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BIOCHEMICAL TREATMENT TECHNOLOGIES FOR GAS INDUSTRY WASTES

by

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ABSTRACT

Sequential chemical and biological amendments as well as sequential biological processes (e.g. anaerobic-aerobic) may have potential in reducing pollutants present in Gas Industry wastes. Several Town Gas soils have been characterized regarding PAH levels and soil particle distributions prior to and following biological treatment. Multivariate statistical analyses have revealed that the presence of biodegradable PAHs such as naphthalene in a sand matrix have significant influence on the effectiveness of biological treatment schemes. Integrated chemical-biological treatment processes have been devised that are effective in achieving extensive PAH degradation, even in soils that are dominated by persistent and normally recalcitrant PAHs.

Other research is addressing gas industry wastes contaminated with PCBs. Anaerobic dechlorination has been demonstrated for PCBs present in Aroclor 1242. Sequential anaerobic-aerobic treatment is being evaluated for PCB-laden gas condensate waters and contaminated soils.

A focused effort is being directed at testing some of these technologies during field experimentation. A Town Gas soil is being subjected to such a field test this summer using conventional land treatment technology.

BIOCHEMICAL TREATMENT TECHNOLOGIES FOR GAS INDUSTRY WASTES

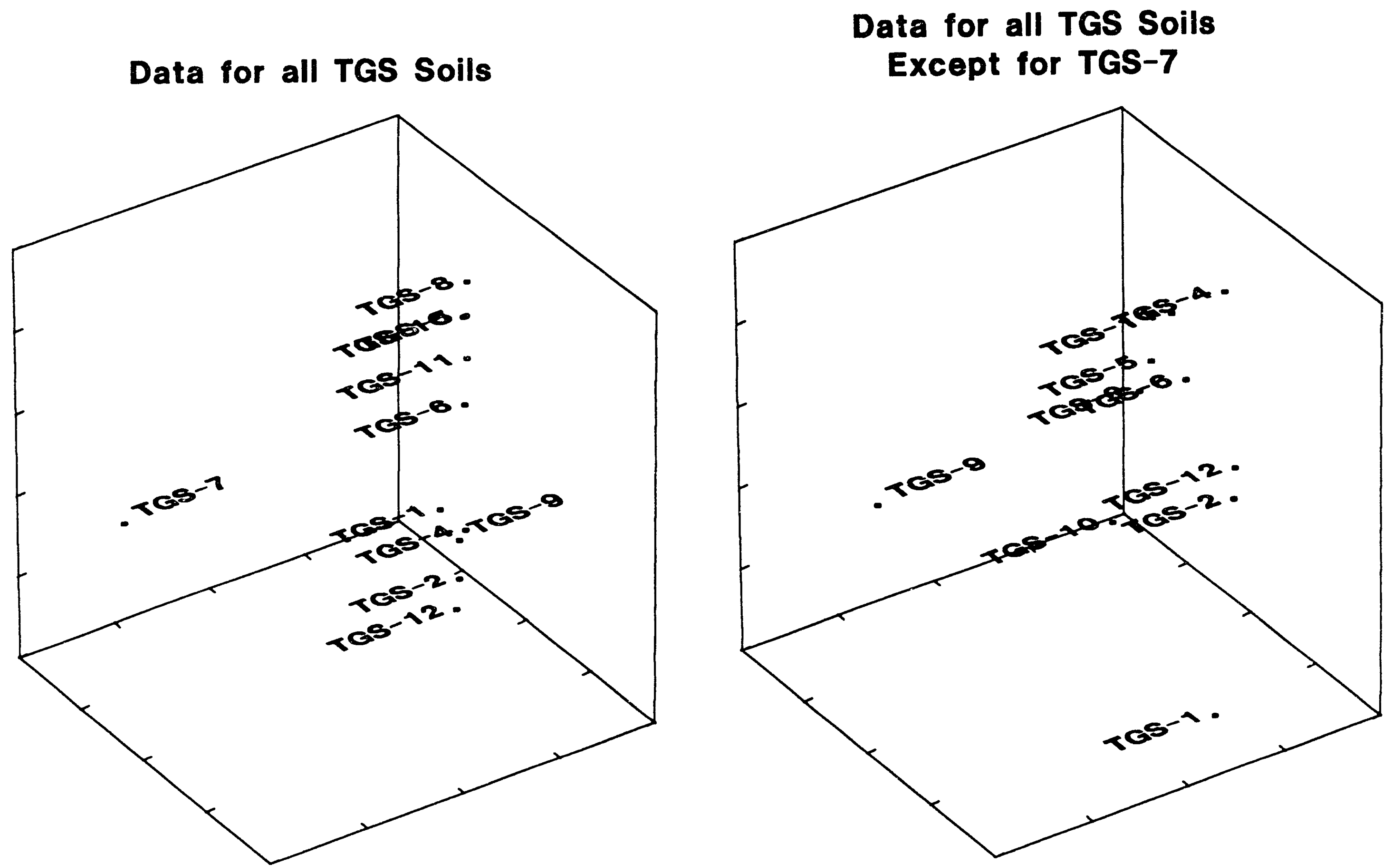
INTRODUCTION

Continued emphasis has been placed in recent years on assessment of technologies appropriate for remediation of gas industry wastes. Among these wastes are polyaromatic hydrocarbons (PAHs) that are contaminants originating from Town Gas operations and polychlorinated biphenyls (PCBs) that were widely used in the gas industry as components of oils used in gas turbines and air compressors and are found as pollutants in gas line condensates. Technologies that have been studied by scientists at the Institute of Gas Technology (IGT) include both biological and chemical treatment used individually and as integrated processes. In the following discussion, emphasis will be placed on work detailing degradation of PAHs using combined biological and chemical treatment processes. Results of research on biological dechlorination of PCBs under anaerobic conditions will also be described.

The ultimate means of evaluating these technologies is to test their waste treatment effectiveness at a field scale. That goal will be realized later this year for PAHs in field experimentation. Details of the scientific approach to be implemented are also reported.

Comparison of Different Manufactured Gas Plant Soils

Over the past several years, numerous research investigations have been undertaken to study PAH degradation in contaminated Town Gas soils (TGS). Several of these soils have been examined and found to vary considerably in their characteristics. Figure 1 maps these soils. To generate this map, data were used regarding selected PAHs (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, phenylnaphthalene, 1-methylphenanthrene, fluoranthene, pyrene, benzo(b)fluoronthene, benzo(k)fluoranthene, benzo(a)pyrene, and benzo(g,h,i)perylene) that range from 2 to 6-rings in size as well as data about the particle distribution as percent sand, percent silt, and percent clay in these test soils. A multi-variate statistical technique called multidimensional scaling was used to reduce the data to 3 dimensions for viewing. These data are plotted in Figure 1 to show the relationships between the various soils tested.



Ordinates are dimensionless parameters which show relationships between the various soils tested for 14 PAHs and their particle distributions (i.e., percent sands, silts and clays).

Figure 1. MULTIDIMENSIONAL DATA REDUCED AND MAPPED IN 3 DIMENSIONS FOR SEVERAL TOWN GAS SOILS USING MULTIVARIATE STATISTICS

It is clear that TGS-7 is much different from the other soils analyzed in this fashion (left panel of Figure 1). This soil was dominated by free tar phase and could almost be described as coal tar contaminated with sand. When TGS-7 data are removed from the data set, TGS-9 appears isolated from the other PAHs as shown on the right panel of Figure 1. This soil contains 35% clay. When cluster analysis is used to portray the same data, both TGS-7 and TGS-9 soils stand apart from the other soils (Figure 2). Further analysis of the data indicates that relative presence or absence of naphthalene and sand are parameters that impose distinguishing characteristics as can be seen in Figure 3.

Integrated Biological-Chemical Treatment

Given the variety of characteristics that exist in these soils an important process consideration is that treatment technologies should be developed and implemented in a manner that is applicable to a broad range of soils. It has been determined that 2 and 3-ring PAHs can usually be removed from town gas soils by bioremediation, and that the more persistent 4 to 6-ring PAHs are most amenable to chemical treatment (Gauger et al., 1990; Kelley et al., 1990). We have also devised and tested an integrated treatment approach that is schematically depicted in Figure 4. When initial soil screening indicates that a soil is dominated by 4 to 6-ring PAHs, chemical treatment is performed as a pre-treatment step. The specific chemical treatment we have found beneficial for PAHs is called Fenton's reaction.

Fenton's reaction involves the formation of highly reactive free hydroxyl radicals during a catalytic reaction involving hydrogen peroxide and ferrous iron. The free radicals then react with PAHs to form readily biodegraded aromatic hydrocarbons (Kelley, et al., 1990). A biological treatment process then follows as shown in Figure 4. An example of this was tested for a soil designated TGS-11 that is dominated by 4 to 6-ring PAHs (>98%) and that has previously been shown not amenable to biological treatment alone. After this soil was amended with hydrogen peroxide at a level of 5% (wt of 100% H_2O_2/ml of a 10% solids slurry), PAH levels dropped 26% from about 900 ppm to 680 ppm as shown in Figure 5. Added aerobic biological treatment reduced these levels further such that combined chemical and biological treatment reduced concentrations to about 350 ppm (60%). These findings represent a single

TREE DIAGRAM

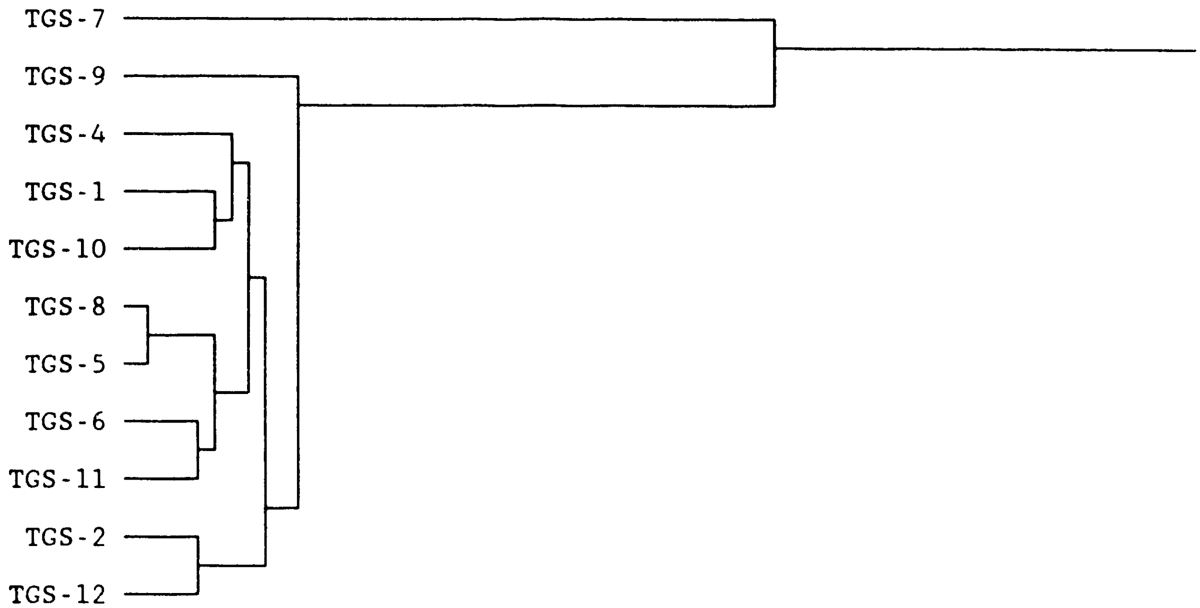


Figure 2. TREE DIAGRAM COMPARING SEVERAL TOWN GAS (MANUFACTURED GAS PLANT) SOILS USING CLUSTER ANALYSIS

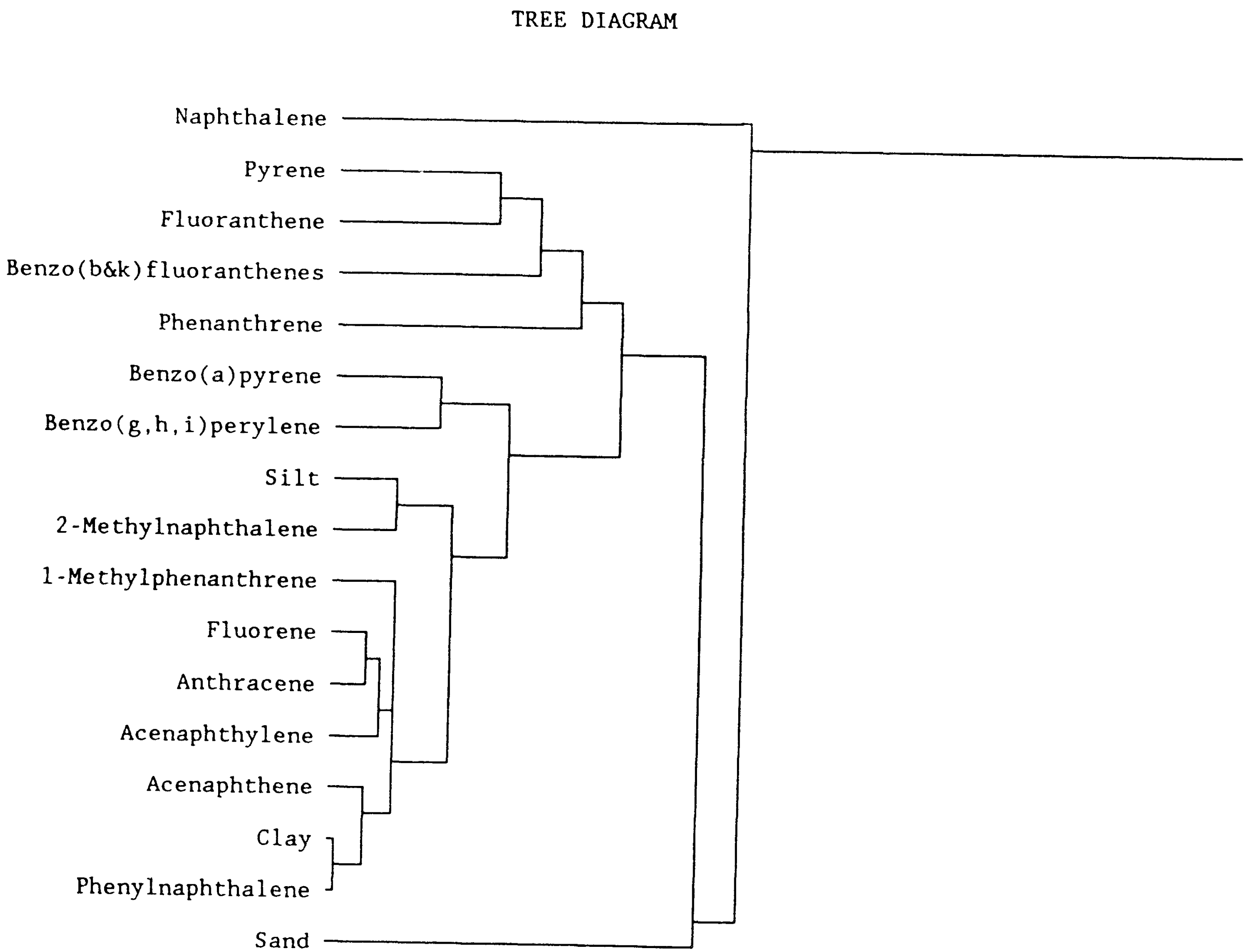


Figure 3. TREE DIAGRAM OF VARIOUS POLYAROMATIC HYDROCARBONS AND SOIL COMPONENTS AS DISTINGUISHING PARAMETERS IN THE CLUSTER ANALYSIS OF TOWN GAS (MANUFACTURED GAS PLANT) SOILS

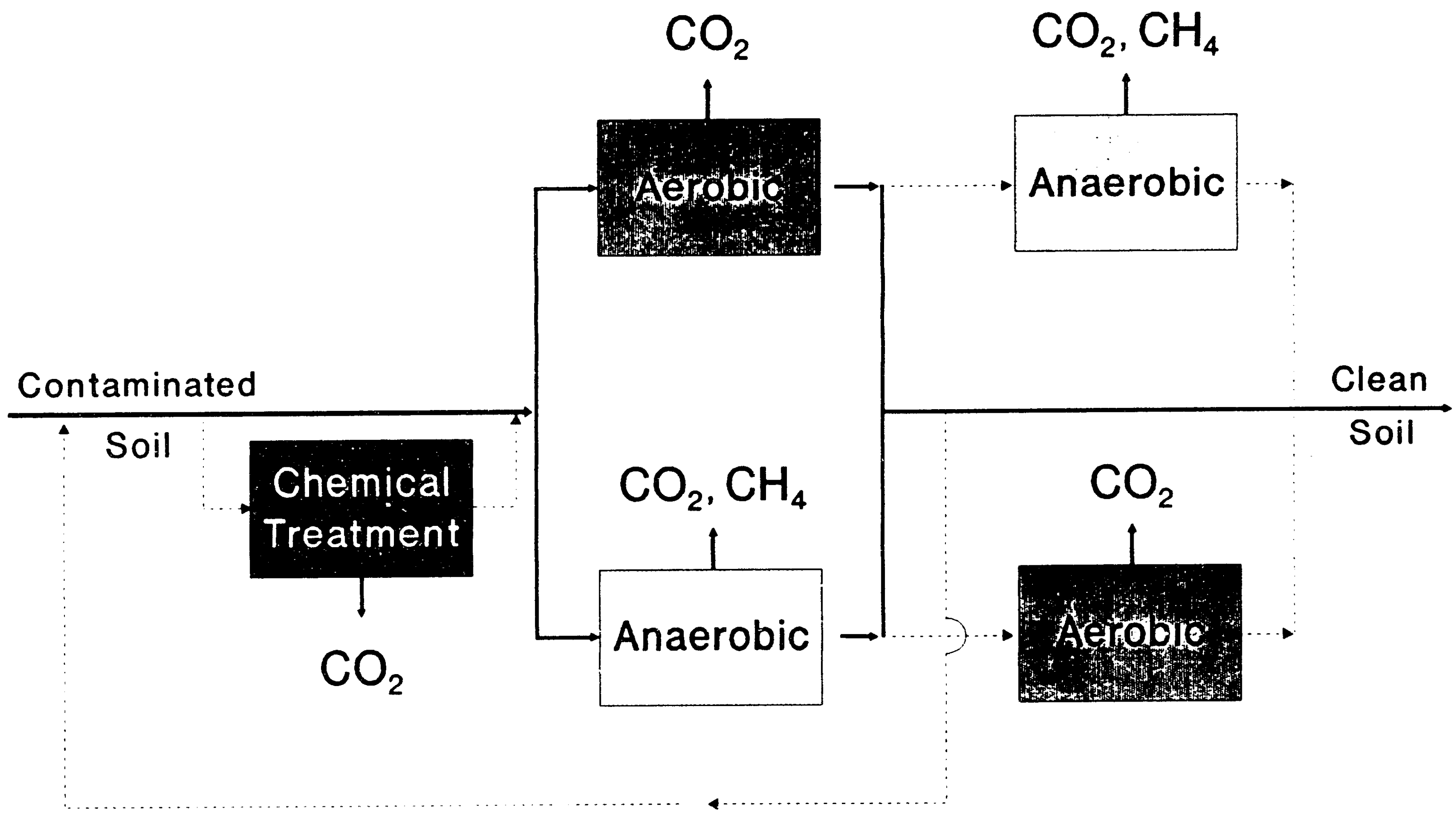
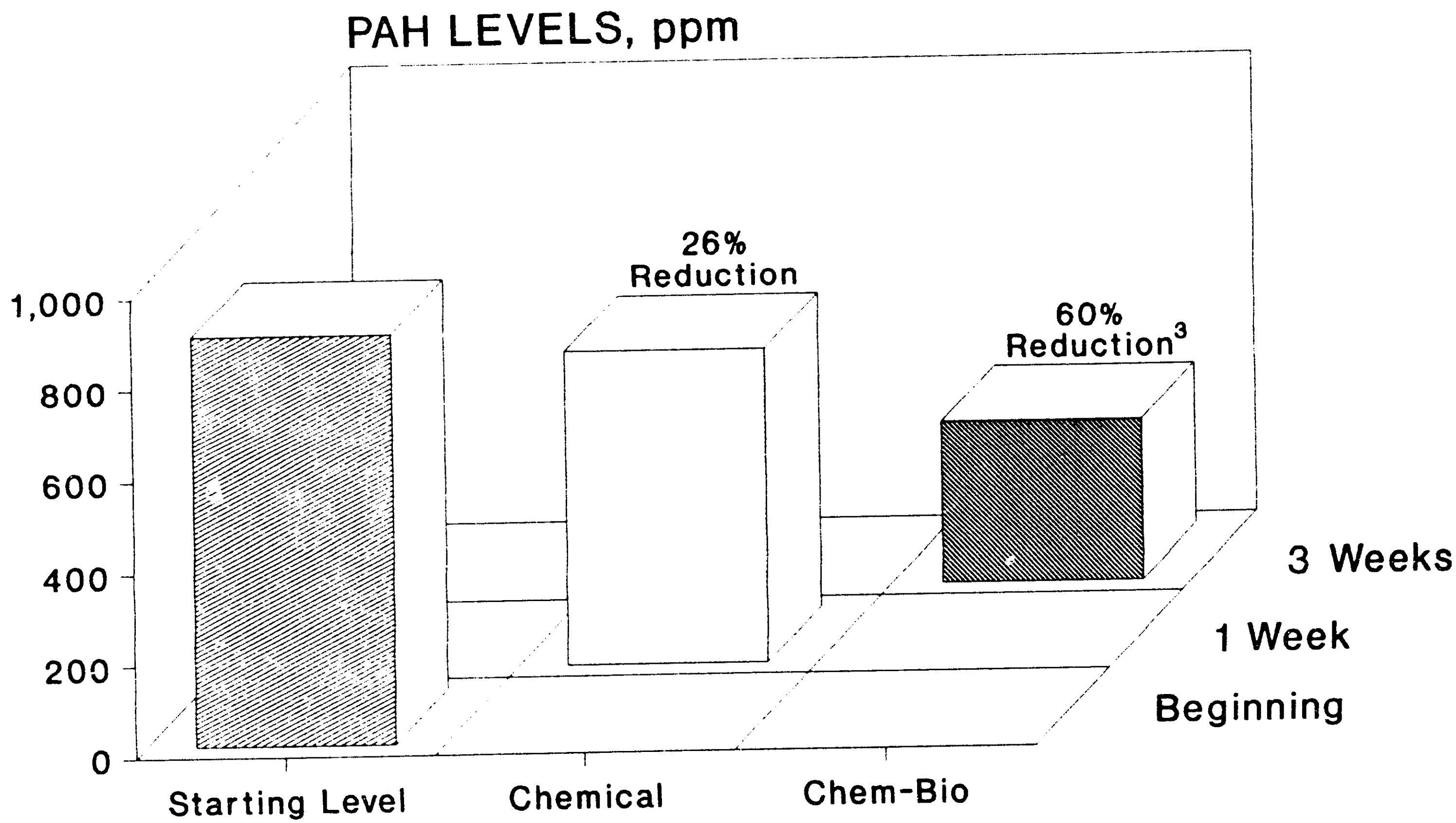


Figure 4. SCHEMATIC OF INTEGRATED CHEMICAL-BIOLOGICAL TREATMENT OF TOWN GAS (MANUFACTURED GAS PLANT) SOIL



[1]5% hydrogen peroxide
[2]Three-week incubation
[3]Subsequent cycles of chemical and biological treatment should reduce levels even further.

*TGS-11 contains › 98% persistent (4-6 ring) PAHs

Figure 5. TOTAL PAHS IN TGS-11 SOIL AFTER CHEMICAL TREATMENT ALONE FOLLOWED BY BIOLOGICAL TREATMENT

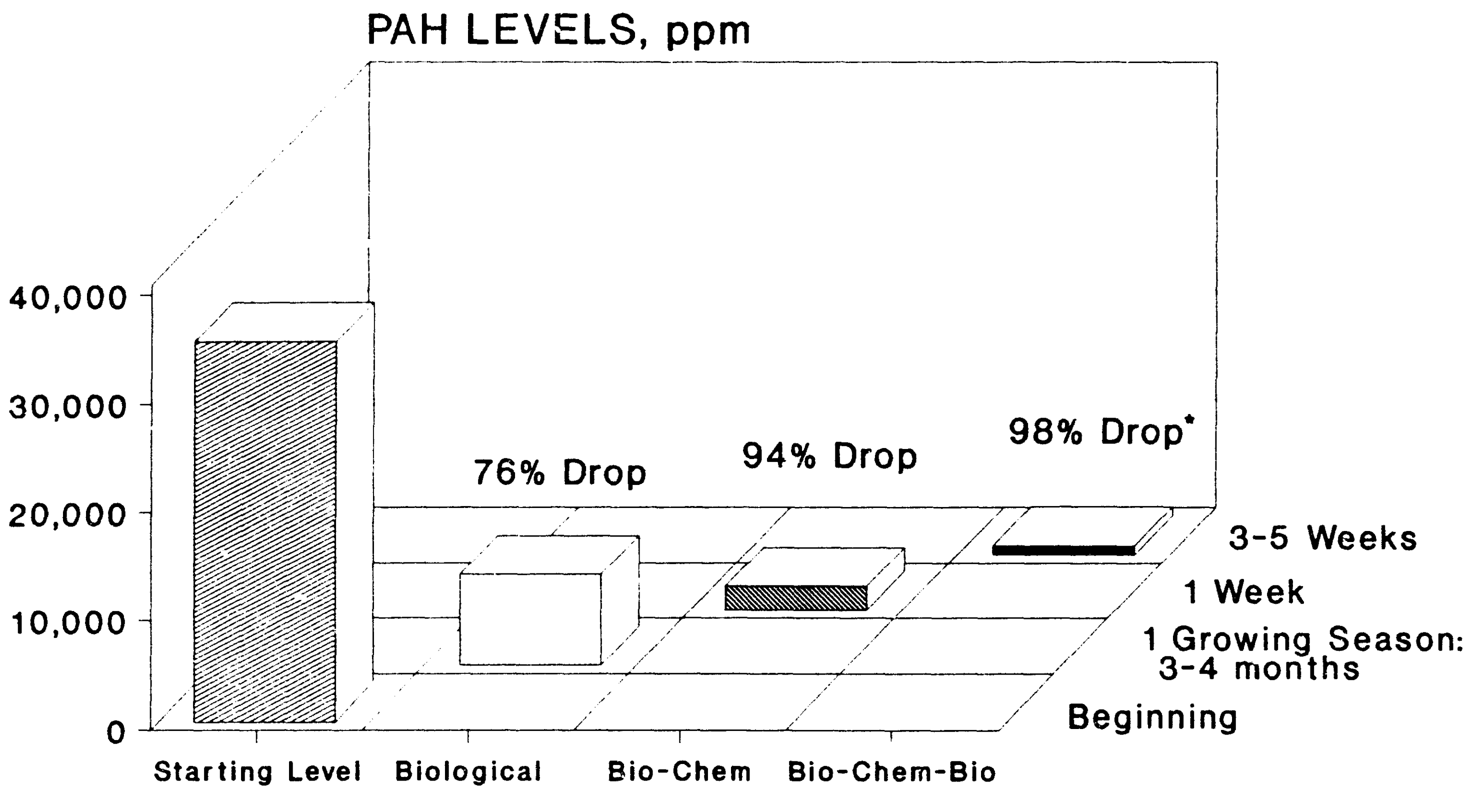
cycle of combined chemical-biological treatment. Added treatment cycles are expected to reduce these levels even more.

When initial soil screening indicates that a soil contains 2 and 3-ring PAHs in significant amounts, biological treatment is recommended as the initial step to remove as many of these compounds as possible. This is then followed by chemical treatment using Fenton's reaction to reduce the remaining persistent PAHs. This was demonstrated using the highly contaminated soil, TGS-7 which, as was noted above, was much different from the other soils that have been studied. TGS-7 soil was used in experiments involving Fenton's reaction applied following an initial period of aerobic biological treatment. Figure 6 shows the initial period of aerobic biological treatment had reduced total PAHs by 76% from 35,000 ppm to about 8,400 ppm. When Fenton's reaction was used as a post-treatment, PAH levels dropped by an additional 18% to 2,200 ppm and when coupled with a second round of biological treatment the total PAH reduction approached 98%. As mentioned previously, added cycles of combined chemical and biological treatment could be implemented as deemed necessary to reduce the endpoint further.

Anaerobic Dehalogenation PCBs

Another feature of this integrated approach is that it is applicable for processes suited to either aerobic or anaerobic treatment. For example, a sequential approach may be the most appropriate scenario for dehalogenation of PCBs. Aerobic microorganisms are generally able to degrade only PCB congeners that harbor 3 chlorines and fewer, whereas anaerobic microorganisms effectively dehalogenate PCB congeners with greater than 3 chlorines. It is easy to envision a sequential biological process for PCBs that involves anaerobic treatment first, followed by aerobic treatment.

The first component of such a process has been tested for Aroclor 1242 using anaerobic bacteria derived from Hudson River sediment and reported previously (Gauger and McCue, 1990). More recent investigations using a similar system have revealed the decline in the levels and numbers of all congeners present in Aroclor 1242 (Figure 7). After a period of 8 weeks, all PCBs in the mixture have dropped in magnitude as well as the number of peaks. Similar types of experiments are being undertaken to determine the effectiveness of this system using gas pipeline condensates and to quantify



*Subsequent cycles of chemical and biological treatment should reduce levels even further.

Figure 6. TOTAL PAHS IN TGS-7 SOIL AFTER SEQUENTIAL BIOLOGICAL-CHEMICAL-BIOLOGICAL TREATMENT

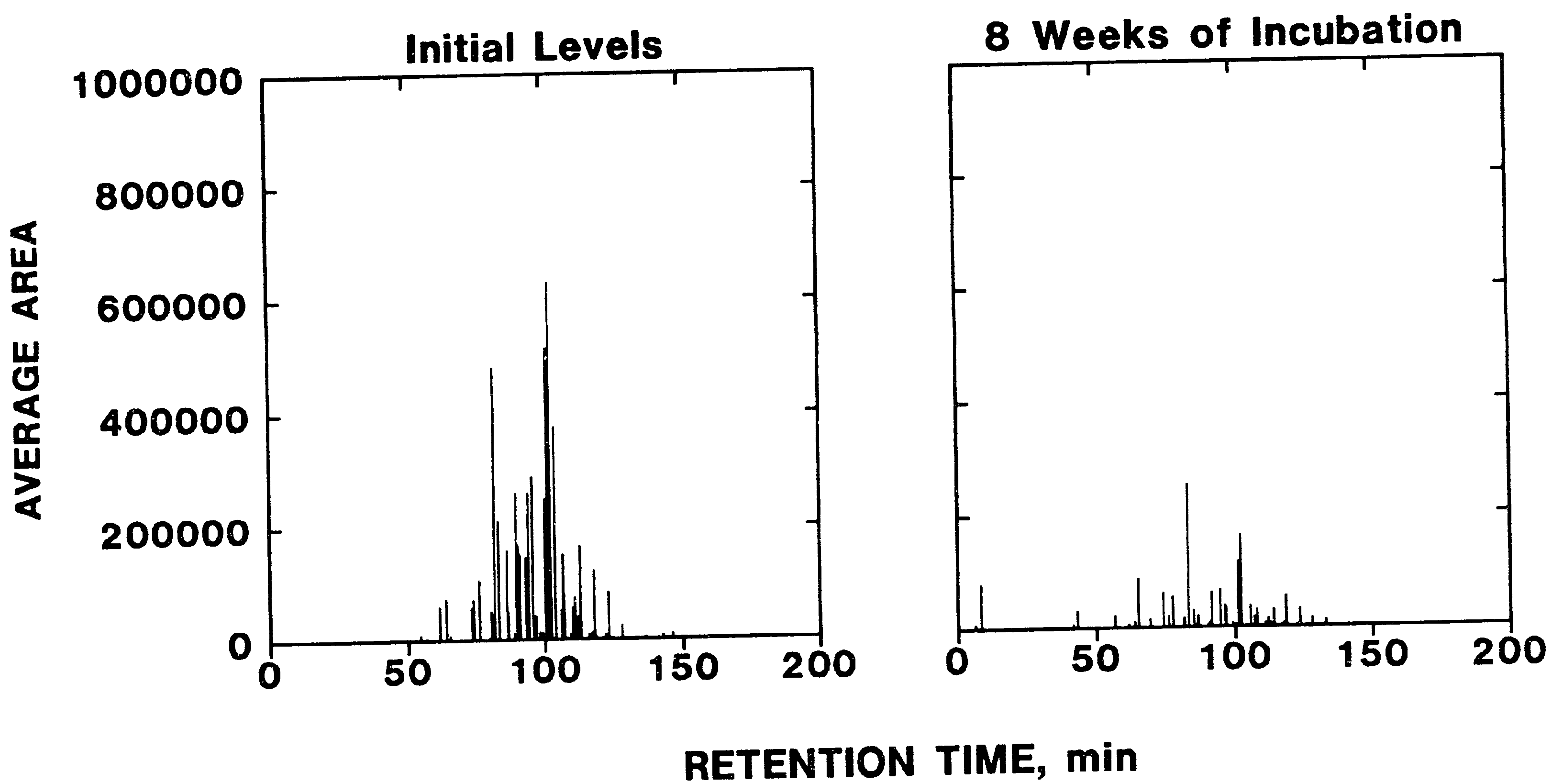


Figure 7. ANAEROBIC DEHALOGENATION OF AROCLOR 1242 POLYCHLORINATED BIPHENYLS (PCBS) AFTER 8 WEEKS OF INCUBATION

the benefit that might be gained by following this treatment by aerobic degradation.

Field Testing of Integrated Chemical-Biological Treatment for PAHs

Field experiments to evaluate the efficacy of integrated chemical and biological treatment of PAHs are to be carried out this year. One such experiment will be performed using land treatment technology this summer. Plans for the land treatment technology experiment will use a soil designated as TGS-12. It contains between 2,500-7,000 ppm total PAHs and is a sandy loam with 64% sand, 30% silt, and 6% clay.

The primary objective of this field experiment is to ascertain whether or not enhanced PAH degradation occurs as a direct consequence of amendment with nutrients alone to enhance the activity of soil microorganisms (i.e., biological processes), or from chemical co-treatment using Fenton's reaction in conjunction with biological processes. The conditions (each with four replicates) to be evaluated (and depicted in Figure 8) are: TREATMENT 1 -- unamended control; TREATMENT 2 -- amendment with nutrients, tilling and irrigation; TREATMENT 3 -- amendment with Fenton's reagents at the beginning of the study by making a hydrogen peroxide slurry of TGS-12 soil (on the order of 80% w/v) and following with nutrients, tilling, and irrigation; and TREATMENT 4 -- amendment with nutrients, tilling, moisture, and Fenton's reagents at the beginning of the study and on a periodic basis by adding hydrogen peroxide directly to the TGS-12 soil during irrigation or by injection into the soil across the test plot. A form of a split plot statistical design will also be imposed on the unamended control (TREATMENT 1, above). Two of the replicated plots will exist throughout the study without any soil management or amendment. The remaining two replicated plots will be tilled and irrigated (but not otherwise amended).

A liner system will be established under each of the treatment blocks to facilitate water management (e.g., irrigation, leachate collection, and disposal) and to prevent contamination of the underlying soil. Above this liner there will be a layer of rock or gravel, then clean sand, and finally, 6" of the contaminated TGS-12 soil. Each of the treatment plots will be bounded by 2" x 12" or similar boards. This will make it possible to till the various plots using a garden tractor fitted with a rototiller on a weekly or biweekly basis and eliminate the need to decontaminate the rototiller between

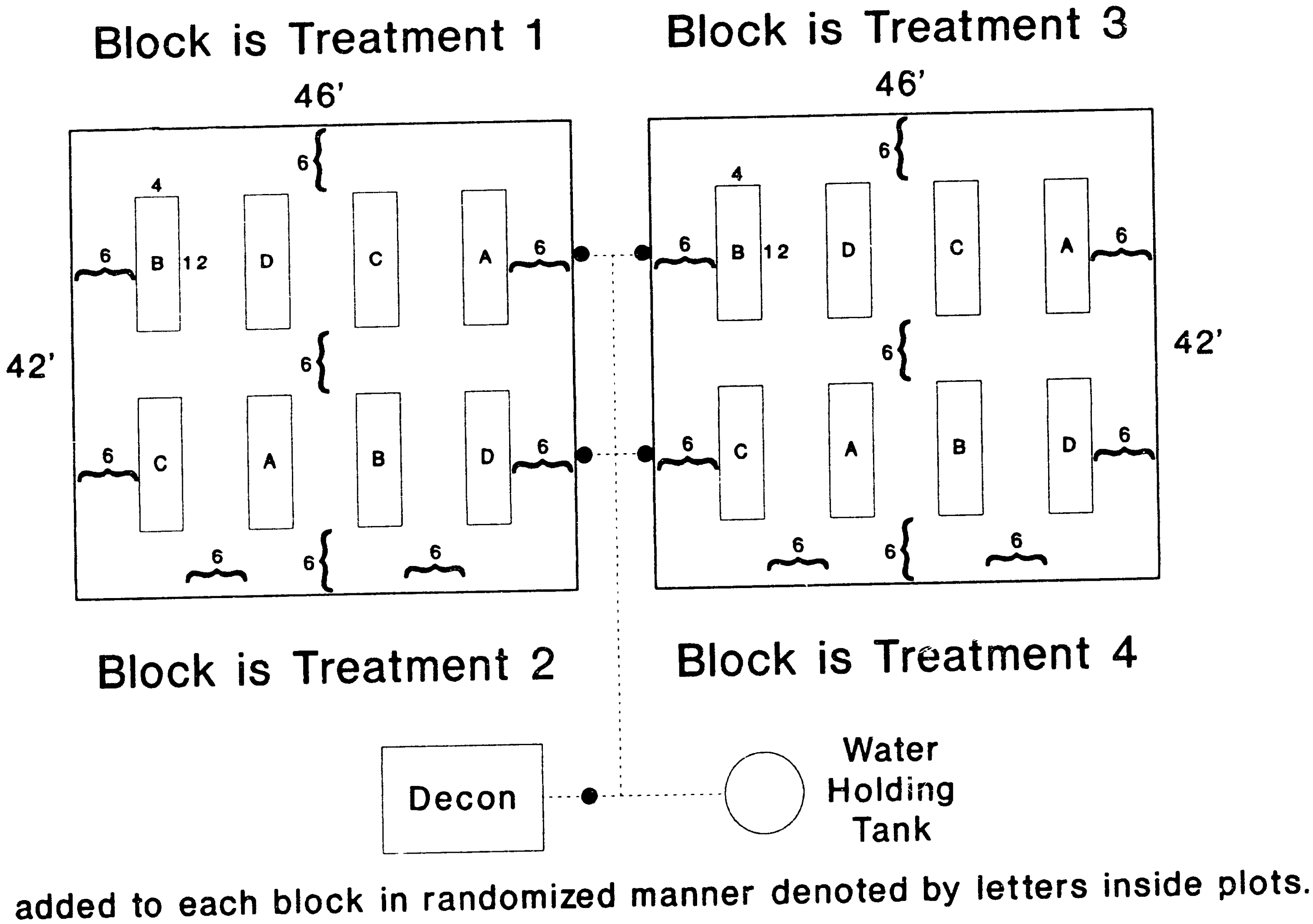


Figure 8. BALANCED COMPLETE BLOCK DESIGN USED IN TGS-12 FIELD EXPERIMENT

plots. Decontamination will only be performed between treatment blocks. A water management system will be established to hold water derived from each of the treatment blocks and the decontamination zone in an on-site impoundment. Collected water will be used for irrigation during the experiment. Meteorological data will be collected so ambient temperature, wind speed and direction, precipitation, etc. are known for weather conditions at the site. Soil samples will be collected at the beginning of the experiment and after 1 day, 1 week, 2 weeks, 4 weeks, 8 weeks, 12 weeks, and approximately 6 months of treatment. Parameters measured will include PAHs, nutrient levels, microbial population levels, pH and moisture. By the fall, the effectiveness of the integrated treatments evaluated in this field experiment when compared with controls and conventional land treatment, will be understood. At that time, engineering management recommendations can be made to ensure that optional PAH degradation is achieved. In the not-too-distant future similar tests may be possible of hazardous wastes laden with PCBs.

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