. During a period of cold weather in early January, the 4A-2,6-DNT concentration increased dramatically, apparently caused by the consortium's inability to process the 4A-2,6-DNT generated by TNT degradation. After the temperature returned to greater than 20°C, the removal of the 4A-2,6-DNT continued. The other two reactors, which operated at a lower soil loading and reduced replacement rate, achieved TNT removal to less than 20 mg/kg. The 4A-2,6-DNT level was less than 50 mg/kg.

The reactor experiments indicated that HMX and RDX concentrations below 10 mg/kg can be achieved. The concentrations of all explosives in reactor liquid (water) fell below 1 mg/L when the temperature was above 25°C and the system was operating to reduce concentrations of soil explosives. It should be noted that during periods of cold weather, TNT removal and levels of 2A-4,6-DNT or 4A-2,6-DNT are impacted.

Small subsamples were obtained from the pilot reactors to determine the metabolics of carbon-14-labeled TNT. The distribution of the radiolabel in the reactor contents was similar in both reactors. Approximately 17-22% of the radiolabel was found in carbon dioxide, indicating mineralization. The remainder was in fatty acids and biomass, which could be removed from the system by increasing the amount of air added to the reactors.

CONCLUSION

The biological soil slurry reactor with molasses and surfactant has the potential to degrade TNT in contaminated soil to levels below 50 mg/kg. HMX and RDX were also removed but at much lower input concentrations. The accumulation of 2A-4,6-DNT and 4A-2,6-DNT was minimized; these compounds were also degraded to levels below 100 mg/kg. In applications of

this technology in cold environments, the temperature of the reactor must be maintained at 20-25°C. Other site-specific issues to be addressed include the residual concentration of explosives allowable in the treated soil and the availability of inexpensive cosubstrates that are effective in promoting microbial activity.

Reference

Manning, J.F. Jr., R. Boopathy, and C.F. Kulpa, 1995, *A Laboratory Study in Support of the Pilot Demonstration of a Biological Soil Slurry Reactor*, report SFIM-AEC-TS-CR-94038, prepared for the U.S. Army Environmental Center, Environmental Technology Division, Aberdeen Proving Ground, Maryland, by Argonne National Laboratory, Argonne, Illinois, July.

BIOREMEDIATION FLOW DIAGRAM

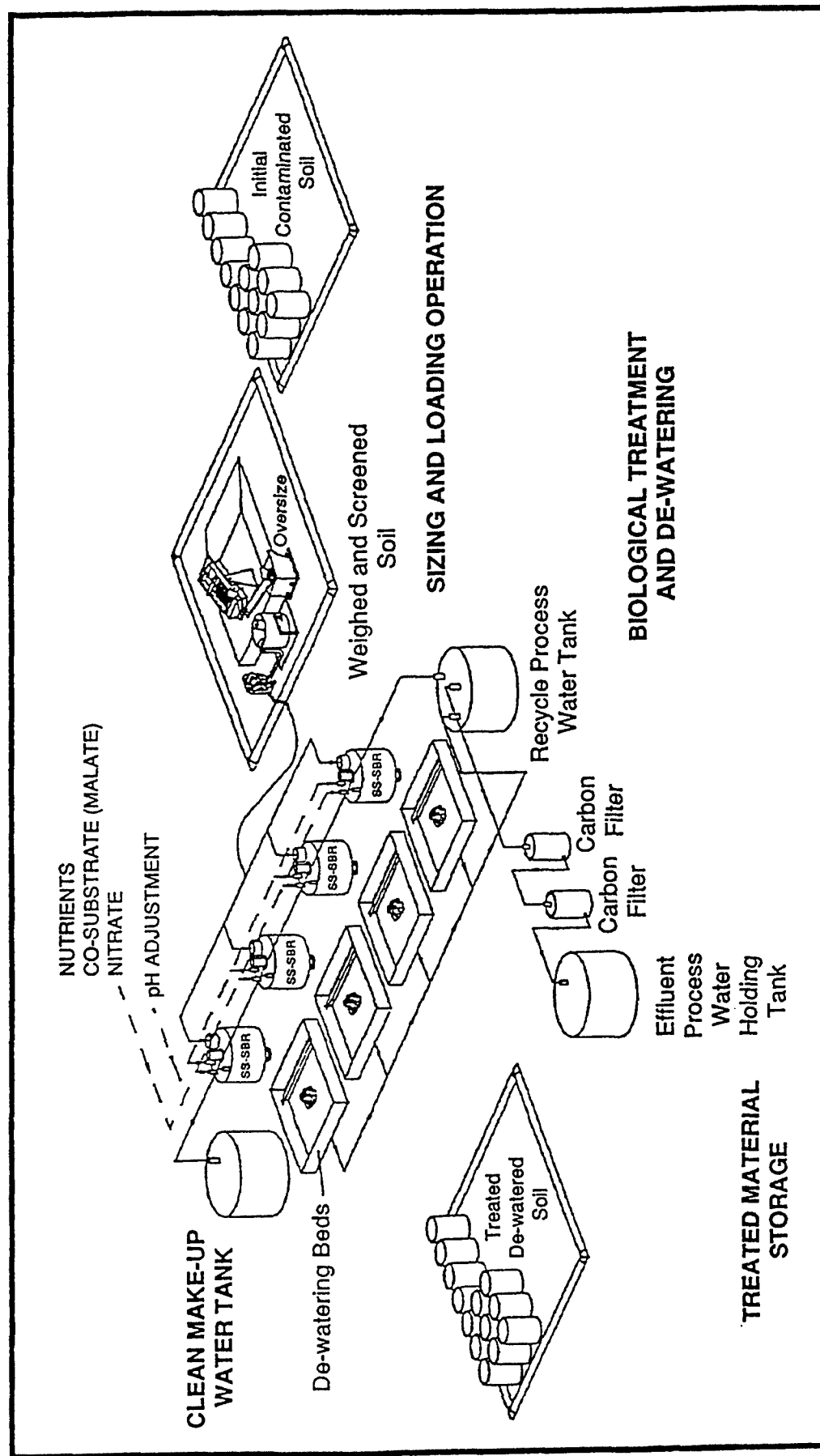


Figure 1 Pilot System

Molasses Bioslurry Reactor

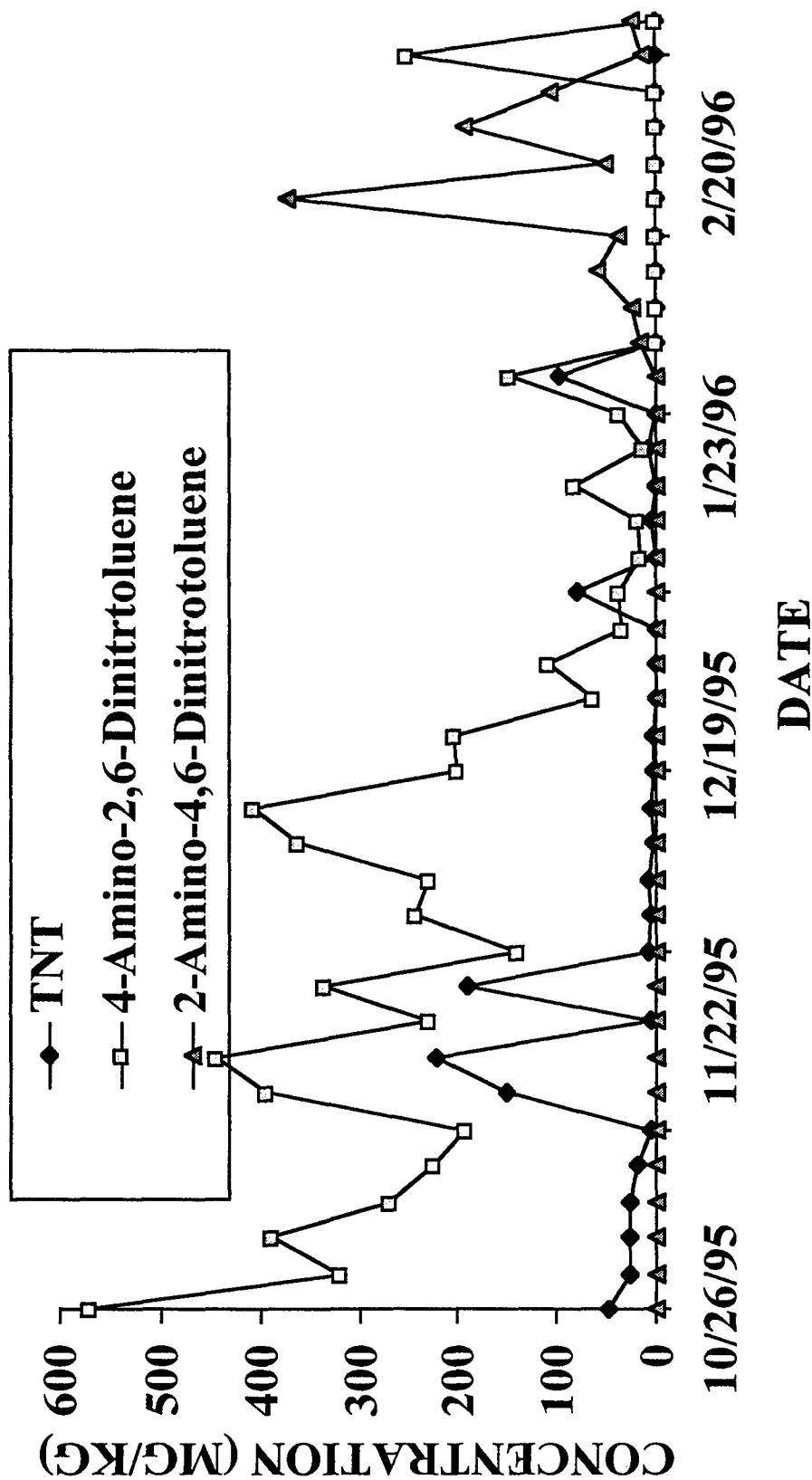


Figure 2 Reactor with 20% Soil Replacement and Molasses

Surfactant Enhanced Degradation

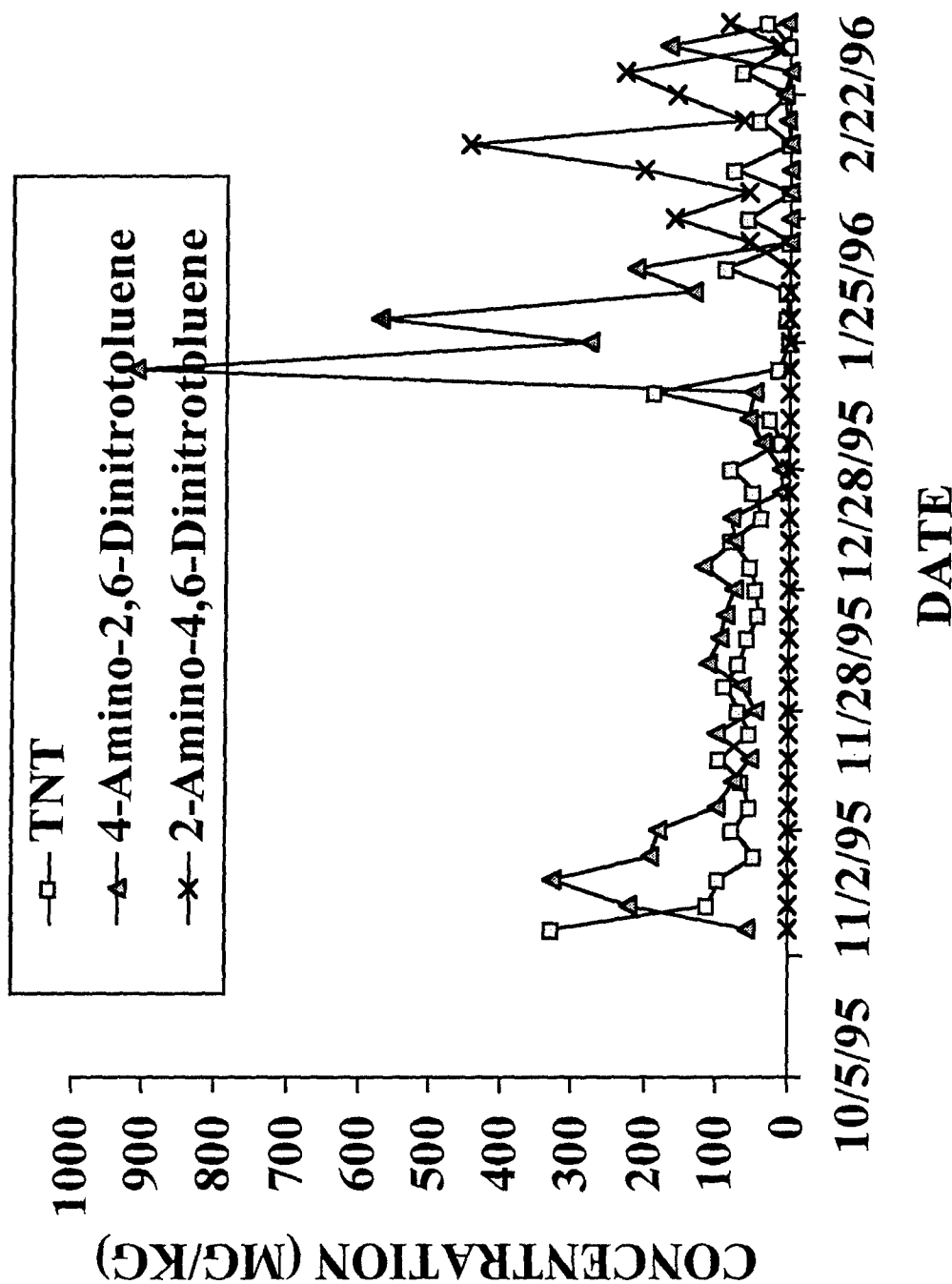


Figure 3 Reactor with 20% Soil Replacement and Surfactant as Cosubstrate