Comparison of Biostimulation, Bioaugmentation and Chemical-Biological Stabilization for Remediation of Hydrocarbon Contaminated Sediments

Francisco Javier Guzman O. and Randy H. Adams
Juarez Autonomous University of Tabasco (UJAT), Academic Division of Biological Sciences
Km 0.5 Carretera Villahermosa – Cárdenas, Villahermosa, Tabasco, México CP 86104
Tel.: (52-993) 391-6538, Fax: (52-993) 354-4308
e-mails: franjaguoso@hotmail.com, drrandocan@hotmail.com

and Juan Avila G.
Pemex Gas and Basic Petrochemicals (PGPB), UMT
dom: Av. Veracruz 614, Col. Petrolera, Coatzacoalcos, Veracruz, Mexico CP96500

ABSTRACT

Treatment methods were studied for remediation of sediments in a man-made lake, previously used to collect acid run-off from a sulfur mine in southern Veracruz state, Mexico. The lake had been restored to neutrality, but remained contaminated with very weathered hydrocarbons (<1,000 to >300,000 ppm TPH). Biostimulation and bioaugmentation (with native microorganisms) both resulted in reductions in TPH concentrations of approximately 20 % within one month (starting concentrations of approx. five to six percent) with no further reduction thereafter. The biostimulation showed greater reduction in toxicity, though, resulting in complete elimination of acute toxicity. The chemical-biological stabilization also completely eliminated toxicity, presented no TCLP leachates, and maintained a stable pH (7.9). Furthermore, this method only requires initial mixing of the chemical and organic reagents instead of daily aeration, reducing operating costs. The results of this study are currently being used to formulate an integrated remediation strategy for this site.

INTRODUCTION

Due to the damage which may be caused by residual hydrocarbons in contaminated soil and sediment, several technologies are being studied which are oriented towards the use of physical, chemical, or biological processes, or the combination thereof. The objective of all of these methods is to transform potentially toxic substances into less dangerous forms, either by totally destroying the toxic substances, or by reducing or eliminating concentrations of said substances in media which come in contact with human populations. The latter strategy may be accomplished by chemically modifying these substances and the matrix in which they are found. This results in a qualitative change which reduces the probability that these contaminants produce significant exposure. Furthermore, it is important that the technologies developed be implementable in reasonable time frames and at a reasonable cost.

Among the technologies which can be used, a common one is bioremediation, and within this technology there are two common practices for implementation: biostimulation and bioaugmentation (1,2). Alternatively, stabilization technologies may be used which reduce the impact of toxic substances by immobilizing them and thereby reducing the bioavailability (and therefore toxicity) as well as the potential for leachates and subsequent groundwater contamination (3). These (stabilization) methods often consist of the addition and incorporation of calcium oxides and organic amendments.

These technologies have produced favorable results in the treatment of hydrocarbon contaminated drilling cuttings, soil, and sediments. None-the-less, they don't always produce good results when the hydrocarbon concentration is very high. For these reasons treatability studies were performed prior to the selection and implementation of a treatment method for this site. In theses studies reductions in toxicity, and leachates were measured in addition to hydrocarbon concentrations.

BACKGROUND

During the first part of the 1990s, the price of sulfur in the Mexican market plummeted, resulting in the closure of several sulfur mining companies in this country. One of these companies, Compañía Exploradora del Istmo (CEDI, Isthmus Exploring Company), closed its installations in Texistepec, in southern Veracruz state in 1993, leaving several areas contaminated. In 1999 resources were assigned to conduct an environmental audit, which found an "environmental passive" consisting of 2,800 poorly finished wells some of which were leaking, 35 Km of rural roads covered with residues containing charcoal and sulfur, 18 dumps of weathered hydrocarbons, 550,000 tons of charcoal and sulfur residues (tailings pile), a 75,000 m^3 acid water holding pond which received leachates from the tailings pile, and an overflow holding reservoir of approximately 350 hectares which contained sedimented hydrocarbons and supernatant, with a volume of 12 billion cubic meters (4).

Today these installations have been assigned to PEMEX Gas y Petroquímica Básica (PGPB, PEMEX Gas and Basic Petrochemicals), whose intention is to restore the overflow holding reservoir "Presa Agua de Minas" and nearby areas. To achieve this end it is necessary to conduct solid phase treatability studies to determine with greater precision the treatment method and important parameters for the remediation of this site, thereby reducing treatment times and associated costs.

The objective of our study was to determine which treatment method (biostimulation, bioaugmentation or chemical-biological stabilization) is the most convenient technology for site restoration of hydrocarbon contaminated soil and sediment in the "Presa Agua de Mina" overflow reservoir, to estimate the efficiency of hydrocarbon removal at this site with these techniques, and to compare the reaction rates, remediation times and achievable levels with respect to reductions in hydrocarbons, toxicity, and leachates for this site.

METHODOLOGY

This study was carried out between the Spring and Fall of 2004. Sediments were collected from a beach area and transported to the UJAT, where they were thoroughly mixed and divided into four equal volumes representing three treatments and a control. Each of these volumes was further divided into three replicate treatments, each replicate consisting of a treatment cell of 0.4 m x 0.4 m x 0.2 m deep. The different treatment methods are described below:

- Biostimulation: addition of inorganic nutrients (Grow-Feed 20-30-10 commercial fertilizer) sufficient to provide 100 ppm of nitrogen, daily aeration and periodic moisture addition (to maintain approx. 15 -22 % moisture)

- Bioaugmentation: addition of autochthonous microorganisms, followed by fertilizer addition, aeration, and moisture control

- Chemical-Biological Stabilization: addition of 4 % (w/w) hydrated lime, mixing, followed by addition of 4 % (w/w) organic amendment (sugar cane process waste) three days latter (5). Fifteen days latter humidicola grass (*Brachiaria humidicola*) seeds were planted on the surface of the treatment cells.

Hydrocarbons were determined using EPA method 418.1 (6), and acute toxicity using the Microtox bioassay (7). Leachates were determined using a TCLP equivalent extraction technique (PECT extract, ref. 8). Hydrocarbons were measured in the leachate extract by extraction with perchloroethylene, solvent evaporation, redissolution in methanol, and TPH determination using EPA method 9074 (9).

RESULTS

Results of TPH reductions in the three treatments investigated are shown in figure 1. In the biostimulation treatment a reduction of 5,900 ppm was observed, representing 18.3 % of the initial concentration, reaching a final, stable concentration of 26,500 ppm. In the bioaugmentation treatment, similar results were obtained; we observed a reduction of 7,300 ppm TPH representing 21.1 % of the initial concentration, stabilizing at 27,400 ppm. In the chemical – biological stabilization treatment we observed a reduction in the initial concentration of 15.6 % (6,000 ppm) reaching a final concentration of 32,300 ppm. All three treatments had final pH values of 7 – 8.

With respect to toxicity, the biostimulation treatment reduced the toxicity from toxic (EC50 = 65,200 ppm, background ≈ 95,000 ppm (10)) to completely non toxic (all samples with EC50 ≥ 100,000 ppm). In the bioaugmentation treatment very little change in toxicity was observed. Averages both before and after treatment were slightly more toxic than background, but within the precision of the method (11). In the treatment with chemical – biological stabilization the toxicity was greatly reduced from toxic (EC50 = 65,500 ppm) to completely non toxic, even showing stimulation of the test organism used in the bioassay. In these treatments the humidicola grass planted grew profusely and developed an extensive root system in about two months (see figures 2 and 3). TCLP leachates were also completely eliminated in this treatment.

CONCLUSIONS

All three methods studied showed similar reductions in TPH concentrations of roughly 15 – 20 %, the remainder of the hydrocarbons being recalcitrant to further biodegradation. During the final months of the experiments there was little change in the hydrocarbon concentration, however it is possible that some humification reactions were taking place. Humification results in the stabilization of hydrocarbons in soil organic matter (humus) which helps to reduce toxicity and leachate potential. Two of the three methods studied (biostimulation, chemical – biological stabilization) demonstrated complete reductions in toxicity and leachates, suggesting this as a possible stabilization process, and demonstrating the necessity to evaluate not only hydrocarbon concentrations, but rather toxicity and leachates as remediation criteria.

Of the two most promising methods evaluated (biostimulation and chemical – biological stabilization) the second has an advantage in terms of materials handling. This method does not require continual mixing as does most bioremediation methods, and therefore is easier to implement, and more economical. The growth rate of the humidicola grass (a C4 metabolizer) probably plays an important role in the humification process, which could be applicable to a variety of production areas in tropical and semitropical climates (southeast Mexico, eastern Venezuela, southern Louisiana, Niger River delta, etc.).

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REFERENCES CITED

1. King R. B., Long, G. M., and Sheldon, J. K. Practical Environmental Bioremediation. Boca Raton, Florida, Lewis Publishers (1992).

2. Adams S., R. H., Domínguez R., V. I, García H., L., "Potencial de la Biorremediación de Petróleo en el Trópico Mexicano," *Terra*, **17** (2), 159 – 174 (1999).

3. Al-Tabbaa, A. and Evans, C., "Deep Soil Mixing in the UK: Geoenvironmental Research and Recent Applications*,"* *Land Contam. Reclam.* **11** (1), 1 – 14, (2003).

4. Universidad Nacional de México, Instituto de Ingeniería, "Diagnóstico de las Presas Existentes en la Unidad Minera Industrial Texistepec," México, D.F., UNAM/Pemex Gas y Petroquímica Básica (2002).

5. Adams, R. H., "Chemical – Biological Stabilization of Hydrocarbon Contaminated Soil and Drilling Cuttings in Tropical Mexico," *Land Contam. Reclam.*, **12** (11) in review (2004).

6. Environmental Protection Agency (EPA), "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," Publicación No. EPA 530/SW-846 (ed. 1997).

7. Secretaría de Comercio y Fomento Industrial (SECOFI), "Norma Mexicana NMX-AA-112-1995-SCFI, Análisis de Agua y Sedimento - Evaluación de Toxicidad Aguda con *Photobacterium phosphoreum* - Método de Prueba," México, D.F. (1995).

8. Secretaría de Desarrollo Social, "Norma Oficial Mexicana NOM-053-ECOL-1993, Que Establece el Procedimiento para Llevar a Cabo la Prueba de Extracción para Determinar los Constituyentes que Hacen a un Residuo Peligroso por su Toxicidad al Ambiente," México D.F., Diario Oficial de la Federación de fecha 22 de octubre de (1993).

9. Adams S., R. H. y Ramírez A. J., "Optimización del método EPA 9074 como alternativa para análisis de hidrocarburos totales de petróleo," presentado en el VI Congreso Inter – Americano Sobre el Medio Ambiente. Monterrey, Nuevo León, México, Red Interamericana para la Calidad Ambiental/Intituto Tecnológico de Educación Superior de Monterrey (ITESM),. (29 Sept. – 2 Oct. 1999).

10. Adams S., R. H., y Ricalde Z., S. Del C., "Determinación de Toxicidad en Suelos Representativos del Activo de Producción Petrolera Cinco Presidentes, Veracruz y Tabasco," *Rev. Inter. Contam. Ambient.*, en revisión (2004).

11. Cornelio G., Y de J., "Evaluación Preliminar de Toxicidad por Plaguicidas (Mancozeb) en Agua y Sedimentos en la Zona Platanera del Río Teapa, Tabasco, México," Tesis de Licenciatura en Ingeniería Ambiental. Villahermosa, Tabasco, México, División Académica de Ciencias Biológicas, Universidad Juárez Autónoma de Tabasco (2001).

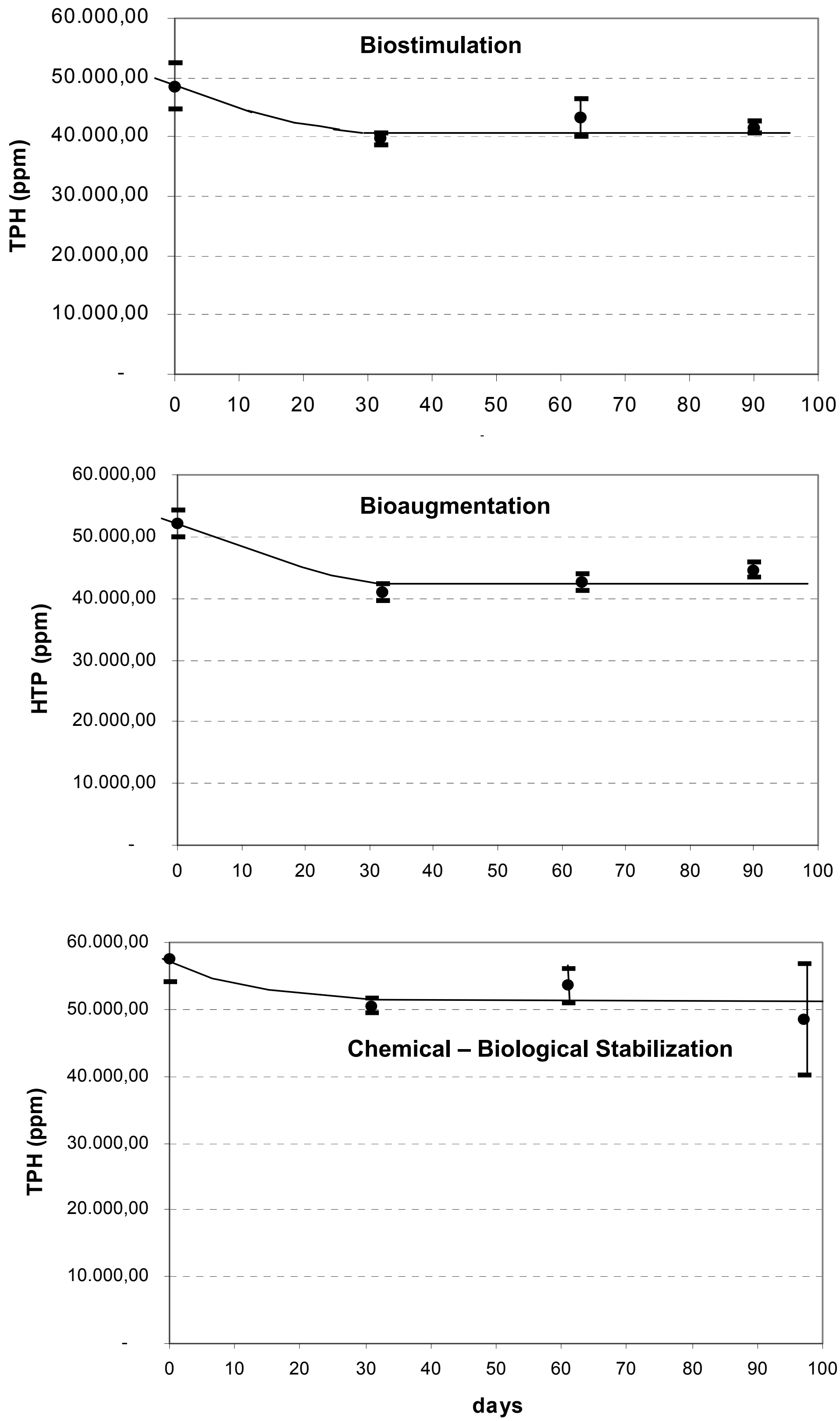

Figure 1. TPH reductions in three treatment methods for sediments with weathered hydrocarbons.

Figure 2. Growth of humidicola grass on sediments treated by chemical – biological stabilization.

Figure 3. Root development (*Brachiaria humidicola*) in stabilized sediments.