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- Corporate Headquarters 30423 Canwood Street, Suite 201 Agoura Hills, California 91301 818/991-7361
- Legal Department and Public Affairs 9200 Shelbyville Road, Suite 300 Louisville, Kentucky 40222 502/423-9400
- Governmental Affairs 1700 North Moore Street, Suite 1925 Arlington, Virginia 22209 703/522-2570

7 THE DESIGN, ECONOMICS, AND OPERATION OF A BIOLOGICAL TREATMENT SYSTEM FOR KETONE CONTAMINATED GROUND AND SOLVENT RECOVERY PROCESS WATERS

George J. Skladany, Research Manager DETOX, Inc. Dayton, Ohio 45459

Jeffrey M. Thomas, Western Regional Manager DETOX, Inc: San Francisco, California 94103

Greg Fisher, Corporate Environmental Engineer

Rom Ramachandran, Staff Safety & Corporate Environmental Engineer Memorex Corporation Santa Clara, California 95054

INTRODUCTION

The MEMOREX Computer Tape Plant in Santa Clara, California uses several solvents in the production of magnetic tape. The discovery of contaminated ground water due to a leaking underground solvent storage tank prompted the company's engineering staff to initially investigate different ground water remediation technologies as well as search for ways to improve the facility's overall hazardous waste handling program. The immediate need was to locate, control, and remediate a ground water plume containing several solvents. Secondary needs at the plant included instituting a hazardous waste treatment program, and to reduce both the liability and costs associated with off-site disposal of hazardous materials.

INITIAL GROUND WATER CONTAMINATION PROBLEM

An environmental investigation at the plant identified a localized ground water contaminant plume downgradiant of the underground solvent tank farm. A leaking storage tank was identified and removed. Monitoring wells were installed at the facility to identify the vertical and horizontal extent of the problem, and an extraction well was installed to hydraulically contain the contamination and transfer water to the surface for treatment. A single well pumping at 15 gpm was able to capture the entire plume. Chemical analysis of the ground water identified the presence of methyl-ethyl ketone (MEK) up to 500 mg/L, xylenes & ethyl benzene up to 40 mg/L, cyclohexanone up to 30 mg/L, cyclohexanol up to 10 mg/L, acetone up to 10 mg/L, and toluene, tetrahydrofuran, 2-butanol, and methyl-propyl ketone each less than 1 mg/L. Initial MEK concentrations were expected to decrease rapidly with treatment. The treatment system was required to handle a continuous flow of 15 gpm, and had to attain effluent MEK concentrations of less than 1 mg/L and other total organics concentration less than 100 μ g/L.

Initially, a carbon adsorption system was installed at the site to provide emergency treatment of the contaminated water. Required effluent treatment levels from the carbon system were set at 1 mg/L for discharge to the local sanitary sewer. The carbon system had many operational problems treating the ground water. Activated carbon has only limited affinity for MEK, thus the system was not able to consistently reduce MEK concentrations to less than 1 mg/L. In addition, odor problems developed within the system. Bacteria able to readily biodegrade the contaminants present in the ground water began growing on the activated carbon, depleting the water of dissolved oxygen. Without free oxygen, the bacteria then began using oxygen present in dissolved sulfates as a terminal electron acceptor, reducing sulfate to hydrogen sulfide. Hydrogen sulfide caused the characteristic "rotten egg" smell present in the system effluent.

Operational problems and costs associated with the carbon system led MEMOREX to investigate alternative ground water remediation technologies. Air stripping, steam stripping, and biological treatment system removal efficiencies and capital/operational expenses were compared in order to select a more permanent remediation technology.

Air stripping is usually the least expensive technology applicable to ground water treatment. However, air stripping is not efficient at removing chemicals that are highly soluble in water. MEK is such a compound. Steam stripping can be used to overcome stripping problems with soluble compounds, but at considerable added expense for high-temperature operation. Air strippers also have the inherent problem of merely transferring chemicals from a water phase to an air phase. In addition, air pollution concerns are beginning to severely limit the types and quantities of compounds that can be released into the atmosphere. The low removal efficiencies for MEK using standard air stripping equipment effectively removed this technology from further consideration. The high-temperature air stripper would require up to three times the capital cost, and up to ten times the operational cost, as that of a comparable biological treatment system.

Biological treatment systems, while initially more expensive than air stripping systems, offer complete destruction of contaminants to carbon dioxide and water. The major obstacle to biological treatment at the site was concern over system operation and performance.

BIOLOGICAL TREATMENT SYSTEM

DETOX, Inc. provided MEMOREX with a biological treatment system consisting of two H-50 submerged fixed-film biological reactors in series. The reactor design provides a high surface area inert plastic media as a support system for attached biological growth, and incorporated a built-in clarifier. A diagram of the H-50 bioreactor is shown in Figure 1. Bacteria attach as a film to the plastic surface, and grow at the expense of organic compbunds removed from water flowing past. Each reactor (12 feet square by 12 feet tall) was sized to handle a flow of 15 gpm and an organic loading rate of 50 pounds per day. By operating the reactors in series, the first unit could be operated to remove the bulk of the contaminants present, while the second unit would act as a biological polishing unit. Cartridge filters (to remove suspended solids) and two carbon units (each containing 600 pounds of carbon) followed the bioreactors to ensure that the final effluent met all applicable discharge criteria. The overall system was engineered so than one of the bioreactors could be bypassed or removed as the ground water contaminant concentration decreased over time.

Biological treatment systems require sufficient amounts of organic carbon, inorganic nutrients, dissolved oxygen, and an adequate pH to properly function. The contaminants in the ground water served as the source of organic carbon. Oxygen to the microorganisms was provided via submerged aerators, which also served to keep the contents of each bioreactor completely mixed. A concentrated



Figure 1. DETOX II-Series submerged fixed-film biological reactor.

inorganic nutrient solution containing stoichiometric amounts of nitrogen and phosphorus was metered into the reactors to maintain the nitrogen (as ammonia) concentration at 5-6 mg/L and the phosphorus (as orthophosphate) concentration at 3-4 mg/L. Dissolved oxygen concentrations were kept in the 2-4 mg/L range, and the pH was maintained between 7 and 8.

The biological treatment system required four weeks for complete start-up. A two week period was used to develop a bacterial population able to metabolize the compounds present in the water. In early June, the tanks were filled with ground water containing approximately 500 mg/L of MEK. The reactor was inoculated with 5 pounds of dried bacteria and 600 ml of concentrated nutrient solution. The treatment system was operated in a batch mode until analytical results showed that MEK levels had been reduced to discharge criteria levels. Foaming problems encountered during this period were eliminated by metering in low amounts of a liquid antifoam agent. Limited ground water treatment started in the third week of June. Influent analysis on June 11, 1986 showed MEK concentrations to the system were 510 mg/L. A total of 65,000 gallons of water were treated by the end of June. Detailed influent and effluent MEK concentrations for the month of June were not available for inclusion in this paper.

REVISED REMEDIATION SYSTEM RESPONSIBILITIES

It was clear from monitoring the MEK concentration in the well water that the contaminant concentration was dropping very quickly. If the trend continued, the overall biological treatment system would be underloaded with organic substrate. This would make one of the bioreactors super-fluous after only several months use. MEMOREX and DETOX personnel at this point evaluated the suitability of treating other plant waste streams with the system. The plant had the following additional solvent-contaminated wastes available for treatment: 1) The current solvent recovery scrubber blowdown system produced about 1-7 gpm of wastewater containing approximately 500 mg/L of cyclohexanone; 2) Equipment steam cleaning wastewater generated approximately 15,000 gallons per year containing approximately 10,000 mg/L miscellaneous organics; and 3) Miscellaneous solvent containing approximately 10,000 mg/L miscellaneous organics; and 3) Miscellaneous solvent 10,000 mg/L miscellaneous organics.

Previously, the solvent recovery wastes were discharged directly to the sanitary sewer. Concerns over future environmental liabilities and changes in environmental regulations limiting discharges to the sanitary sewer system suggested that the blow-down wastes would be a good candidate for on-site treatment. The equipment steam cleaning and miscellaneous wastes were previously disposed of offsite. Disposal costs and new regulations severely limiting off-site disposal of hazardous materials suggested that these waste streams should also be considered for biological treatment if they could be properly fed into the system.

MEMOREX and DETOX investigated the possibility of treating the aforementioned additional waste streams with the already installed ground water treatment equipment. The solvent present in the solvent recovery waste (cyclohexanone) was readily biodegradable, and in late June/early July the plant was repiped in order to introduce this waste stream into the treatment system. At this time a heat exchanger was also installed following the biological treatment system. Water passing through the exchanger qualified for classification as non-contact cooling water, and could be discharged with solvent concentrations as high as 5 mg/L. Solvent recovery wastes were not fed into the bioreactors until late July. The solvents present in the steam cleaning waste water and miscellaneous solvent wastes were also biodegradable, and this material was also periodically pumped into the biotreatment system.

Figure 2 presents a process diagram for the revised ground water/solvent wastes biological treatment system. Chemical analyses of the well water, treatment system influent, first bioreactor effluent, and second bioreactor effluent were performed twice a week (on the average). The major contaminants treated at the facility continued to be MEK and cyclohexanone.

RESULTS

The ground water MEK concentrations continued to rapidly decline. Analyses showed MEK at 72 mg/L on 22 July, 34 mg/L on 4 August, and 39 mg/L on 7 August 1986. Figure 3 shows the combined system influent and effluent MEK concentrations over the 34 week period in which contaminated ground water, solvent recovery process water, and miscellaneous plant solvent wastes were fed to the biological treatment system. Figure 4 shows the combined influent cyclohexanone concentrations for the same period. Lastly, Figure 5 presents total combined solvent influent and effluent concentra-



Figure 2. Process diagram for revised groundwater and solvent wastes biological treatment system.

tions. The total organic concentration includes acetone, tetrahydrofuran, toluene, ethyl benzene, total xylenes, and cyclohexanol in addition to MEK and cyclohexanone concentrations.

Overall, influent MEK concentrations were quite consistent, and ranging from 0 to less than 100 mg/L. Influent cyclohexanone concentrations, however, were extremely variable, and ranged from



Figure 3. Average weekly treatment system influent (n) and effluent (\bullet) MEK concentrations. Data from weeks 1-10 not available.



Figure 4. Average weekly treatment system influent (o) and effluent (•) cyclohexanone concentrations. Data from weeks 1-10 not available.



Figure 5. Average total organic treatment system influent (o) and effluent (\oplus) concentrations. Data from weeks 1-10 not available.

zero to as high as 700 mg/L. In spite of these wide fluctuations in influent concentration, the twostage biological treatment system consistently removed the contaminant to concentrations less than 5 mg/L. Typically MEK was removed to greater than 99% in the system, while cyclohexanone was removed to a slightly lesser extent. Infrequent excursions above the discharge limits were the result of organic shock loads applied to the treatment system, generally through the introduction of steam cleaning and miscellaneous solvent wastes containing high (approximately 10,000 mg/L) concentrations of contaminants. This problem has since been eliminated by more careful system loading and operational control.

The DETOX biological treatment system has been in continuous operation from start-up on 29 May 1986 through 30 March 1987. In that period, approximately 3,092,919 gallons of ground water and various solvent wastes have been successfully treated. Specifically, 2,537,089 gallons of ground water, 448,000 gallons of solvent recovery wastes, and 107,830 gallons of miscellaneous wastes were processed.

SYSTEM CAPITAL AND OPERATING EXPENSES

Total capital cost for the biological treatment system, with modifications to allow it to receive solvent recovery and miscellaneous solvent wastes, was \$207,500. This includes the two submerged fixed-film bioreactors, cartridge filters, activated carbon filters, pumps, blowers, concrete pad, stairs, heat exchanger, piping, and instruction in system operation.

Operating expenses can be divided into three major categories: DETOX service contract, MEMOREX supplies and monitoring, and MEMOREX personnel. Initially, DETOX supplied MEMOREX with a service contract allowing a total of 30 site visits for \$7,000. Since that time, a revised service contract at \$1,000 per month has been established. DETOX personnel visit the installation every other week to measure the concentration of dissolved oxygen, nitrogen, and phosphorus. In addition, personnel evaluate the day to day performance of the system and recommend any changes to the operation of the system.

MEMOREX supplies and monitoring expenses cover antifoam addition (one drum per month at \$600 per drum), nutrient addition (one drum every six weeks at \$500 per drum), laboratory testing (once per week at \$600 per test), and fees for discharge to the sanitary sewer (\$405 every six months). These costs total \$32,510 per year, or \$2,709 per month. Electricity to run the 5 horsepower blower runs approximately \$9.00 per day (based on \$0.10 per kwhr), or \$270 per month.

MEMOREX personnel time required for system operation and project management were kept at a minimum because of the design and type of remediation equipment used. Actual MEMOREX operator requirements are estimated to be 12 hours per week at \$35 per hour. This translates into a yearly total of \$25,480, or \$2,123 per month.

The capital cost for the equipment provided is \$67.60 per day or \$2,029 per month. This is based on a cost of \$207,000 depreciated over a 20 year period at a 10% interest rate. Assuming that electricity, nutrient solution, antifoam agent, DETOX service contract, and MEMOREX personnel time comprise the typical system operating expenses, and that 300,000 gallons of water are treated per month, the overall expense (capital and operating) per gallon for treatment is 2.1 cents. As noted previously, the capital cost of the biological treatment system was estimated to be onethird of the cost of a high-temperature air stripping system. In addition, operating expenses were estimated to be one-tenth of that of the high-temperature system. It is evident that the biological treatment system provided MEMOREX with significant cost savings in treating the contaminated ground water. However, the biological treatment system now successfully processes solvent recovery and miscellaneous solvent wastes produced at the plant. In terms of treating the solvent recovery waste stream, there is no direct cost savings because this material was previously discharged to the sanitary sewer. Indirect savings were obtained by eliminating the liability for discharging this material, and also expenses that would be incurred as future environmental regulations prohibited dumping of this material to the sewer. The steam cleaning solvent wastes and the miscellaneous solvent wastes were previously disposed of off-site, at a cost of \$1:00 per gallon. Thus treating these wastes on-site both reduces potential liabilities and has a direct cost savings of \$115,000 per year. This translates into a simple return on investment of 60%, with less than a two year payback for the system.

SUMMARY AND CONCLUSIONS

Ground water at the MEMOREX Computer Tabe Plant (Santa Clara, CA) contaminated with several organic solvents (primarily methyl-ethyl stone) was successfully treated using DETOX submerged fixed-film biological reactors. As the commination level in the ground water decreased, the plant piping and biotreatment system was reconfit and to allow it to receive both solvent recovery and miscellaneous solvent wastes produced at the factory. Combined waste stream organics in fluctuating concentrations as high as 700 mg/L could be consistently treated to less than 5 mg/L. The biological treatment system has successfully remediated approximately 3.1 million gallons of water over a 43 week period. On-site treatment of hazardous wastes has significantly reduced potential future environmental liabilities while allowing the company to save \$115,000 per year in off-site disposal costs.

'DECAY THEORY' BIOLOGICAL TREATMENT FOR LOW-LEVEL ORGANIC CONTAMINATED GROUNDWATER AND INDUSTRIAL WASTE.

George J. Skladany DETOX, Inc. 1600 Dove Street, Suite 408 Newport Beach, CA 92660

> Kevin M. Sullivan DETOX, Inc. P.O. Box 4735 Ithaca, NY 14852

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George J. Skladany DETOX, Inc. Newport Beach, California---

> Kevin M. Sullivan DETOX, Inc. Ithaca, New York

ABSTRACT

A "decay mode" biological submerged fixed-film reactor has been designed to treat groundwater and industrial waste waters containing less than 50 parts per million (ppm) total influent organics. The ability of this reactor to successfully treat organic concentrations below those generally thought to be amenable to biological treatment is based upon the application of microbial "decay", rather than "growth", processes. Briefly, a healthy biofilm initially grown at high organic concentrations within the reactor is able to continue scavenging organics from water after it has been switched to a feed consisting of low (<50 ppm) influent organics. Because very low organic concentrations are insufficient to support an actively growing biomass, the reactor biofilm slowly deteriorates (or decays) with time. When appropriate, the biofilm can be regrown in the reactor through exposure to high organic concentrations. Specific organic concentrations have been reduced from the parts per million to the low parts per billion range using this reactor design.

INTRODUCTION

Three of the most common remediation technologies for treating contaminated groundwater and industrial wastewaters are air stripping, carbon adsorption, and biological treatment. Air stripping is a mass transfer, rather than destruction, technology. Chemicals dissolved in water are brought into contact with large volumes of air, and the compounds with low water solubilities pass from the water phase into the air phase. As such, the contaminants removed from water are not actually treated, just transferred from one media to another. Chemicals highly soluble in water (such as acetone) are removed to only a limited extent. While air stripping has the advantage of being a relatively inexpensive treatment technology, increased concern over air pollution and its possible human health effects is limiting the applicability of air stripping technology.

Carbon adsorption is a natural process in which molecules of a liquid or gas are attracted and held at the surface of a solid. This physical attraction is caused by the surface tension of the carbon. Organic chemicals have different affinities for carbon, making carbon adsorption more applicable in some cases than in others. Carbon adsorption is also a separation technique, not a destruction technology. Spent carbon still retains the organic contaminants removed, and must itself be disposed of as a hazardous waste. Carbon systems have the advantage of being effective as soon as they go on line. However, costs for replacement carbon and disposal of spent carbon make this treatment technology relatively expensive. This is especially true if it is used to treat waters at both high flow rates and organic concentrations.

Biological processes (such as activated sludge, trickling filters, and rotating biological contacters) have been successfully used for many years to treat waters containing high (>50 ppm) concentrations of biodegradable influent organics. These treatment systems foster the aerobic growth of microorganisms in order to convert biodegradable contaminant mass into carbon dioxide, water, and additional biomass. Biological treatment of contaminated waters containing less than 50 ppm was not practical because these low organic concentrations generally would not support the growth of additional biomass. Thus aerobic processes were considered to have a lower influent threshold of approximately 50 ppm.

However, laboratory work by microbiologists and microbial ecologists showed that organisms can indeed degrade organic compounds to the parts per billion (ppb) range (1). New information about microbial processes that take place under low nutrient growth conditions also revealed that biofilm technologies have specific advantages when applied to the pollution control field. For example, healthy biofilms grown at a high specific organic concentration can effectively reduce the feed organic concentration down to some minimal level, usually designated as $S_{\rm min}$ (for minimal substrate level). If that biofilm is then switched to a feed concentration less than $S_{\rm min}$, the compound can continue to be effectively scavenged to concentrations far below $S_{\rm min}$. Under these conditions, however, the biofilm does not actively grow but rather decays with time (2). The decay method of treating water containing low contaminant concentrations was used as the basis of a research plan for the development of a functional "decay" biological reactor.

This paper describes the theory, development, field testing, and operation of a DETOX "decay" submerged fixed-film bioreactor designed to treat influent organic concentrations below 50 ppm. The non-conventional technology utilized capitalizes on the slow decay, rather than growth, of organisms present in a biofilm. A healthy biofilm is initially grown within the bioreactor using a liquid recirculation system and supplemental feed organics. When the biofilm has sufficiently matured, the recirculation system is disconnected, and the waste stream to be treated (containing low influent organic concentrations) is fed into the reactor. The decay submerged fixed-film technology is especially applicable to the remediation of hydrocarbon contaminated groundwaters, such as those typically found at sites containing leaking underground storage tanks.

DECAY THEORY

Decay theory of biodegradation is the culmination of biological advances made in understanding the growth of microorganisms under low nutrient conditions and also engineering advances made in the understanding of fixed-film processes. This section of the paper will attempt to briefly explain some of the fundamental biological/engineering processes involved.

Microorganisms possess a wide variety of metabolic capabilities and live under many different environmental conditions. While the almost endless diversity of microbial capabilities may seem confusing to someone unaccustomed to dealing with biological processes, all living organisms have the same basic goals. These goals are: first, to remain alive; and second, to grow and multiply if environmental conditions are favorable.

The state of being alive requires energy and organic/inorganic nutrients. Microorganisms use the organic/inorganic compounds found in their environment as food to supply themselves with energy and materials for new biomass. When environmental conditions are favorable, organisms continue to grow and multiply until conditions change. In general, the growth rate of an organism is proportional to the concentration of any required factor that limits growth. Assuming that all nutrients are present in excess, this growth limitation reverts to that amount of food (or substrate) available. Using batch culture experiments and non-inhibitory substrates, Monod was among the first to attempt to relate microbial growth rate to substrate concentration (3). He developed the empirical relationship:

$$u = u_{max} \frac{S}{K_s + S}$$

where: u = specific growth rate (units of 1/time),

- umax = maximum specific growth rate (units of 1/time),
- S = concentration of growth limiting nutrient in solution (units of mass/unit volume),
- K_s = half-velocity constant, that is the nutrient concentration at one-half of the maximum growth rate (units of mass/unit volume).

The growth rate/substrate concentration relationship is shown in Figure 1. At low substrate concentrations, the growth rate is also low. As more substrate becomes available (as S increases), the microbial growth rate increases until some maximum growth rate (u_{max}) is attained. Later research has shown that two major types of microorganisms exist: those with high growth rates requiring high substrate concentrations (these organisms have high K_S values), and those with low growth rates that grow best at low substrate concentrations (as low as 1 mg/L per day; these organisms have low K_S values) (4, 5).

These findings have several important implications for the pollution control field. First, treatment of low concentrations of organics will most likely be performed by microorganisms that grow very slowly. It is important therefore to engineer bioreactors that are able to maintain slow growing biomass within the treatment system. Fixed-film systems can maintain sludge ages of 20 to 100 days, as compared to 4 to 20 days for most activated sludge systems with recycle. This corresponds to growth rates (in units of 1/day) of 0.3 or less, compared to 0.3 to 1.2 for the aforementioned activated sludge systems (6). In addition, growth under low nutrient conditions seems to favor microbial attachment to surfaces, where substrate organics may accumulate (7). This finding also supported the idea that fixed-film processes may be ideal in the treatment of waters containing low concentrations of organics.

Rittmann and McCarty developed a biofilm model for treating low organic concentration solutions such as those found in groundwater (8, 9). The model considered mass transfer of the substrate through the bulk liquid to the biofilm, diffusion of substrate through the biofilm, biological utilization of the substrate, growth of the biofilm, and decay of the biofilm. They predicted that the concentration of substrate needed to keep the biofilm in a steady-state (that is, no net gain or loss in the biofilm) condition is given by:

$$S_{min} = K_S \frac{b}{Yk - b}$$

where: Smin = the minimum substrate concentration (units of mass per volume),

 $K_S =$ the Monod half-velocity constant (units of mass per volume),

b = the specific decay rate for the biofilm (units of 1/time), and

Y = true cell yield (mass of cells produced per mass of substrate removed), and

k = maximum specific utilization rate (units of mass of substrate removed per mass of bacteria per time).

Laboratory biofilm reactors using 3 mm glass beads held in a 12 cm long by 2.5 cm diameter glass columns were constructed. Once a healthy biofilm had been established, the fixed-film bioreactors received a feed solution containing a target chemical (such as acetate) as a substrate source. Biological activity occurring in the column as the water passed through the reactor reduced the contaminant concentration down to a limiting minimal concentration (S_{min}) in good agreement with their steady-state model predictions (8).

However, if the bioreactors were operated under nonsteady-state conditions in which the feed substrate concentration was below the S_{min} value, the biofilm was able to effectively scavenge the feed organic to concentrations much less than S_{min} (2, 9). A nonsteady-state biofilm process using galactose as a substrate was able to sustain good (greater than 85%) removal of trace substrate concentrations for one year without the need to regenerate the biofilm (2). An example of acetate removal under both steady and nonsteady-state conditions from Rittmann's work is shown in Figure 2 (9).

While the theoretical basis for nonsteady-state biofilm treatment of organics was being established, laboratory and pilot-scale work on the development of submerged fixed-film bioreactors to treat high levels of organics was also progressing (10 and 11, for example). Submerged fixed-film reactors were small, easily portable, resistant to shock loads, and required a minimal amount of operator attention.

DETOX, Inc. saw that successful development of a decay (or nonsteady-state) submerged fixed-film bioreactor would offer new opportunities for the pollution control field in treating groundwater and industrial process waters contaminated with low levels of organics. The next sections of the paper present data obtained during development of the reactor, as well as results obtained during pilot and full-scale field application of the treatment system.

LABORATORY DEVELOPMENT OF DECAY REACTOR

A laboratory reactor using stacked packing material as a support for biofilm growth was designed. The test column was 0.3 feet in diameter and 6 feet tall. Water pumped to the reactor was initially saturated with oxygen through the use of air stones placed in a holding tank. Water pumped from the holding tank received metered amounts of a concentrated organic feed stock solution. Water flowed down through the column while air introduced into the bottom of the reactor passed up and out.

Approximately two months were required to initially establish a benzene degrading biofilm within the stacked-pack reactor. Over the next 200 days, the reactor was used to test the effects that hydraulic retention time, air flow rates, and other parameters had on the biodegradation of low (<10 ppm) concentrations of benzene and methyl ethyl ketone (MEK).

The overall results obtained using benzene as the target substrate are shown in Figure 3. Over the initial 108 day test period, the flow rate of water to the reactor was increased from 2.5 to 10 gallons per hour (gph) while maintaining a relatively constant benzene concentration. From days 0 to 31, the reactor received a flow of 2.5 gph, corresponding to a hydraulic retention time within the bioreactor of 90 minutes. Different air flow rates were tested during this period, and overall benzene removal rates greater than 96% were attained. The reactor was next operated (days 32-49) at a flow of 3.5 gph, giving a hydraulic retention time of 64 minutes. As before, different air flow rates were tested, and removal efficiencies of greater than 97% were observed. A flow rate of 5 cph (hydraulic retention time of 45 minutes) was tested for a little over one week (days 50-59), with greater than 98% benzene removal. The flow rate was next increased to 7.5 gph (hydraulic retention time of 30 minutes) for 4 weeks (days 60-90), and the system continued to achieve excellent (98%) benzene removal rates. However, nutrient addition to the bioreactor was stopped on day 88. Finally, the water flow rate was increased to 10 gph (23 minute hydraulic retention time) for over 2 weeks (days 91-108). Treatment efficiencies dropped to approximately 92% during this period, presumable due to both the lower hydraulic retention time and changes in other operational parameters. Overall, average benzene removal efficiencies of greater than 96% were attained during the 108 day test. This was achieved in spite of fluctuations in organic concentrations, air flow rates, and water flow rates.

After this first round of benzene experiments was completed, the biofilm within the reactor was regrown in anticipation of the second round of tests investigating the biodegradability of low concentrations of MEK. Flow to the reactor was reduced to 2.5 gph for 4 weeks, and benzene was again fed into the reactor.

The test reactor was then operated for 9 weeks at MEK concentrations of 2-10 ppm and flow rates of 2.5-4.5 gpm (corresponding to hydraulic retention times of 90 and 45 minutes, respectively). Removal efficiencies were consistently greater than 98% throughout the test, as shown in Figure 4.

Data obtained during the bioreactor laboratory development period confirmed that biological decay processes could be effectively used to treat low concentrations of environmentally significant chemicals. Reaction rates were sufficiently fast so that hydraulic retention times as low as 30 minutes could be used for treatment. Air flow and inorganic nutrient concentration feeds rates were also important factors to consider when optimizing the treatment process (data not shown). Thus the theory and technology associated with biological decay reactors appeared to be viable, and awaited field testing under real world conditions.

FIELD PILOT TESTING OF REACTOR

An opportunity arose to pilot-test a prototype decay reactor in the field at an industrial site in New Jersey. Water discharged from the facility periodically exceeded discharge standards set for benzene (200 ppb), Biochemical Oxygen Demand (BOD5), and Total Suspended Solids (TSS). It was hoped that the bioreactor could consistently reduce benzene levels to below 200 ppb and also reduce BOD concentrations.

Water from the facility consisted of both contaminated groundwater and various plant process waters, including well filter backwash and cooling tower wash waters. The actual total organic and inorganic composition of the water was not available. It was known that benzene concentrations typically varied from 240-1,400 ppb. A diagram of the prototype DETOX reactor used at the site is shown in Figure 5. The pilot study was conducted over a 75 day period (December 1986 to February 1987), and tested the effects of 3 different hydraulic retention times and 2 different mixing schemes within the reactor. Data from the study is presented in Figure 6.

Overall, benzene removal efficiencies of greater than 89% were attained. For the first 37 days of the test, the reactor was operated in a plug-flow mode with an influent flow of 4-5 gph, giving a hydraulic retention time of approximately 90 minutes. From days 38 to 61, the reactor operated in a plug-flow mode at 2.0-2.5 gpm, or a hydraulic retention time of approximately 180 minutes. Lastly, aeration to the reactor was increased and the system was operated for 14 days in a completely mixed fashion at a flow rate of 1 gph (hydraulic retention time of 360 minutes). Benzene removals throughout the test were consistently good, but BOD, COD, and TSS values varied widely and did not meet discharge criteria (data not shown).

Upon further evaluation of the test results, it appeared that the plant water treated was inhibitory to suspended growth microorganisms, and that the fixed-film system actually succeeded in reducing at least part of the inhibition. This hypothesis was supported by routinely finding higher BOD concentrations in water tested after treatment (data not shown). While the prototype system could not meet the dual demands of the client (both benzene and BOD reductions), it did demonstrate that the decay biological reactor could effectively treat low concentrations of environmentally significant chemicals under real-world conditions.

FULL SCALE TREATMENT OF HYDROCARBON-CONTAMINATED GROUNDWATER

CALE

Improvements were made to the design of the decay biofilm reactor following the field pilot testing. In January 1987, one of the first DETOX L-Series decay submerged fixedfilm reactors was used to remediate a site in California (south of San Francisco) in which groundwater became contaminated with gasoline as the result of a leaking underground storage tank. The client believed that total organic concentrations would be in the 25 ppm range with flow rates less than 5 gpm. The proposed treatment system consisted of a groundwater recovery well, above ground oil-water separator, bioreactor, sump, roughing filter, and activated carbon polishing filter. The activated carbon filter was needed to meet the stringent California water discharge criteria, such as effluent benzene concentrations of 0.7 ppb or less.

The DETOX L-6 reactor was installed and started up in early 1987. When the treatment system was put on line in March of 1987, influent total hydrocarbon concentrations were in the 250-270 ppm range, far above the maximum design concentration of an L-Series reactor (25-50 ppm). However, the bioreactor was able to adapt to the higher organic concentrations by functioning as a growth reactor, not as the anticipated decay reactor. Since March, the influent total hydrocarbon concentration to the system has steadily declined, and in June typical concentration values were approximately 50 ppm. Throughout the 100 days of operation thus far (18 March 1987 to 20 June 1987), the system has removed greater than 90% of the total hydrocarbons present. Also during this period, benzene concentrations were reduced by more than 93%, toluene concentrations by more than 96%, and xylene concentrations by more than 91%. Operating data for total hydrocarbon and benzene removal are shown in Figures 7 and 8, respectively.

It is important to realize that accurate design data (such as influent organic concentration) is frequently unavailable when treatment equipment is sized and sold. Thus a treatment system that has flexibility in terms of handling influent concentrations and flow rates may not only be desirable but required. As groundwater pumping continues at this site, influent organic concentrations are expected to continue to decline. As they do, the biological processes within the reactor will shift from growth to decay mode. This will allow effective treatment to continue at the site using the same treatment equipment. However, since growth mode reactors cannot typically reduce specific organics to the low ppb range, larger amounts of activated carbon will be used for polishing as long as the reactor is operated in the growth mode.

Decay reactors use aerobic biofilm processes, and must be supplied with minimal amounts of air during operation. Because of strict air emission requirements in California, state regulatory personnel were concerned than some of the volatile gasoline groundwater contaminants were being removed by air stripping, rather than biological, processes. Off gases emanating from an air vent in the top of the covered bioreactor were sampled in triplicate on 3 June 1987 for total hydrocarbons, carbon dioxide, and oxygen using Source Test Method 1-100 of the California Air Resources Board. Carbon dioxide from the reactor was continuously monitored for three 30 minute periods using a Horiba Model PIR-2000 NDIR carbon dioxide analyzer. Total hydrocarbons were quantitated similarly using a Beckman Model 400 Hydrocarbon analyzer, and oxygen concentrations were quantitated with an Infrared Industries Model 2200 Oxygen analyzer. Estimated air flow rates from the system were 1 cubic feet per minute (CFM). Total hydrocarbon concentrations (as C-1) were determined to be 300, 371, and 423 ppm. Methane concentrations were measured at 2, 2, and 2 ppm. Total nonmethane hydrocarbons (as C-1) were measured at 298, 369, and 421 ppm. Oxygen concentrations were close to normal (21.6, 20.2, and 20.6%), and carbon dioxide concentrations varied (0.32, 0.60, and 0.95%). Total hydrocarbons (as C-1) released to the environment averaged 0.000678 pounds per hour. Total non-methane hydrocarbons (as C-1) released to the environment averaged 0.000678 pounds per hour.

Unfortunately, a mix-up with the water sampling crew occurred, and water samples were not taken while the air monitoring was being done. This prevented a total contaminant mass balance analysis from being performed on the treatment system. Water samples taken the next day (4 June 1987), however, can provide at least an estimate as to the treatment efficiency of the system. Assuming that contaminant concentrations were approximately the same over the 48 hour period, 0.44 pounds of total hydrocarbons were calculated to have passed through the system per day at a flow rate of 1.94 gpm and a total hydrocarbon concentration of 19 ppm (This value for hydrocarbon (as C-1) value released to the atmosphere of 0.000678 pounds per hour, approximately 0.0162 of hydrocarbons are released into the air per day from the bioreactor. This corresponds to an air stripping rate of approximately 3.68%. The minimal rates of air flow to the biotreatment system help to ensure that readily biodegradable volatile organics are biodegraded, not air stripped.

Concern over the limited air discharge from the site does not appear to be warranted at this time, as the performance of the bioreactor was evaluated and approved by the appropriate California regulatory personnel. Further treatment of off gases was not deemed to be necessary.

CONCLUSION

Decay fixed-film reactors can be designed and operated in to biodegrade low (<50 ppm) influent organic concentrations. These low starting concentrations are below the treatment thresholds associated with typical biological growth mode reactors.

Expanding on concepts developed for nonsteady-state biofilms, a healthy biofilm is initially grown within the reactor using a water recirculation system and high influent organic concentrations. Once the biofilm is established, the reactor can be switched to a feed containing low organic concentrations, and the biomass can continue to reduce these compounds to the low ppb range. With time, this biofilm slowly decays, and must eventually be regrown to continue effective treatment.

DETOX, Inc. has developed, tested, and installed submerged fixed-film reactors utilizing the biological decay concept. Benzene, toluene, xylene, methyl ethyl ketone, and petroleum constituents are especially amenable to remediation using this technique. The ability of the decay reactor to treat low influent organic concentrations, such as those typically found in groundwater or dilute industrial process waters, makes it a valuable tool for use by the pollution control field.

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Limiting Nutrient Concentration, S

Figure 1. Monod growth kinetics showing relationship between growth rate (u) and limiting nutrient concentration (S). K_Sis the nutrient concentration at one-half the maximum growth rate (u_{max}).



Figure 2. Examples of acetate removal under both steady-state and unsteady-state biofilm conditions. Figure 2-A shows that under steady-state conditions, acetate concentrations can be reduced from 7.6 ppm to an min concentration of approximately 0.7 ppm. Figure 2-B shows the same biofilm under nonsteady state conditions. Influent acetate concentrations of 0.76 ppm can be reduced to less than 0.2 ppm. min is denoted by dashed line in each graph. Adapted from Rittmenn and McGarty (9).





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Figure 4. MEK removal during laboratory bioreactor development. Keÿ: influent MEK (©); effluent MEK (O).





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Days of Operation



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Figure 8. Benzene removal using DETOX L-6 Bioreactor to treat gasoline contaminated groundwater. Key: Influent benzene (Φ); affluent benzene (O).

Biological Treatment of Groundwater, Soils, and Soil Vapors Contaminated with Petroleum Hydrocarbons

by

Edward G. Galaska George J. Skladany and Evan K. Nyer

> DETOX, Inc. Dayton, Ohio

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Edward G. Galaska George J. Skladany and Evan K. Nyer

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INTRODUCTION

Leaking underground storage tanks and pipelines have recently become one of the most widespread and talked about environmental problems. Across the country, service station gasoline storage tanks are being tested for leaks and replaced as either necessity or as precaution dictates. While the total number of underground storage tanks is unknown, it is estimated to be in the vicinity of 1.4 million tanks and, of these tanks, between 10 and 30 percent are thought to have leaked gasoline into the ground (1). For a leak to be considered a contamination problem, at least 1,000 gallons of gasoline has usually been spilt. Leaks of up to 270,000 gallons have been reported, and leaks in the range of 20,000 to 50,000 gallons are not uncommon. Most of this gasoline has contaminated the subsurface soils and groundwater, and in many cases poses a major threat to drinking water supplies, since a single gallon of gasoline can render 1,000,000 gallons of water unsuitable for consumption.

In most cases, the cleanup operation at petroleum contaminated sites involves the remediation of groundwater, soils, and air emissions. Typically, heavily contaminated soils are excavated and incinerated or transported to secure landfills. The remediation of contaminated groundwater and air emissions has focused primarily on air stripping and carbon adsorption technologies. Although both of these technologies have had varying degrees of success, each has limitations in removing all of the organic compounds commonly found in petroleum products. In addition, both of these technologies are considered to be non-destructive, meaning that the contaminants are not destroyed but simply transferred to another medium (air and/or carbon) requiring further treatment. Biologic methods have had wide application in the remediation of sites contaminated with petroleum hydrocarbons. This technology uses the action of naturally occurring microorganisms to aerobically metabolize the contaminants present, usually converting the organic compounds into carbon dioxide, water, and additional bacteria. Above-ground and in-situ biological treatment of contaminated gasoline service stations and oil terminals has been quite successful, since most petroleum constituents are biodegradable. Further, biological treatment can cost-effectively and efficiently destroy the specific hydrocarbons present, thus eliminating potential future liability problems associated with other remediation technologies. This paper will present several case histories describing the biological treatment of petroleum hydrocarbon contaminated groundwater, soils, and air emissions.

PROPERTIES OF PETROLEUM HYDROCARBONS

The most common petroleum products contaminating soils and groundwater are gasoline, diesel, and fuel oils. While these products are generally spoken of as single entities, each is actually a complex mixture of many organic chemicals. Figure 1 (2) shows some of the major petroleum hydrocarbon constituents as they would appear in a gas chromatograph separating compounds by increasing the bolling point. Each of these specific compounds has its own properties and behavior when in contact with soils and water. For example, gasoline contains a mixture of chemicals with bolling points less than decane (C-10) and within the range (rom 36° to 173°C. More specifically, gasoline contains relatively large concentrations of the aromatic compounds benzene, toluene, and the xylenes (BTX). In comparison diesel fuels consist primarily of higher boiling-point straight chain alkanes. Therefore sites contaminated with diesel fuel would not be expected to contain high concentrations of aromatic compounds (3).

Above-ground or in-situ biological remediation of petroleum contaminated soils and waters must address the specific organic compounds present. The physical, chemical, and biological properties of these chemicals in a complex petroleum product have a major effect on the distribution of the compound in a soil/gas/liquid matrix. The problem with remediating a site contaminated with petroleum products is that not all of the chemical constituents of "gasoline" can be found in each of the three different phases. The organic compounds that make up gasoline and have low solubility, low volatility, and strong adsorption characteristics, will be most prevalent within the site soils (3). The compounds with high solubility will be most prevalent in the aquifer, and the compounds with relatively high volatility will be found in the soll gases and the atmosphere. This is why, in most cases, the complete remediation of petroleum contaminated sites involves the combined treatment of the groundwater, soils, and air emissions.

It is important to point out that most regulatory agencies require only BTX concentrations be monitored at sites involving petroleum hydrocarbon contamination. From an environmental point of view these aromatic compounds are the most important group of chemicals contained in petroleum.

ASPECTS OF BIOLOGICAL TREATMENT

The basis of all biological treatment methods is the use of microorganisms to convert soluble organic compounds into insoluble organic material (more bacteria). Under aerobic conditions this process will also produce carbon dioxide and water to the environment (see Figure 2). Thus, biological methods are considered to be true destruction processes by which the contaminants are permanently remediated and require no further treatment.

For biological treatment to be effective, a proper growth environment for the bacteria must be created. Major factors to consider include pH, oxygen concentration, influent organics concentration, concentration of inorganic nutrients (primarily nitrogen in the form of ammonia and phosphorus in the form of orthophosphate), temperature, and the absence of high concentrations of toxic and/or inhibitory compounds (4). In order for any biological treatment system to perform properly, it is important that the <u>only</u> limiting factor for biological growth should be availability of the organic food source. All nutrients and oxygen should be available in excess of that required for metabolism of the available substrate. Environmental conditions of temperature, pH, absence of heavy metals, etc. should be in reasonable ranges to ensure successful operation and biological growth and optimum treatment efficiency.

BIO-REMEDIATION OF GROUNDWATER

There are two major strategies employed to remove petroleum hydrocarbons from contaminated aquifers: pump and treat in above-ground systems and in-situ bioremediation. The latter of these methods, in-situ bioremediation is frequently an effective technique because all of the compounds are biodegradable. Conversely, one of the advantages of treating the contaminated groundwater in above-ground systems is the ability to constantly maintain optimal growth conditions for the bacteria. In either case, both treatment methods require the addition of supplemental nutrients, dissolved oxygen, and the maintenance of several environmental factors (pH, temperature, etc.) to work efficiently.

DETOX employs above-ground aerobic submerged fixed-film biological treatment systems (H-Series and L-Series) to remediate groundwater contaminated with petroleum hydrocarbons. The H-Series units are designed to treat contaminated water supplies containing from 50 to 10,000 ppm as BOD (Biochemical Chemical Oxygen Demand), while the L-Series bioreactors are designed to treat water contaminated with less than 25 ppm total organics. These systems are more efficient than conventional activated sludge processes bedause they are resistant to shock loads, require minimal operator attention, and have low operating expenses. Further, they can assure treatment of an entire flow stream when discharge to sewer, stream, or re-injection into the ground is required. All of these factors are important when deciding upon a cost-effective and environmentally sound remediation method.

Above-ground biological processes (such as activated sludge, trickling filters, and rotating biological contactors) have been successfully used for many years to treat waters containing high concentrations (greater than 50 ppm) of biodegradable influent organics. These treatment systems foster the aerobic growth of microorganisms in order to convert biodegradable contaminants into carbon dioxide, water, and additional biomass. Biological treatment of contaminated waters containing less than 50 ppm was, in the past, not practical because these low organic concentrations generally would not support the growth of additional biomass. Thus, aerobic processes were considered to have a lower influent threshold of approximately 50 ppm (5).

Within the past five years, DETOX has developed a decay-mode submerged fixed-film bioreactor (L-Series) designed to treat influent concentrations below 50 ppm (Figure 3). This non-conventional technology capitalizes on the slow decay, rather than growth, of organisms present in a biofilm. A healthy biofilm is initially grown within the bioreactor using a liquid recirculation system and supplemental feed organics. When the biofilm has sufficiently matured, the recirculation system is disconnected, and the waste stream to be treated (containing low influent organic concentrations) is fed into the reactor (5). Since most petroleum hydrocarbon-contaminated groundwaters usually contain soluble organics from 1 to 50 ppm, L-Series bioreactors are especially applicable at sites where this type of contamination exists. In addition, these systems can treat the contamination at 1/10th to 1/40th the cost of activated carbon methods. The following case studies illustrate the effectiveness of these above ground biological systems in remediating groundwater contaminated with petroleum hydrocarbons.

Case Study #1

Groundwater and soils at a gasoline service station in West Virginia were contaminated with petroleum hydrocarbons as the result of an underground storage tank leak. DETOX was contracted by the consulting firm involved with the investigation to determine the most cost-effective treatment system for remediation of the contaminated groundwater.

The organic concentrations measured in the groundwater were less than 25 ppm total BTX. The flow rate of this system was estimated to be at 10 gpm (gallons per minute). State EPA officials set effluent ground water criteria for this treatment process at less than 150 ppb (parts per billion) total BTX. In addition, any contaminated air emissions from the treatment system must be remediated prior to discharge into the atmosphere.

Under this set of guidelines the most cost-effective technology available to remediate the contamination was biological treatment. The system selected to treat the contaminated groundwater was an L-6 bioreactor, designed to handle a 6 gpm flow rate. Figure 4 illustrates the influent and effluent concentrations by compound of BTX which were measured in the groundwater during 140 days (5 months) of system treatment. The influent groundwater concentration of total BTX compounds remained relatively constant during this period at between 17 and 20 ppm. Effluent total BTX concentrations have been consistently measured at less than the required 150 ppb (parts per billion) discharge level. Comparison of the two sets of results indicates that the biological treatment system installed at this site was successful in removing over 99.3 % of the BTX compounds found in the groundwater.

Case Study #2

Groundwater and soils at a gasoline service station in Michigan were contaminated with petroleum hydrocarbons as the result of an underground storage tank leak. The groundwater remediation was to be addressed separately from the soil contamination. DETOX was contracted by the property owner to evaluate and provide the most cost-effective treatment system for remediation of the contaminated groundwater.

The groundwater contained 2 to 5 ppm each of benzene, toluene, and the xylenes, or less than 20 ppm total BTX. The flow rate of the system was estimated to be at 25 gpm maximum. The Department of Natural Resources for the state of Michigan set effluent ground water criteria at less than 20 ppb. In addition, any contaminated air emissions from the treatment system must be remediated prior to discharge into the atmosphere.

DETOX selected biological treatment as the most cost-effective technology for remediation of the groundwater. Although air stripping alone would have been the least expensive technology, the air emission limitation would have required vapor phase carbon to treat highly contaminated air stripper discharge gases, thereby significantly increasing the cost of the treatment.

The system selected to treat the contaminated groundwater was an L-20 bioreactor, designed to handle a 20 gpm flow rate. Figure 5 illustrates the influent and effluent concentrations by compound of BTX which were measured in the groundwater during 250 days (8 months) of system treatment. Influent groundwater concentrations of total BTX compounds ranged from 8 ppm at the start of the cleanup down to approximately 2 ppm after 8 months. Effluent total BTX concentrations were consistently measured at 5 ppb or less. Comparison of the two sets of results indicates that the biological treatment system installed at this site was successful in removing over 99.9 % of the BTX compounds found in the groundwater.

BIO-REMEDIATION OF SOILS

The use of contained land farming methods or in-situ biological treatment to remediate soils contaminated with petroleum hydrocarbons has been well documented. The basis behind both of these treatment methods is identical to other types of bioremediation technologies. A suitable environment is established for the indigenous microorganisms present in the soil, i.e. proper pH, inorganic nutrient levels (ammonia and phosphorus), and oxygen. In the case of land farming this process is performed after the contaminated soil has been excavated and removed to a contained area. For in-situ biological treatment the soil is treated on site.

The application of biological methods for soils remediation must be approached with caution however. Previous work has shown that not all soils are applicable to bioremediation technology. For this reason, subsurface conditions at the site should be investigated prior to implementing any type of biological treatment to determine if this technology is feasible. Whether land farming methods or in-situ treatment is being considered to remediate the contaminated soils, certain environmental parameters (moisture content, inorganic nutrient levels, etc.) must be determined.

Laboratory treatability work will help to develop clean-up strategies in a very cost-effective manner. These studies determine the basic microbiological as well as the physical/chemical growth conditions present at a site. They are designed to investigate whether the contaminated site already contains indigenous organisms able to degrade petroleum hydrocarbons, as well as determine if the biodegradation rate can be enhanced by improving site subsurface conditions. This information is needed in order to evaluate if biological treatment should be considered as a possible remediation technology. The following case study illustrates the importance of this approach.

Case Study #3

A petroleum hydrocarbon spill has resulted in the contamination of 35 to 40 square yards of surface soil. The use of in-situ biological treatment is under consideration due to the biodegradable nature of these compounds. To determine if biological methods would be successful in reducing petroleum hydrocarbon concentrations at this site an aerobic laboratory treatability study was conducted.

This study was set up to determine the effect that aeration and/or addition of supplemental inorganic nutrients would have on bioremediation processes within the contaminated soil. Soil samples collected from three pre-determined locations at the site were homogeneously mixed and separated into four portions and labeled as "control", "poison", "aeration only", and "aeration and nutrients". The sample labeled as "control" was left undisturbed throughout the duration of the project. The "poison" sample served as the negative biological control and was sprayed with a mercuric chloride solution the first two days of the study. The sample labeled as "aeration only" was aerated daily by simple hand mixing, while the "aeration and nutrient" sample was aerated daily and sprayed occasionally with an inorganic nutrient solution containing nitrogen and phosphorus. The moisture content of all of the soil samples was kept constant by the periodic addition of sprayed water.

Samples collected during the fourteen week study were each analyzed for the total number of indigenous microorganisms present, the total number of hydrocarbon degrading bacteria present, and petroleum hydrocarbon concentrations. Along with these analyses, each soil was tested for pH and soluble ammonia and orthophosphate concentrations. Figures 6 and 7 summarize the total plate counts and the hydrocarbon degrader plate counts received for each soil over the length of the study (14 weeks). Figure 8 illustrates the petroleum hydrocarbon concentrations measured in the soils over time (EPA Method 418.1). For the "control", "poison", and "aeration only" soil samples the number of indigenous and hydrocarbon degrading bacteria was similar and relatively constant. Petroleum hydrocarbon concentrations for these three soils ranged from 35,000 to 45,000 ppm (mg/Kg) initially, and eventually dropped to levels between 30,000 and 35,000 ppm after 14 weeks. The "aeration and nutrient" soil sample, which had been supplied inorganic nutrients as well as being aerated, contained significantly lower numbers of indigenous and hydrocarbon degrading bacteria after 14 weeks. Further, the concentration of petroleum hydrocarbons present in this soil had dropped to approximately 10,000 ppm, corresponding to a 75% removal, indicating that biological treatment had occurred and was somewhat successful.

The results obtained from this study indicate that biological treatment of the petroleum contaminated soil should be considered. Also, the bioremediation process may be enhanced by the use of supplemental nutrients such as oxygen, nitrogen, and phosphorus.

BIO-REMEDIATION OF AIR EMISSIONS

At the present time several technologies produce contaminated air streams as a result of their actions. For example, in-situ soil venting systems can cost effectively remove many volatile organic compounds from the subsurface, as can air stripping of contaminated waters. Increasingly, however, notable contaminants now present in the off gases must be treated, not discharged directly to the atmosphere. The most common treatment technologies for the contaminated air streams are vapor phase activated carbon or incineration. Each of these technologies can become very expensive, in essence negating the the cost advantages usually associated with soil venting and air stripping. Since many volatile compounds are known to be biodegradable, specifically BTX constituents, it seems logical to attempt to develop an above ground biological reactor to treat air stream contaminants.

The biological degradation of hydrocarbons from air streams is roughly analogous to the biological unit processes (e.g., trickling filters, activated sludge units, etc.) which degrade hydrocarbons in water. In both cases, bacteria are provided with both a hospitable environment (in terms of oxygen, temperature, nutrients, and pH) and a carbon source for energy. The bacteria utilize these favorable conditions to metabolize the carbon source to its primary components (i.e., carbon dioxide and water). The result is a "clean" water or, in this case, an air stream (6).

The use of biological degradation for waste waters has been established for the past century. Research into the biological treatment of air stream materials is a relatively recent occurrence, existing for only the past thirty years. Many applications of this technology have been developed in European countries, where soil or peat was used as the biological filtering media (6). In the U.S. this type of technology has recently been licensed for application in the hazardous waste field (7). DETOX has decided to pursue a different track, employing biofilm technology to treat air emissions contaminated with petroleum hydrocarbons.

Bio-Airtower Research Project

The prototype DETOX air stream bioreactor (bio-airtower) was designed similar to an air stripping unit, as shown in Figure 9. High surface area inert plastic media within the column was used to support the biofilm growth. Water containing inorganic nutrients was recirculated over the packing material in order to keep the biofilm moist and provide a working medium for biological degradation. The carbon source for the system was provided in the form of contaminated air produced from a gasoline service station soil venting project. The air was introduced into the bio-airtower unit at the bottom and forced up through the column for treatment.

The initial microbial population within the bio-airtower was established by inoculating clean sump water with hydrocarbon degrading bacteria, inorganic nutrients (primarily nitrogen and phosphorus), and a suitable food source. Petroleum products and chemical structural analogs served as the carbon food source during this growth phase, which lasted approximately one month. After a sufficient biofilm was established with water recirculation, actual soil vented air was introduced into the column and testing procedures were started.

Unfortunately, like in all new equipment development, the mechanical and operational problems had to be initially worked out. During this period, however, the hydrocarbon concentrations in the soil venting gases decreased significantly and prevented the wells from being used. In order to maintain high gasoline vapor concentrations throughout the tests, the equipment was modified to continuously ingest small quantities of vaporized gasoline into the bio-airtower influent air line. The hydrocarbon concentration was maintained at a constant level for a three week period prior to sampling the unit.

The sampling and analytical methods chosen to test the efficiency of the system were both NIOSH and EPA approved. The method of sampling involved the use of charcoal trap tubes to capture the contaminated material over a set period of time (usually 30 minutes). The specific organic compounds were then identified and quantitated by approved gas chromatography methods.

The first operational tests on the bio-airtower were conducted in March, 1989. Once system stabilization was achieved, three major factors were tested for their effects on air stream bioremediation efficiency. The factors investigated were sump water recirculation rate, influent air flow rate, and influent hydrocarbon concentrations. Changing the water recirculation rate and influent concentration appeared to have very little effect on either the BTX or total petroleum hydrocarbons percent removal, so these variables will not be discussed further.

The most important variable affecting petroleum hydrocarbon removals in this system appears to be air flow rate. The contact time between the airborne contaminants and the biomass is very limited in this type of system. Therefore it is not unreasonable to assume that a minimal air residence time would be required for effective treatment. The unit was tested at flow rates of approximately 10 and 17.4 CFM (cubic feet per minute). Table 1 presents the percent removals of BTX and total petroleum hydrocarbon compounds from the contaminated air stream. Its obvious from the data listed that the percent removal for both BTX and total petroleum hydrocarbons approximately doubled when the air flow rate through the bloairtower was lowered. Specifically, BTX removal increased from approximately 40.8% up to 74.5%, and total petroleum hydrocarbon removal increased from approximately 30.6% up to 60.8% after the flow rate was lowered. This finding supports the initial theory that the removal efficiency will be dependent on residence time through the column.

This preliminary investigation of the operational parameters of the system has only recently been concluded. However, data received from these initial tests indicate the overall effectiveness of using biological treatment on compounds not very soluble in water. The next step is to set the system to run at 10.4 CFM with steady influent concentrations (HNu instrument \bullet 165 mg/L) for several weeks to collect additional data about reliability and operational costs. After this period the design of the system will be modified to optimize removal efficiency.

SUMMARY

In summary, it is quite apparent that biological processes are increasingly applicable to the remediation of contaminated ground and industrial process waters, soils, and air streams. The use of this technology to remediate sites contaminated with petroleum hydrocarbons is a logical choice, considering that most of the constituents are readily biodegradable. Organic compounds thought of as being non-susceptible to bioremediation, specifically the chlorinated aliphatics, have also been metabolized in these systems (non-specific biodegradation) when they are treated in a mixture with other biodegradable contaminants. Further, biological treatment can cost-effectively and efficiently destroy the specific hydrocarbons present, thus eliminating potential future liability problems associated with other remediation technologies.

The application of this technology has been limited however, primarily due to the lack of understanding of biological processes by practitioners in the field as well as an unconscious bias towards physical/chemical methods. As more environmental professionals become familiar with biological treatment and the advantages associated with its use, this technology will play an increasingly important role in the remediation of petroleum contaminated soils, liquids, and air emissions.

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FIGURE 1. Approximate Boiling Ranges for individual Hydrocarbon Products. Benzene (B) has a boiling point of 80.1 °C and n-Hentriacontane (C-31) has a boiling point of 302 °C.

Adapted from Senn and Johnson, 1985. (2)



FIGURE 2. Bacterial Conversion of Organics



FIGURE 3. L-Series Bioreactor







FIGURE 4. Summary of L-6 Influent and Effluent BTX concentrations.



Part B. Effluent



FIGURE 5. Summary of L-20 Influent and Effluent BTX Concentrations.



FIGURE 6. Summary of Total Plate Count Data.

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FIGURE 7. Summary of Hydrocarbon Plate Count Data.



FIGURE 8. Summary of Petroleum Hydrocarbon Concentrations after 14 Weeks of Treatment.



FIGURE 9. DETOX Prototype Airstream Bioreactor

TABLE 1.Bio-Air Tower Removal Rates at High Concentration
(HNu @ 165 mg/l) and Variable Air flow.

Part A. At low air flow (10.4 CFM)

Sample Number*	Total Petroleum Hydrocarbon Concentration (mg/l)**		Benzene, Toluene, and Xylenes Concentrations (mg/1)**		% Removal	
	influent	effluent	influent	effluent	TPH Cpds.	BTX Cpds.
1	14.71	4	1.85	0.39	67.6	78.6
2	10.66	4.9	1.73	0.51	53.9	70.3

* These two samples represent the high and low influent concentrations received after seven trials.

** All concentration results were determined from charcoal trap analyses (NIOSH Mtds.).

Part B. At high air flow (17.1 CFM)

Sample Number*	Total Petroleum Hydrocarbon Concentration (mg/1)**		Benzene, Toluene, and Xylenes Concentrations (mg/1)**		% Removal	
	influent	effluent	influent	effluent	TPH Cpds.	BTX Cpds.
1	2.49	1.84	0.34	0.25	26.1	32.6
2	1.35	0.96	0.21	0.11	28.7	47.8
3	1.08	0.68	0.075	0.034	37.1	55.2

* These three samples represent the high, medium, and low influent concentrations received after nine trials.

** All concentration results were determined from charcoal trap analyses (NIOSH Mtds.).



P.O. Box 324 Dayton, OH 45459 513/433-7394

Diane C. Kroplin Sales Manager



DETOX, Inc.: Your Solution to Ground Water Treatment

The Leader in Ground Water Treatment

Since 1983, DETOX has been providing effective above-ground and in-situ treatment systems. DETOX offers a full range of technologies and equipment, backed with the knowledge and experience required to get the job done. We specialize in biological treatment, as well as systems that cost-effectively combine other unit processes such as air stripping and carbon adsorption.

DETOX supports all equipment with a wide range of services, including design conceptualization, laboratory treatability studies and field pilot testing, to ensure your system is technically and economically effective.

State-of-the-Art Equipment

DETDX has developed technologically superior equipment which has been proven in over 30 installations. Our proprietary designs for fixed-film bioreactors have placed us on the forefront of biological treatment for hazardous waste. These bioreactors are successfully employed throughout the nation and have been selected by the U.S. Environmental Protection Agency's S.I.T.E. program.*

Our bioreactors use a destruction technique for removing organics

* The U.S. Environmental Protection Agency's Superfund innovative Technology Evaluation (SITE) program identifies and tests promising new technologies for Superfund and other hazardous waste clean-ups. and hydrocarbons from the water or soil with little or no discharge. This environmentally sound technique virtually eliminates your future liability.

Each DETOX system is designed to require minimal operator attention. In addition, our systems possess the flexibility to respond and adapt to the changing needs of your site conditions.



Effective Treatment at a Reasonable Cost

DETOX systems are specifically designed





to reduce your costs <u>and</u> concerns. At DETOX, we combine innovative equipment with professional training ant. Factical judgment.

Be servery site is unique, we begin with texter / review reports to analyze your treatment options and potential costs. We have also developed extensive laboratory treatability studies to yield data duickly and economically. In addition, DETOX conducts a variety of field pilot tests which duplicate the real-world rigons of your treatment site. Together, these procedures give you comprehensive answers, with a minimum investment of your time and money.

We Continue to Grow

At DETOX, our personnel combine hands-on experience with state-of-theant knowledge of nemediation systems. DETOX staff members regularly participate in technical conferences, author papers, and conduct seminars on site nemediation for the U.S. EPA, universities, and private industry. Our continuing professional growth ensures that you receive an advanced and costeffective treatment system.



JOIN OUR LIST OF SATISFIED CUSTOMERS.

Here are just a few of the organizations that DETOX, inc. serves:

IBM Corporation

Memorex Corporation

Marathon Oil Company

Stauffer Management Company

Chevron USA

ATEC Environmental Consultants

Harding Lawson Associates

Canonie Environmental

Hangis & Associates, Inc.

Peer Consultants, P.C.

Wright Patterson Air Force Base

US Environmental Protection Agency

McCiel and Air Force Base

Call DETOX today.





an American Ecology company + 561 Congress Park Drive, Dayton, Ohio 45459 Office: [513] 433-7394 FAX: [513] 433-1572



BIOLOGICAL TREATMENT SYSTEMS

H - Series & L - Series

WHY BIOLOGICAL TREATMENT?

- Biological Treatment is Environmentally Sound contaminants are destroyed, not transferred into the air or onto carbon. Potential liability is ended.
- Biological Treatment is Economical >99% destruction at 1/40th the cost of activated carbon.
- · Biological Treatment is Proven at over 70,000 sites over the last 80 years.

ABOVE-GROUND BIOREACTORS OR IN-SITU TREATMENT?

Both biological treatment technologies have their place and their advantages; indeed, DETOX often employs them together on the same site. Above-ground bioreactors are easier to control and require less monitoring. They can assure treatment of an entire flow stream when discharge to sewer, stream or re-injection into the ground is required.

WHEN IS BIOLOGICAL TREATMENT MOST EFFECTIVE?

For contaminants with low volatility (poor strippability) such as ketones, phenols, and petroleum hydrocarbons, biological treatment is best. If vapor-phase treatment is required on air strippers, even easily stripped compounds like benzene are good candidates for biodegradation (see graph on back). Generally, heavily chlorinated compounds are poor candidates for biotreatment.

WHAT BIOLOGICAL TREATMENT PROCESS IS BEST SUITED FOR GROUNDWATER?

Our R&D efforts have developed two submerged fixed-film designs that avoid the operational problems caused by activated sludge, trickling filters and RBC's. Both are very suitable for effective Life Cycle Designs.



Step 1 - DEGRADABILITY STUDIES

These studies are often suggested by the inexperienced to "prove" the biodegradability of a compound, but they are usually NOT REQUIRED. Because of our experience in biological treatment, we can generally predict a contaminant's degradation characteristics without resorting to expensive, time-consuming studies trying to identify the proper microbes and environmental conditions to use. When necessary, our laboratory can perform full biodegradation studies.

Step 4 - DESIGN & FABRICATION

All DETOX units are designed to provide effective treatment with minimal operator attention, in keeping with our "LIFE-CYCLE DESIGN" concept. Removal efficiencies of greater than 99% and effluent levels as low as 1 ppb of specific organics are achievable. We are constantly improving and updating our designs in response to operational experience at a variety of sites. Fabrication can be in a variety of materials to suit site conditions and relevant structural codes.

Step 2 - TOXICITY/INHIBITION TEST

Because many different factors can be toxic or harmful to micro-organisms (such as pH, heavy metals, or pesticides) we usually suggest a brief (less than one week) test at our Dayton laboratory to check for the presence of these potentially harmful compounds. We can usually provide a **PERFORMANCE GUARANTEE** for your particular waste stream after this test.



Step 3 - FIELD PILOT TESTING

For extra security, or for regulatory approval, we offer pilot scale models of all our reactors to run at your site. These tests take two to three months, and subject a system to the actual conditions that will be encountered. EXACT design specs, nutrient usage rates, and performance predictions can be made from this test.

Step 5 - INSTALLATION & START-UP SERVICES

DETOX can provide turnkey installation services. Our portable units require a minimum of site disruption and support equipment. After start-up, most biological systems take 3-6 weeks to develop a healthy biomass and become fully operational. DETOX can assist with system monitoring and control during this time, and we can provide training for your personnel. We also offer complete "Operations and Maintenance Contracts" to ensure excellent performance during the life of your cleanup.

Biological treatment costs compared to air stripping and carbon adsorption.





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inc. LABORATORY & FIELD PILOT ul groundwater treatment equipment design is accurate data. The first step is a theoretical Nost probable treatment technologies (see PREVIEW/REVIEW data sheet). The next step is ul groundwater treatment equipment design is accurate data. The first step is a theoretical nost probable treatment technologies (see PREVIEW/REVIEW data sheet). This data should bilit: study to provide the initial data on the actual water that will be treated. Inst probable treatment technologies (see PREVIEW/REVIEW data sheet). The next step is the initial data on the actual water that will be treated. This data should with the initial data on the actual water that will be treated. This data should with end Pilot Testing under actual treatment conditions. Stvice capabilities for providing the data to design a groundwater treatment system. We have full scale tensive series of laboratory treatability tests and field pilot equipment to simulate full scale Srvice capabilities for Providing the data to design a groundwater treatment system. We have tensive series of laboratory treatability tests and field pilot equipment to simulate full age of tensive series and equipment. These procedures are based on our thorough knowledge tensive series of laboratory treatability tests and field pilot equipment to simulate full scale atment processes and equipment. These procedures are based on our thorough knowledge of eatment and equipment design. Inexpensive laboratory tests can produce design information atment processes and equipment. These procedures are based on our thorough knowledge of eatment and equipment design. Inexpensive laboratory tests can produce design information is atment and equipment design. Inexpensive laboratory tests our designs to the real-world rigors of your one is a subject of the real-world rigors of the real-world rigors. eatment and equipment design. Inexpensive laboratory tests can produce design information onomically, while our field pilot equipment subjects our designs to the real-world rigors of your Together or separately, these services can provide you with the extra margin of safety required on inomically, while our field pilot equipment subjects our designs to the real-world rigors of your and the extra margin of satety required on the role of separately, these services can provide you with the extra margin **of satety required** of the test in the test in the test in the test in the test is and the assurance that your treatment system will work right the tirst time. Together or separately, these services can provide you with the extra margin of saft cts, and the **assurance that your treatment system will work right the first time**. ATORY TREATABILITY dwater, soils and vapor-phase NG: obiology laboratory for complete biodegradaboratory-scale facilities for heavy metal Physical/chemical treatment studies for advan-FIELD PILOT TESTING: • Easily portable small-scale equipment designed ced treatment methods. , Field sampling and shipping services. to duplicate full-scale installations. Rapid testing - as little as a single day on-site for • Equipment can be operated by our trained technicians or by your personnel. • Flow rates from 1-40 gpm.

Listed below are descriptions of a few of the more common popular laboratory tests and pilot studies DETOX can provide. This list is by no means complete, but rather is intended to give a representation of the types of problems that can be addressed. Our staff of scientists and engineers is ready to design the exact test or series of tests to provide you with answers at minimum cost.

AIR STRIPPING - ON-SITE PILOT TEST

A single day, on-site test using our portable 22' tall air stripper. This test will determine the design parameters of an air stripper such as tower height, tower diameter, air:water ratios and blower sizing. Samples taken at different water and air flow rates are analyzed by gas chromotography to determine contaminant removal efficiencies and mass transfer characteristics.

BIOLOGICAL TREATMENT -- LABORATORY TOXICITY/INHIBITION TESTS

A quick one-week laboratory test that is suggested as a first step for most biological treatment systems. This test is designed to discover if any chemicals or factors present in a water or soil will inhibit or prevent biological growth, thereby making biotreatment impossible.

BIOLOGICAL TREATMENT -- FIELD PILOT STUDIES

All DETOX biological processes can be piloted in the field. Field testing determines the exact level of treatment obtainable, defines the sizing and design parameters of a unit, and exposes a system to the natural shocks and changes that will be encountered on a full scale site. Most biological pilot tests take one to three months.

IN-SITU BIODEGRADATION --- SAMPLING & LABORATORY ANALYSIS SERVICES

This packaged analytical service tests for the important physical and chemical properties that effect insitu degradation. Soil, soil gas and groundwater samples are analyzed for dissolved oxygen, nutrients, micronutrients, pH, temperature, contaminant levels, total bacteria, specific organic degrading bacteria and other factors. This test is especially helpful for determining the feasibility of in-situ treatment, and also for monitoring an in-situ cleanup process.

CARBON ADSORPTION - LABORATORY AND/OR FIELD PILOT TESTS

Isotherms or column tests run in the laboratory on a small sample, or in the field on a small slip-stream. Testing determines the required contact time, contactor sizing and carbon usage rates. Especially useful for multi-contaminant sites.

METALS & INORGANIC REMOVAL - LABORATORY & FIELD STUDIES

DETOX has a variety of equipment to simulate most metal and inorganic removal processes. Included are precipitation, flocculation, clarification, filtration and ion exchange. Laboratory tests can usually be completed in one week.



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AIR STRIPPING SYSTEMS

Air stripping is usually the least expensive method of removing Volatile Organic Compounds (VOC's) from groundwater. In the proper design of an efficient air stripping tower, contaminated water and large volumes of air are brought into close physical contact. The contaminants are "stripped" out of the water and into the air, and carried off into the atmosphere or to further vapor-phase treatment. The clean water is then suitable for potable use, recharge to the aquifer, or discharge to a sewer or stream.

>ETOX understands the air stripping process. With our pilot equipment, analytical laboratory, computer design capabilities, and our field experience, we have the resources to provide you with the most economical, effective treatment available on the market today. Through proper selection of design parameters, construction materials and packing, we have been able to provide systems for as little as 1/3 the cost of other air strippers.

- EFFECTIVE DETOX Air Strippers can remove more than 99% of many compounds; higher removal with multiple towers.
- ECONOMICAL Capital costs as low as 1/3 of competing systems; operating costs are just a small blower; systems are designed for low maintenance.
- ENGINEERED Designed to avoid common operational problems such as plugging and flooding.
- EASILY INSTALLED All our equipment is portable, designed for easy installation and possible removal at the end of a cleanup.
- EXPANDABLE Should your treatment requirements change, our units are readily adaptable to new flows or influent levels.
- ENDURANCE Our use of durable, noncorrosive materials and complete structural analyses assure years of trouble-free operation.



DETOX Air Stripper Wright-Patterson AFB Flow: 2000 gpm Contaminant: TCE Application: Potable Water Supply Installed Cost: \$54,000 Total Operating Cost: \$0.02/1000 gal treated (includes capital and 0 & M costs)

PILOT TESTING

DETOX pilot testing equipment is available for short on-site tests run by our personnel, to accurately determine design parameters such as air:water ratio, liquid loading rates, and packing height. Samples from the pilot testing can be analyzed by our in-house lab, or an independent lab of your choice.

DESIGN SERVICES

Using either pilot results or our past operating data, we run computerized analyses to determine the most economical stripper configuration, not only in terms of initial capital outlay, but also considering operational costs over the life of your unit. All DETOX systems come with a 100% performance guarantee.

HIGH-FLOW AIR STRIPPERS

Our high-flow air strippers were specially designed for low-concentration high-flow situations, such as a municipal water supply. Through the use of special, less expensive, low-pressure drop polypropylene packing, and very high air:water ratios, we have designed a tower that is shorter, less expensive to install, and efficient to operate. The significantly lower tower heights result in smaller foundation requirements, reduced material requirements, and fewer aesthetic objections. Suitable for flows over 250 gpm.

HIGH-CONCENTRATION AIR STRIPPERS

This series of DETOX air strippers have been designed for high influent concentrations of VOC's, and also for use on less volatile compounds. These towers utilize a high-efficiency random polypropylene packing, and can be supplied in any required height through the addition of modular tower sections. Suitable for flows from 0-1000 gpm.

CUSTOM DESIGNED SYSTEMS

DETOX can also provide custom designed systems, tailored to your exact site requirements. Air stripping is especially effective in conjuction with other technologies, such as carbon adsorption, aboveground biological systems, and in-situ treatment. DETOX provides all these technologies to assure you of the most effective system for your treatment concerns.

VAPOR PHASE TREATMENT

In those localities with strict air emission requirements, DETOX can help with a variety of technologies for off-gas treatment, including vapor phase carbon adsorption, incineration or flaring, and solvent extraction and recovery.

INSTALLATION/INSPECTION/ANALYSIS SERVICES

DETOX service does not stop with equipment supply. Most of our work is performed on a turnkey basis, where we are responsible for installation and startup. Although air strippers require virtually no maintenance, we also offer periodic visits to assure continuous operation, as well as sampling and analytical services to meet regulatory monitoring requirements.

EQUIPMENT RENTAL

All equipment is available on either a lease or purchase basis. Many short duration cleanups are economically carried out with the use of rental equipment. Contact DETOX for more information.



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GROUNDWATER TREATMENT PREVIEW/REVIEW

PREVIEW/REVIEW is a concise analysis of treatment alternatives for removing contaminants from groundwater.

COST-EFFECTIVE -

Save time, money, and resources by quickly eliminating inappropriate treatment methods.

FAST -

Rush projects can have a full report delivered in two to three weeks.

ECONOMICAL -

PREVIEW or REVIEW usually will cost less than 1% of the completed cleanup.

COMPLETE -

All applicable treatment technology is reviewed (including innovative treatment methods), and the most cost-effective treatment system is highlighted.

PREVIEW FEATURES

- GROUNDWATER DESCRIPTION A summary of the groundwater contaminants and the environmental conditions, with an emphasis on the factors which are important for treatment.
- PHYSICAL PROPERTIES A table listing the physical properties of the contaminants found in the groundwater.
- TREATABILITY PROPERTIES A table listing properties that are important for determining the treatability of the specific compounds found in the groundwater.
- TECHNOLOGY REVIEW A list is provided of all of the treatment technologies that can be applied to the contaminants. Each technology is reviewed. A general description of the technology is provided and the advantages and disadvantages of applying the specific technology to the groundwater treatment is summarized.
- TREATMENT SYSTEM OPTIONS A specific discussion on several possible treatment systems, utilizing single or combined technologies, that will remove the contaminants from groundwater.
- PROCESS DRAWINGS A process drawing is provided for each of the treatment systems discussed in the report.
- ECONOMIC SUMMARY The projected capital and operating costs for each of the treatment systems are summarized and compared in a final table.

"Don't wait for full scale operation to discover problems"

Before a project starts, have DETOX *PREVIEW* your contaminated groundwater and develop a cost-effective direction for your studies. Or, after your engineers have finished, have DETOX *REVIEW* their report to insure that the most cost-effective treatment methods will be utilized.

REVIEW FEATURES

DETOX will customize a *REVIEW* to fit the specific needs of your project. Our senior engineers/ scientists will read and study the contents and recommendations of your project engineers. We will use our years of experience in field application of groundwater treatment systems to insure that the recommended treatment method is both appropriate and cost-effective.

DETOX will also evaluate the proposed treatment system for practical problems that may arise as the project is implemented in the field.

All of the features that are considered in our *Preview* reports are also included in our *REVIEW* report.

EXPERIENCE

DETOX has years of experience from the application of our groundwater treatment equipment to aquifer restorations. Our staff has detailed knowledge of all of the technologies that are widely applied to cleanups. DETOX is on the leading edge of the application of innovative technology. Clients such as the U.S. EPA, IBM, Memorex Corp., the United States Air Force, and consultants such as Pioneer Consultants, Bendix Field Engineering Corp. and Kleinfelder Engineers have benefited from our groundwater treatment knowledge. "Groundwater Treatment Technology" and "In-Situ Treatment of Soils and Groundwater" are examples of authorative books by DETOX personnel. No one knows equipment better than DETOX.



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