United States
Environmental Protection
Agency

EPA/540/SR-94/531
March 1995

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Emerging Technology Summary

Bench-Scale Testing of Photolysis, Chemical Oxidation, and Biodegradation of PCB Contaminated Soils, and Photolysis of TCDD Contaminated Soils

The tests reported herein were conducted by IT Corporation, Knoxville, TN, to investigate the feasibility of a two-phase detoxification process that would potentially have application to the treatment of soils contaminated with PCBs and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The first step in the process was to degrade the organic contaminants by using ultraviolet (UV) radiation. The source of UV radiation was either artificial UV light or natural sunlight, but generally photolytic processes are more rapid with artificial UV light. Alternatively, advanced oxidation processes, such as iron catalyzed hydrogen peroxide (Fenton's Reagent), were used to provide primary contaminant degradation. Both photolysis and chemical oxidation were expected to convert contaminants to more easily biodegradable compounds. Biological degradation, the second step, was then used to further destroy organic contaminants and detoxify the soil. Biodegradation is enhanced by the addition of microorganisms and nutrients to the UV-treated soil.

The results of bench-scale testing on degradation of TCDD by using UV photolysis, and PCB degradation by using both UV photolysis and chemical oxidation, indicate that there was no apparent destruction of the dioxin on the soil, 23% to 69% destruction of PCBs in UV Tests, and 0% to 53% reduction in chemical oxidation tests.

Bioslurry experiments evaluated the biological reduction of PCB congeners in surfactant/UV-treated and untreated soils. Experiments were also conducted to evaluate the impact of PCB-blodegradation inducers, biphenyl and 4-bromobiphenyl, on congener removal. Bioslurry treatment did not provide significantly different results for the UV-treated surface soil versus the untreated soil.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE emerging technology that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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environmental contaminants. To remove or destroy contamination on soils, relatively high-temperature thermal treatment or harsh chemical treatment is required. These treatments are expensive and can significantly alter the composition of the soil.

The use of UV light to destroy dioxins or PCBs in solutions has long been known. More recently, the use of UV light to destroy these compounds on soils was investigated. Typically, the reaction is aided by the presence of a solvent or solubilizing aid, such as a surfactant, which is transparent to the UV radiation in the region of activity (generally 254 nanometers) and which has increased solubility for the contaminants being destroyed. The irradiation process can be performed on excavated soils or in situ with the use of enhanced radiation from lamps or natural sunlight. The process usually involves the continued application of the solubilizing aid and continued exposure of fresh surface to the irradiation source. The solubility aid helps to transfer the contaminant from the pores of the soil to the surface of soil where the reactions can take place. The surfactant or solubilizing aid may also act as a medium for the degradation process by providing labile protons to allow the reaction to proceed more easily.

Chemical oxidation by Fenton's Reagent has been used to destroy organic compounds such as formaldehyde, azo dyes, and chlorinated phenols in groundwaters and wastewaters. The reaction is ideally performed at a pH of 2 to 4 by using hydrogen peroxide as the oxidant in the presence of a ferrous salt. Ferrous ions catalyze the decomposition of hydrogen peroxide. In the process of decomposition, the reactive hydroxyl radical is produced, and it is capable of oxidizing organic contaminants. If, however, the desired oxidation reaction is slow, significant amounts of hydrogen peroxide can be consumed in unproductive decomposition instead of participating in the desired process. Reaction conditions must be established to provide useful rates of contaminant oxidation with efficient use of hydrogen peroxide reagent.

Aerobic biodegradation of the lower chlorinated PCB congeners (1 to 3 chlorines) has been well documented. The more highly chlorinated congeners are, however, generally resistant to microbial attack, although there have been reports of microbial degradation of the higher-chlorinated PCB congeners (>4 chlorines). Biological degradation of PCB congeners is highly affected by the chlorination pattern and the number of chlorines per biphenyl. Further hindering microbial biodegradation of PCB is their hydrophobicity, which inhibits their bioavailability. To increase the rate and extent of PCB biodegradation, two conditions are necessary: the bioavailability of the PCB should be increased, and the chlorination level per biphenyl ring should be decreased. This study addressed the bioavailability and microbial attack of PCB after the combined surfactant/UV treatment of highly contaminated PCB soil.

Process Description

This two-phase treatment is envisioned as a potential in-situ process for shallow contamination on soils. More probable, however, is the use of the technology for ex-situ on-site treatment of excavated soils in a specially constructed shallow treatment basin—one meeting the requirements of the Resource Conservation and Recovery Act (RCRA). The entire process may require longer treatment times than other technologies, but have a trade off in economy. In addition, the only residue generated from this combination of technologies is soil contaminated with surfactants and the end metabolites of the biodegradation processes. The end metabolites will depend on the original contaminants, and the surfactants are common materials used in agricultural formulations.

UV Photolysis Performance

UV photolysis testing was performed on three soils, one containing TCDD contamination and two containing PCB contamination. The tests were conducted independently by using a medium-pressure Hg lamp, a 10-Hz pulsed lamp and sunlight, and by employing different surfactants and surfactant application procedures. Tests were carried out with either the 450-watt medium pressure Hg lamp or the 70 watts/in. pulsed lamp operating approximately 10 in. above the soil with a parabolic reflector above the lamp.

A composited TCDD soil from a Vertac site in Jacksonville, AR, using two surfactant levels, 2.5% and 5% by weight of the dry soil, was tested. TCDD concentrations on the soil ranged from about 200 to 300 ppb. The soil was mixed and sprayed at 1/2-hr intervals with either surfactant solution or water for a total irradiation time of 48 hr. Results from these tests indicated no apparent destruction of the dioxin on the soil in any of the tests.

Surface soil from a Texas Eastern Gas Pipeline site in Armaugh, PA, contaminated with about 10,000 ppm PCBs (Aroclor 1248) and a pit soil from the same site containing about 200 ppm PCBs were tested under the same conditions given above using different surfactants, application procedures, soil mixing, etc. The results of all of the experiments are summarized in Table 1.

Chemical Oxidation Performance

Five batch experiments using the H_2O_2/Fe (Fenton's) reagent system were done at ambient temperature. All five used the same clay/humic surface soil that was used in the UV photolysis testing. This soil provided samples for treatment that ranged from 5000 to 10,000 ppm PCBs (Aroclor 1248). Conditions were established to provide the best opportunity for observing an effect due to treatment. Each experimental mixture was pH adjusted to a pH between 2 and 4 and continuously stirred. Hydrogen peroxide concentration was monitored throughout each experiment and additions were made as necessary to maximize concentration. Reagent-to-soil ratios were high, and Fe concentrations were varied between experiments to investigate the effect. The treated soil was analyzed either at the end of the treatment time or sampled at selected times throughout the run if sufficient soil was used in the test. Results from testing are summarized in Table 2.

Biological Treatment Performance

The ability of selected organisms to biotransform PCB congeners in surfactant/UV-treated and untreated soil was evaluated during two bioslurry treatment experiments. The first bioslurry experiment evaluated the biological reduction of PCB congeners in surfactant/UV-treated and untreated soils. A subsequent enhanced bioslurry experiment evaluated the impact of PCB-biodegradation inducers on congener removal. Previous studies show that the addition of biphenyl, 4-bromobiphenyl (4-BB), 4-chlorobiphenyl, 2-chlorobiphenyl, or other monochlorobiphenyls have induced and enhanced aerobic PCB biodegradation.

The bioslurry experiments were conducted under aerobic conditions at 25°C using PCB-degrading organisms from two sources. PCB-degrading organisms were isolated from an impacted New England Superfund Site soil (BAC 17). In addition, known-PCB degrading microorganisms were obtained from General Electric Corporation (GE; H850). Three PCB-contaminated soils were evaluated for biological reduction of PCB congeners. Soils employed were identified as untreated surface soil from the UV photolysis testing, surfactant/UV-treated surface soil, and New England Superfund Site soil. In separate tests, each soil was treated with the bacteria cultures, BAC 17 and H850. In

Table 1. *Summary of UV Photolysis Results on PCB Contaminated Soil*

Test	Soil Type	Soil Depth in.	Surfactant, %	Lamp Type	Temperature °C	Time (Hr)	Initial PCB Conc., ppm	Final PCB % Reduction
1	surface	0.25	2	pulsed	25	12	7240	<15
2	surface	0.25	2	medium pressure pulsed	28	7	7430	<15
3	surface	0.25	2	medium pressure Hg	40	7	8440	33
4	pit	0.5	2	medium pressure Hg	30	16	140	30
5	pit	0.5	2	pulsed	28	16	157	13
6	pit	0.5	2	pulsed	28	12	170	23
7	pit	1.0	4.5	solar irradiation	30-40	25 days	132	<15
8	pit	1.0	2	solar irradiation	30-40	25 days	159	<15
9	pit	1.0	0	solar irradiation	30-40	25 days	171	<15
10	surface	0.25	2.5	medium Hg		20	10000	52*
11	surface	0.25	2.5	medium Hg		20	10000	32

**Increase in concentration noted for di-PCBs, decrease in concentration for tetra through hepta-PCBs.*

Table 2. *Summary of Chemical Oxidation Testing*

Test	Amount of Soil, g	Water/Soil Ratio	pH	Fe, % of Soil	H_2O_2 Conc. (%) Average	Time (Hr)	Percent Reduction of Starting PCB Concentration
1	10	9.7	2.8	2.5	.07	162	44
2	8.0	8.4	2.5	0.1	1.8	118	55
3	8.1	9.5	2.2	0.5	0.87	118	45
4	170	10.1	3.1	.09	1.6	845*	35
5	196 w/surfactant	8.0	2.9	.09	0.88	184	<15

**No further decrease in PCB concentration observed after 211 hr.*

addition a killed control sample was prepared for each soil. Table 3 summarizes the reductions measured for the PCB homologs after four weeks.

In the enhanced bioslurry experiment, the effect of adding 1,000 mg/L biphenyl inducer and 1,000 mg/L 4-BB inducer on PCB biodegradation was investigated. The BAC 17 culture was used with the New England Superfund Site soil and the untreated soil because these combinations demonstrated the highest PCB reductions in the bioslurry experiment. The soils were tested with both inducers. Table 4 summarizes the reductions measured for the PCB homologs after one week.

Conclusions

UV photolysis treatment gave no detectable decrease in soil TCDD concentration in the tests conducted and minimal reduction of PCBs. The PCB reductions ranged from less than 15% to a maximum of 52%. The decreases in concentration were highest for higher level chlorinated PCBs (tetra through hepta-PCBs). In some cases greater decreases in concentration of lower chlorine level PCBs were noted. These were suspected to have been lost due to volatilization in tests at increased temperatures caused by the heat generated by the UV lamp, along with the high soil surface area exposed.

Chemical oxidation with Fe catalyzed hydrogen peroxide also provided minimal reduction of PCBs on the highly contaminated surface soil tested. The PCB concentration reductions ranged from less than 15% to a maximum of 55% in reaction times of well over 100 hours. Highest reductions were observed with higher Fe-to-soil ratios and maximized concentrations of hydrogen peroxide, up to 2%, by periodic additions. Where concentrations were reduced, the losses of PCBs were observed more from the lower chlorinated homologs (di and tri-PCBs) and less from the higher chlorinated homologs (tetra through hepta-PCBs).

Bioslurry treatment did not provide significantly different results for the UV-treated surface soil versus the untreated soil. This was not surprising since UV treatment was not successful in significantly degrading the higher chlorine level PCB homologs. Percent reductions of PCBs were highest for a New England Superfund Site soil that had a significantly lower concentration of PCB contamination. The culture isolated from the New England soil gave 70%, 20% and 30% reduction of the di, tri, and tetra-PCBs, respectively, in the New England soil. PCB reductions lessened with increasing level of chlorination with no significant reduction noted for penta, hexa, or hepta-PCBs. Similar results were obtained with inducer additions to the soils. Biphenyl addition gave even greater reduction in PCB concentrations for the New England site soil with reductions of 82%, 54%, 63% and 16% for di, tri, tetra, and penta-PCBs, respectively.

Recommendations

Although the percent of PCB degradation was low, meaningful destruction rates may have been masked by the high concentration of PCBs in the surface soil that was used in many of these tests. Although the lower PCB concentration pit soil was used in some of the photolysis tests with little difference in results, a more detailed analysis of the processes would be allowed if soils with lower, but still practical PCB concentrations (<1000 ppm), were used in this early phase of testing.

High amounts of surfactant were carried through the treatment process and may have been inhibitory to bacterial activity or promoted non-PCB degrading activity. Likewise, the treated soil had a pH of 5.5, which may have been inhibitory to the bacteria and probably was a result of surfactant addition. An additional soil washing step may be necessary to remove/recycle surfactant from the soil and neutralize the pH before biological treatment.

In addition, correlations of PCB-degrading activity with soil type, PCB concentration and composition, biphenyl/PCB concentrations, and bacterial populations need to be explored.

Both of these processes may be enhanced by adding surfactants to the soil to solubilize the contaminants and to provide a medium for reaction mass transfer processes.

The full report was submitted in fulfillment of Cooperative Agreement No. CR816817-02-0 by IT Corporation under the sponsorship of the U.S. Environmental Protection Agency.

Table 3. *Percent Loss of Homolog Groups at Four Weeks Bioslurry Evaluation*

Congener Group	*UV-Treated Soil*[a]		*Untreated Soil*[b]		*New England Soil*[c]	
	Treatment B1 (BA 17)[d]	*Treatment B2 (H850)*	*Treatment B4 (BAC 17)*	*Treatment B5 (H850)*	*Treatment B7 (BAC 17)*	*Treatment B8 (H850)*
Dichlorobiphenyl	24	21	67	0*	70	40
Trichlorobiphenyl	0	16	0	0	20	0
Tetrachlorobiphenyl	0	0	0	0	30	0
Pentachlorobiphenyl	0	0	0	0	0	0
Hexachlorobiphenyl	0	0	0	0	0	0
Heptachlorobiphenyl	0	0	0	0	0	0

[a]*Surfactant/UV-treated surface soil - 4000 mg/Kg total PCB.*
[b]*Untreated surface soil - 8400 mg/Kg total PCB.*
[c]*New England Superfund Site soil - 350 mg/Kg total PCB.*
[d]*Bacteria Culture.*
**Percent degradation less than 15% is not considered significant and is reported as zero..*