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SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Technology Demonstration Summary

Biological Treatment of Wood Preserving SITE Groundwater by Biotrol, Inc.

BioTrol's pilot-scale, fixed-film biological treatment system was evaluated for its effectiveness at removing pentachlorophenol from groundwater. The system employs indigenous microorganisms amended with a specific pentachlorophenol-degrading bacterium. The demonstration was performed in the summer of 1989 at a wood preserving site in New Brighton, MN. Groundwater from a well on the site was fed to the system at 1, 3, and 5 gpm with no pretreatment other than pH adjustment, nutrient addition, and temperature control. Each flowrate was maintained for about 2 wk while samples were collected for extensive analyses.

At 5 gpm, the system was capable of eliminating about 96% of the pentachlorophenol in the groundwater and producing effluent pentachlorophenol concentrations of about 1 ppm. At the lower flowrates (1 and 3 gpm), removal was higher (about 99%) and effluent pentachlorophenol concentrations were well below 0.5 ppm.

Review of other data provided by the developer indicates that the process is also effective on other hydrocarbons, including solvents and fuels. The system appears to be a compact and cost-effective treatment for contaminated wastewaters; it requires minimal operating attention once acclimated.

This Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of this SITE Demonstration. These findings are fully documented in two separate report(s) (see ordering information at back).

Introduction

The Superfund Innovative Technology Evaluation (SITE) Program was established in 1986 to promote the development and use of innovative technologies to remediate Superfund sites. Contamination by chemicals from wood preserving operations has frequently been found at Superfund sites on the National Priorities List. Biological destruction of hazardous chemicals such as pentachlorophenol (PCP) and creosote-derived polynuclear aromatic hydrocarbons (PAHs) at wood preserving sites was deemed to be a suitable topic for investigation under the SITE Program.

This Summary highlights the results of an evaluation of BioTrol's Aqueous Treatment System (BATS), a fixed- film aerobic treatment of such groundwater, using a consortium of pentachlorophenol-degrading bacteria. Economics of the process are also assessed.

A wood preserving facility in New Brighton, MN, was selected for pilot-scale evaluation of the technology. The site has been used for wood treatment with creosote, pentachlorophenol, and chromated copper arsenate since the 1920s. Remedial Investigation/Feasibility Study (RI/FS) testwork at the site indicated that both the soil and the underlying groundwater were contaminated with pentachlorophenol and polynuclear aromatic hydrocarbons even though these chemicals are no longer used in wood treatment. The owner and operator of the site, the MacGillis and Gibbs Company, agreed to host the testing of the BioTrol system.

Process Description

Two wells were drilled at locations based on surface and subsurface testing results in the RI/FS. One of these provided adequate flow (over 5 gpm) and contained sufficient pentachlorophenol contamination (~45 ppm) for the study. Although total polynuclear aromatic hydrocarbon levels were well below 1 ppm in these samples, a decision was made to proceed.

The mobile BATS is contained in an enclosed trailer (20 ft long and 8 ft wide) in which all the process equipment is mounted. The only site requirements are a level area about 50 ft square, potable water, and electrical power. The system, shown in Figure 1, consists of a conditioning or temper tank, a heater and heat exchanger, a three-stage fixed-film bioreactor, a blower, process pumps, and a nutrient feed system. The use of a fixed-film reactor allows for a long solids retention time in a relatively small reactor volume, thus reducing production of excess biomass.

Influent groundwater is pumped directly from the well to the conditioning tank on a level-controlled cycle. The pH is adjusted (if necessary) to just above 7.0 with caustic, and inorganic nitrogen and phosphorus nutrients (urea and trisodium phosphate) are added. After passing through the in-line heater and heat exchanger to ensure a process temperature in the vicinity of 70°F (21°C), the groundwater is introduced to the base of the first of the three bioreactor chambers (Figure 2). Each chamber contains an inert support for bacterial growth; in the study corrugated polyvinyl chloride sheets were the support medium used (Figure 3). The influent is passed up through each chamber while air is injected at the base of each chamber through a sparger tube system fed by a single blower motor.

Start-up and acclimation are accomplished by introducing an indigenous bacterial population, usually taken from the local soil. After allowing about 1 wk for acclimation and development of the biomass, the system can be "seeded" (if necessary) with an inoculum of an organism with a specific capability to degrade the target contaminant. For this study, the system was inoculated with a pentachlorophenol-degrading *Flavobacterium* species and acclimated further by recycle with the contaminated wastewater. When the system is fully adapted to the wastewater, once-through processing is ready to begin.

Test Program

Three increasing flowrates, 1, 3, and 5 gpm, corresponding to residence times of 9, 3, and 1.8 hr, respectively, were selected for study to allow the effectiveness of the process to be determined at various contaminant loadings. Each flowrate was tested for 2 wk.

The plan agreed to by EPA and BioTrol called for monitoring of the groundwater from the selected well, the influent to, the effluent from, and the two intermediate stages of the bioreactor for pentachlorophenol and other semivolatile organics using EPA Method 3510/8270 (gc/ms). Chloride and TOC also were monitored to assess BioTrol's claim that pentachlorophenol removal occurred by mineralization to water, carbon dioxide, and salt. BioTrol was responsible for operating the system and maintaining system conditions such as nutrient feed, pH, dissolved oxygen, temperature, etc., whereas EPA's contractor personnel were responsible for the sampling/analysis program.

Other parameters also monitored to provide a complete history of the groundwater as it passed through the system included total and volatile suspended solids, oil and grease, nitrogen and phosphorus, volatile organics, and heavy metals. Because there is always concern when treating wastewaters containing chlorinated aromatics, testing was also done for chlorinated dioxins and furans. Samplings and analyses also were carried out before and after the carbon adsorption units on the air exhaust line and the effluent line to determine if significant quantities of the contaminants were lost by any route other than biodegradation.

Finally, static bioassays using two species, *Daphnia magna* (water flea) and *Pimephales promelas* (minnow) were carried out on the incoming groundwater, the influent to the reactor, and the effluent. These tests were performed to determine whether the groundwater was toxic to aquatic species and whether treatment removed the chemical source of toxicity.

Results

System parameters monitored throughout the course of the project indicated reasonably consistent operation with no deviations from expected results and no upsets were observed during the study. Table 1 summarizes the temperature, pH, and dissolved oxygen data obtained.

Comparison of pentachlorophenol concentrations in the well with the effluent from the bioreactor demonstrated that the BioTrol system is capable of achieving about 96% removal of pentachlorophenol at the highest flowrate, 5 gpm, and, at that flowrate, can produce effluent concentrations – before carbon polishing – of approximately 1 ppm. At the lower flowrates, 3 and 1 gpm, removals were even higher, approaching 100%, and effluent concentrations were well below 1 ppm. Table 2 summarizes the pentachlorophenol removals at the three different flowrates.

The plan to follow the course of the biodegradation by analyses at the intermediate stages in the bioreactor could not be accomplished due to an unexpected sampling artifact. The composite sampler inlet strainers were placed too deep in each downcomer chamber, thus allowing backmixed water from the subsequent chamber to enter the collected samples. The effect was detected as significant lower values for the "influent" concentrations for pentachlorophenol (and other parameters) at sampling point #2 in Figure 2 when compared to the groundwater samples (sampling point #1) or grab samples just before the water entered the bioreactor (sampling point #B). Presumably, the values at the two intermediate sampling points (#3 and #4) were similarly affected.

The changes in chloride and TOC results (obtained once/week) parallel the decrease in pentachlorophenol at all flows (Table 3); however, the results are not sufficiently precise to provide more than supportive evidence for mineralization of pentachlorophenol to sodium chloride, water, and carbon dioxide. The mineralization of PCP by *Flavobacterium* has been studied extensively by Crawford and coworkers; tracer studies have shown that the degradation proceeds completely to CO_2 and that no intermediate byproducts are formed.

As part of the effort to confirm that pentachlorophenol was being removed by biochemical mineralization and not by adsorption on the biosolids or by stripping because of the aeration in the bioreactors, both biomass solids and air emissions were also analyzed for pentachlorophe-

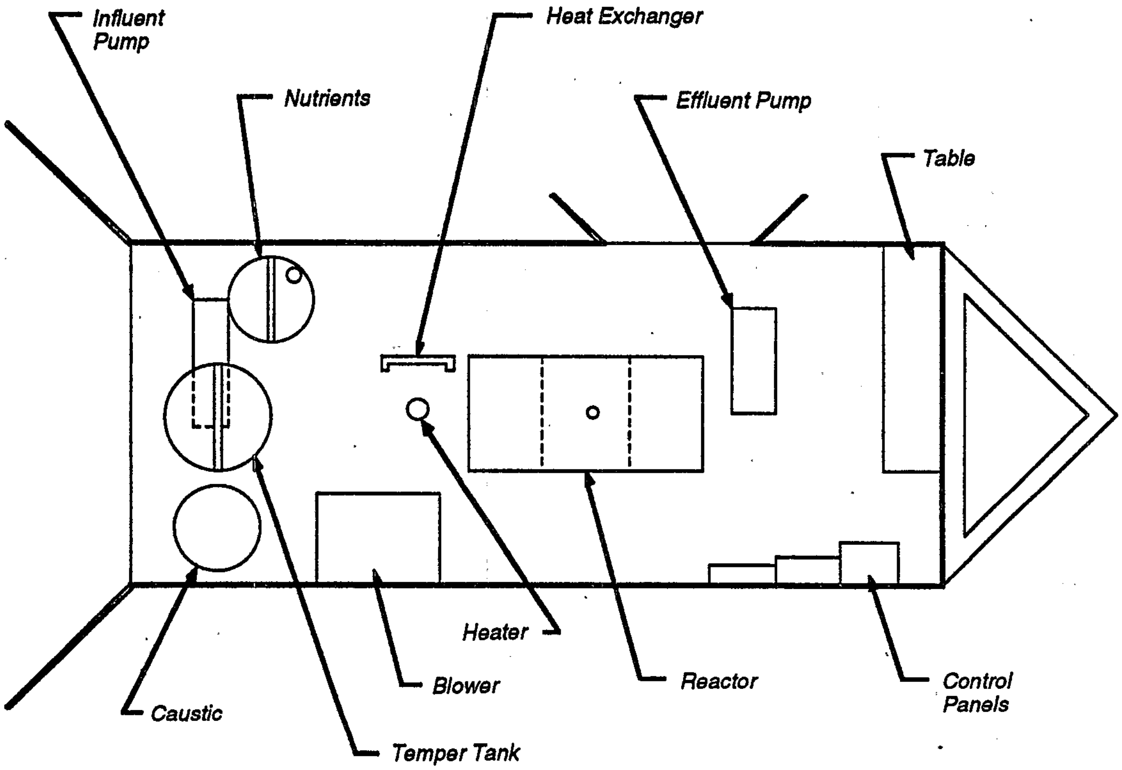


Figure 1. *Biotrol, Inc. Mobile Aqueous Treatment System (ATS).*

nol. Although the sludge trapped in the bag filter was found to contain pentachlorophenol (34 and 170 ppm found in two samples), the amount of sludge was so small that adsorption of pentachlorophenol on the biosolids and removal with the suspended solids (Table 4) does not represent a significant removal mechanism. Similarly, pentachlorophenol was not present above the detection limit (0.2 ppb) in any of the air samples collected from the exhaust from the reactor chamber with a modified Method 5 collection system with an XAD resin trap. Therefore, it does appear that biological degradation is, by far, the primary means of eliminating the pentachlorophenol from the groundwater.

Concentrations of the various polynuclear aromatic hydrocarbons measured as part of the semivolatile fraction were consistently below detection limits in the incoming groundwater. Whereas the detection limits were usually high (2 ppm) in these analyses because of the high pentachlorophenol concentrations in the influent, two analyses of well water during the predemonstration testing indicated total PAHs of 145 and 295 ppb, which would confirm that the PAHs are not major contaminants in this water. Several PAHs, including naphthalene and methyl naphthalene at maximum levels of 34.6 ppb and 47.9 ppb, respectively, and others at considerably lower levels, were found during the modified Method 5 testing of the air emissions from the reactor, suggesting that some air stripping of these constituents may be occurring. The carbon adsorption unit on the exhaust from the bioreactor was successful in collecting most of these emissions.

Small amounts of various chlorinated dioxins were found in the effluent (<340 ng/L, using method SW8280) and, particularly, the sloughed biomass sludge, where one sample did exhibit 1900 ng/g of the OCDD isomer. With the exception

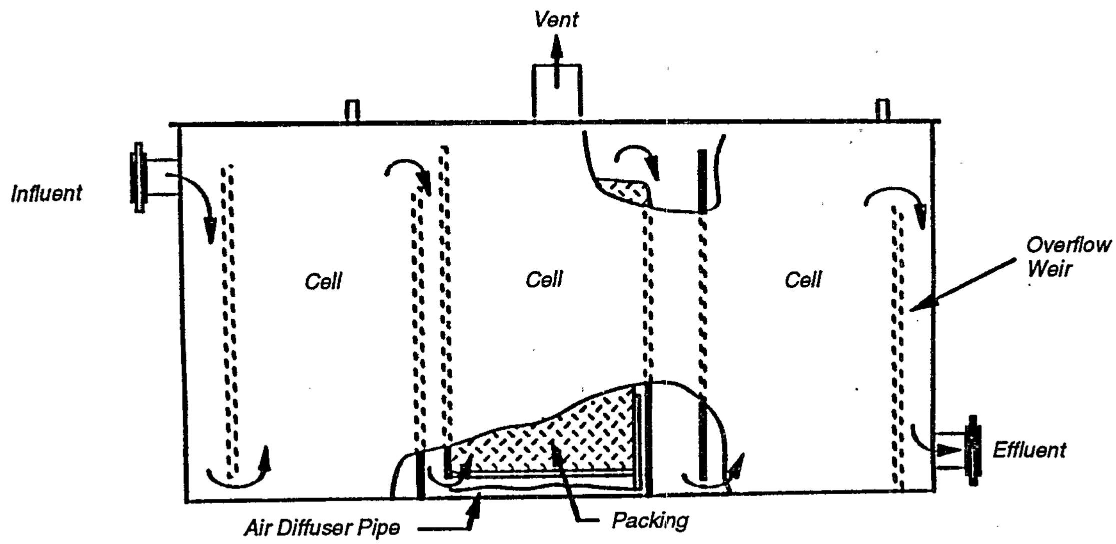


Figure 2. BATS Reactor

of one effluent sample found to contain 62 ng/L, the 2,3,7,8-tetrachlorodioxin of primary concern was not detected in any of the influent, effluent, or sludge samples using high resolution GC coupled with low resolution MS.

The incoming groundwater contained low concentrations of several of the heavy metals, including nickel (<91 µg/L), zinc (<32 µg/L), copper (<25 µg/L), lead (<11 µg/L), and arsenic (<6.5 µg/L). With the exception of one sample which is believed to be an anomaly, the concentrations of the metals in the effluent were similar.

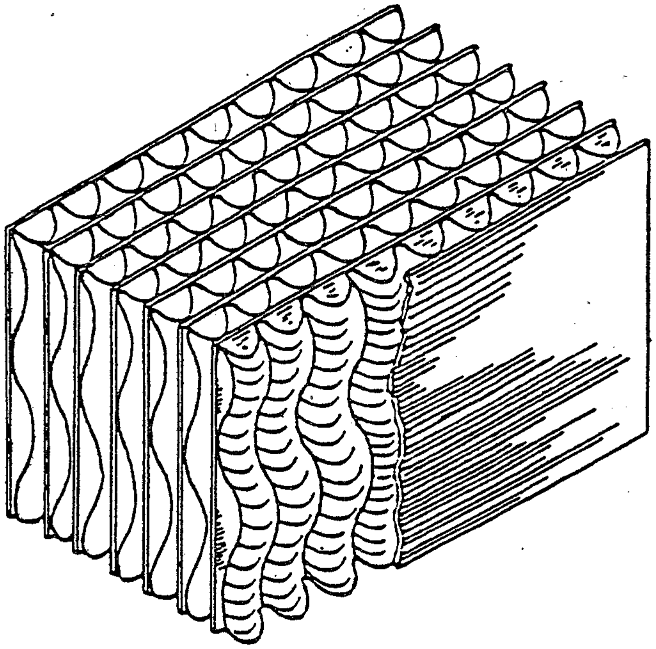
Acute biomonitoring with fresh water minnows (96-hr static test) and *Daphnia magna* (48-hr static test) demonstrated that the toxicity observed with the incoming groundwater and the influent was essentially totally removed by the treatment. LC_{50}'s increased from an estimated low of 0.2% (groundwater/control water) for the groundwater to more than 100% (as calculated from results) in the treated effluent; in other words no toxicity was observed with 100% treated effluent.

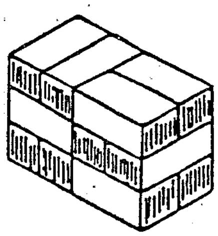
Costs

Estimates were provided by the vendor for the cost of operating the pilot plant at MacGillis and Gibbs including cost for nutrients, electricity, heat, labor, and caustic. Ancillary costs incurred as part of the SITE Demonstration program such as the bag filter, the carbon adsorption units, and the extensive analytical program were not included. BioTrol also extrapolated costs to a large scale system capable of treating 30 gpm of a similarly contaminated (~40 ppm pentachlorophenol) groundwater based on the demonstration study and other information at their disposal (Table 5). As shown in the table, certain costs do not increase at an expected linear rate. For example, unit nutrient cost would decrease because of bulk purchase; operator labor cost also does not increase in direct proportion to the size of the unit.

These costs do not include leasing or amortization of the capital equipment, which are approximately $2,400/mo (5 gpm mobile), $30,000 (5 gpm skid mounted) and $80,000 (30 gpm skid mounted), respectively.

The labor cost is clearly a major component of the total cost. In many instances, heat input is not required; however, if heating is necessary it also is a major cost component. Any site-specific pre- or post-treatment requirements, such as oil/water separation, solids removal, polishing, air emissions control, etc., would have to be factored into the cost calculation for that





Blocks
Cross-Stacked

Figure 3. Corrugated Polyvinyl Chloride Media

site. Regulatory needs before or during a remediation such as permits for wells, discharge of effluent, sludge disposal, etc. are also not included.

Applicability to other Wastewaters

BioTrol, Inc. has carried out several other studies as part of its development and commercial activities related to the BATS. Results from those studies have also been evaluated as a means of evaluating the applicability of the process to other pentachlorophenol-contaminated wastewaters as well as to other contaminants.

BioTrol has successfully demonstrated – at 15 gpm – the ability of the BATS to eliminate the benzene, toluene, xylene, and ethylbenzene components from gasoline-contaminated groundwater. Benzene was reduced from approximately 4000 ppb to about 10 ppb. Similarly, in another bench scale study, toluene, methyl ethyl ketone, and tetrahydrofuran were reduced by over 99%. In various other laboratory, pilot scale, and commercial scale studies summarized in the report, removals of pentachlorophenol consistently averaged over 90% and the removal of other oxygenated and chlorinated organics have been demonstrated.

Conclusions

The following conclusions can be drawn from the available information, relying primarily on the SITE demonstration study but supported by other information provided by the developer.

1. The fixed-film system effectively removes pentachlorophenol from con-

Table 1. System Parameters During Test Program

Flow gpm	Avg. Temperature (°C)			pH (s.u.)		Avg. Dissolved O_2 (mg/L)	
	gdwter	infl.	effl.	infl.	effl.	infl.	effl.
1	21	23.4	24.5	6.9-7.9	8.0-8.4	5.3	5.8
3	11	14.2	20.9	7.1-8.7	7.6-8.1	5.0	5.6
5	13	14.6	20.9	6.8-8.0	7.2-8.0	5.6	5.8

Table 2. Average Pentachlorophenol Removal by the Biotrol Aqueous Treatment System

Flow Rate (gpm)	Ground-water* (ppm)	Effluent (ppm)	Removal (%) Average†	Range
1	42.0±7.1	0.13±.25	99.8	87.4-99.9+
3	34.5±7.8	0.34±.15	98.5	95.8-99.8
5	27.5±0.7	0.99±.49	96.4	79.3-99.4

* decrease with time may reflect drawdown of aquifer
† based on average of daily effluents

Table 3. Comparison of Chloride, TOC, and PCP Results.

Flow Rate (gpm)	Change (delta) (ppm) PCP	Cl_f	Cl_c	TOC_f	TOC_c
1	-41.9	+44.2	+27.9	-24	-11.3
3	-34.1	+40.5	+22.7	-32	- 9.2
5	-26.5	+22.0	+17.6	-21	- 7.0

(f) = found; (c) calculated

Table 4. Average TSS Results

Flow Rate (gpm)	Groundwater (ppm)	Effluent (ppm)
1	2.5± 0.07	53.6± 6.6
3	13 ±12.7	26.3±11.1
5	1.5± 0.7	22.5± 9.5

Table 5. Operating Costs

Cost Item	($/1000 gal) at 5 gpm	at 30 gpm
nutrients	0.042	0.017
electricity	0.216	0.216
heat	1.46	1.46
labor	1.49	0.50
caustic	0.24	0.24
TOTAL	3.45	2.43

taminated groundwaters. Other phenolics also appear to be extensively degraded.

2. Pentachlorophenol removals of 95% and higher are achievable with final pentachlorophenol concentrations well below 1 ppm, making the effluents potentially suitable for direct discharge, discharge to a POTW, or reuse.
3. Biodegradation appears to be the predominant mechanism for pentachlorophenol removal. Adsorption on the biomass or air stripping are not significant contributors to removal.
4. Complete mineralization of pentachlorophenol and other partially chlorinated phenols is consistent with the loss of TOC and the increase in chloride ion observed in the study.
5. Toxicity (acute) of groundwater such as that found at MacGillis and Gibbs is totally eliminated by the BioTrol treatment process.
6. The system is convenient to operate and requires a minimum of operator attention once acclimation has been achieved. Use of the BioTrol fixed-film reactor minimizes sludge production.
7. Operating costs range from $3.45 in a 5 gpm unit to $2.43 in a 30 gpm unit, making the process economically attractive.
8. The process does not appear to be adversely affected by the presence of oil in the 50 ppm range, suspended solids, metals, or other sources of organic carbon.
9. Based primarily on review of BioTrol's data from other studies, it appears that the process would be well suited to the removal of other organic contaminants including hydrocarbons, oxygenated hydrocarbons and even chlorocarbons from various ground and process waters.
10. While it appears from other studies that polynuclear aromatic hydrocarbons are also removed by the BioTrol process, such a conclusion cannot be stated from the results of this SITE demonstration.

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The complete report, entitled "Technical Evaluation Report: Biological Treatment of Wood Preserving Site Groundwater by Biotrol, Inc.," (Order No. PB92-110 048/AS; Cost: $26.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

A related report, entitled "Application Analysis Report: Biological Treatment of Wood Preserving Site Groundwater by Biotrol, Inc. (EPA/540/A5-91/001) is available.

The EPA Project Manager can be contacted at:

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