

Assessment of Radiolysis and Chemical Dehalogenation for Decontamination of PCBs and PCDDs in Soil

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Abstract

Chemical dechlorination with immobilized reagents (CDP) and γ -ray irradiation were evaluated in tandem with solvent extraction for decontamination of PCB and PCDD laden soils from wood treatment and electric power substation sites. Evaluations were carried out on a bench scale in the laboratory and on a semi-pilot scale at contaminated sites.

The results of the study indicate that a solvent extraction in tandem with the secondary degradation technique can yield a low-cost but effective treatment process for soils and other porous solids contaminated with PCBs and related persistent organics. The tandem arrangement of solvent extraction and CDP was effective in removing and degrading up to 95% of the PCBs. The radiolytic degradation of PCBs can be carried out directly in solvent impregnated soil, however, extremely high doses are required for effective degradation.

Introduction

Recent US EPA regulatory guidelines permit soil extraction with innocuous solvents for removal of PCBs from contaminated soils.¹ Solvent extraction technologies offer a convenient and cost-effective means for removal of PCBs and other chlorinated compounds. The principal drawback of this technique lies in the fact that the technique, in itself, just transfers contaminants from one phase to another phase. The contaminants transferred into the solvent still must be destroyed through a secondary treatment. The present study was initiated to evaluate the efficacy of two destruction technologies in tandem with solvent extraction. The integrated approach combined solvent extraction with CDP[®], a chemical dehalogenation process based on immobilized reagents, and radiolysis involving γ -ray irradiation for the destruction of PCBs.²⁻⁶

Experiments

Selection of Extraction Solvents: Experiments were carried out to select optimal solvents for extraction and subsequent destruction of the contaminants. The desired characteristics of solvents in this context were low-toxicity, high-solvent strength for the contaminants, compatibility with soil, and low reactivity towards dechlorination reagents. Mixtures of alkanes and low molecular weight alcohols were deemed acceptable. Soils with known concentrations of contaminants were equilibrated with solvent mixtures. The soil and solvent phases were separated and concentrations of the contaminants in solvent mixtures and soil were determined with a gas chromatography – mass spectrometry system.

Chemical Dechlorination Experiments: A chemical reagent consisting of a non-alkali metal, a polyalkyleneglycol or a Nixolens[®], and an alkali hydroxide or an alcoholate was prepared. Non-

alkali metals were used as dehalogenation accelerators. Polyalkyleneglycols of different molecular weights were evaluated as phase transfer catalysts. Reagents were immobilized on a suitable adsorbent and packed into thermostated columns. The mole ratios of polyglycole or Nixolens[®] and hydroxide to the total halogen content of the contaminated matrix was varied from 1:1 to 30:1 and 10:1 to 200:1, respectively. The concentration of non-alkali metal in the reaction mixture was varied from 0.02% to 5% (w/w basis).

γ -Ray Irradiation Experiments: These experiments were carried out with ⁶⁰Co γ -ray sources at the University of Missouri Research Reactor (MURR). Aliquots of PCB-contaminated materials (soil, dielectric fluids, and solvent mixtures) were placed in clear borosilicate glass vials with PTFE-lined polyphenolic screw caps. Vials were placed at different distances from the ⁶⁰Co sources and irradiated for varied time periods. This arrangement permitted varied exposure doses. Four sets of irradiation experiments were conducted. In the first set, known concentrations of PCBs in solvent mixtures were irradiated at different dose rates. In the second set, dry soils with known amount of homogeneously distributed PCBs were irradiated. The third set of experiments was carried out with PCB contaminated soils saturated with solvent mixtures. The last set of experiments was conducted with solvent extracts of PCB fortified soils.

Field Trials: Field trials to evaluate the applicability of solvent extraction for removal of PCDDs and PCBs were conducted at a contaminated wood treatment site in the San Joaquin Valley, California. Experiments were carried out in batch mode with 8 stainless steel treatment bins, each capable of holding 500 kg of contaminated soils. Soils were homogenized in large batches and packed into the treatment bins to a depth of 90 cm. Solvent was introduced through a sintered stainless steel plate placed one centimeter above the sealed bottom of the treatment bins. The extracted contaminants in the solvent were collected at the top and subjected to degradation techniques.

Quantitative Determination of PCBs, and PCDDs: The quantitative determination of contaminants in soils and organic solvents was carried out with gas chromatographs interfaced to an electron capture detector or a quadrupole mass spectrometer. The gas chromatographic separations of PCB congeners were carried out with a 30m x 0.25mm (I.D.) fused silica capillary coated with methyl:phenyl (95:5) polysiloxane stationary phase. Prepurified helium was used as the mobile phase, and its flow rate was maintained at 1ml min.⁻¹ Separations were achieved through linear temperature programming of the column oven temperature from 100–260 °C. The separated components were monitored with an electron capture detector or a quadrupole mass spectrometer. The mass spectrometer was operated in the selected ion-monitoring mode.

Results and Discussion

Extraction Solvent: The best extraction efficiency was obtained with 5:1 alkane-alcohol mixture. The analysis of soils before and after the solvent extraction showed that up to 95% of PCDDs and PCBs were removed from the soils.

Chemical Dechlorination: Efficiency of the chemical dechlorination process (CDP) was evaluated with transformer oils and alkane alcohol mixtures contaminated with PCBs. The PCB concentration in these matrices ranged from 10-30,000 ppm. In one experiment, hydrocarbon transformer oil with a PCB concentration of approximately 700 parts per million (ppm) was treated with CDP with vigorous mixing. Analysis of aliquots taken at different time intervals showed that PCB concentration was reduced rapidly to 2 ppm in less than 20 minutes (Figure 1).

In the ultrasound augmented treatments, the PCB concentration in transformer oil was reduced from 700 ppm to less than detectable level in less than 5 minutes. In other experiments,

concentration of PCBs in transformer oil was reduced from 8765 ppm to 20 ppm in less than 30 minutes. The most effective reagent was found to consist of a polyalkyleneglycol or an alkene oxide copolymer (molecular weight ≥ 6000) plus a non-alkali metal accelerator such as aluminum (0.1 to 0.2% w/w) and an alkali hydroxide or an alcoholate. The reagent was found to be very effective even in the elimination of contaminants with low chlorine content such as Aroclor 1242 and 1254. The process has been adapted for continuous operation by immobilizing the reagents on solid carriers of specific particle size and pore size distribution. This configuration of the process has been found to be particularly suitable for on-site decontamination of dielectric oil and soil-solvent extracts since it permits treatment in a continuous operation.

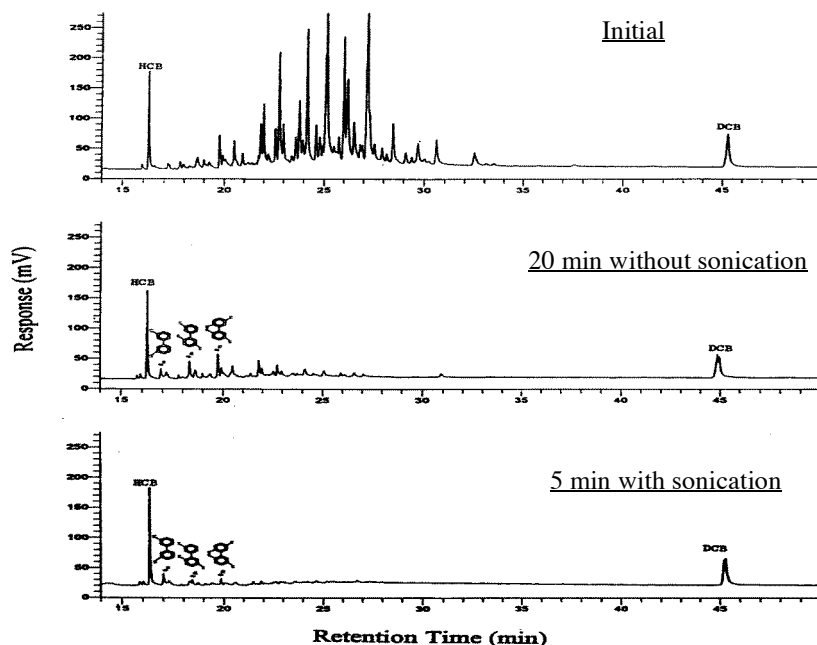


Figure 1. Chromatograms of PCB Residues in Solvent Extract after Chemical Dechlorination

Radiolytic Degradation: The degradation of PCBs was observed in soils irradiated with γ -rays. Residues remaining after irradiation were extracted and measured with a GC-ECD setup. The results showed that the PCB concentrations decreased with an increased γ -ray dose. However, large doses in the mega rad range were required to bring the concentrations down to acceptable levels. Degradation of PCBs occurred at a faster rate when the soils were partially saturated with organic solvents. The degradation rates obtained in these experiments were similar to the degradation rates obtained in the solvent mixtures without soil. These observations are consistent with the mechanism for solvent mediated degradation of PCBs. Nevertheless, high irradiation doses were still needed for effective degradation of PCBs. In one experiment, nearly 60 mega rads were needed to degrade PCBs from 300ppm down to 1ppm in solvent saturated soil. A comparison of radiolytic degradation of PCBs in different matrices is shown in Figure 2.

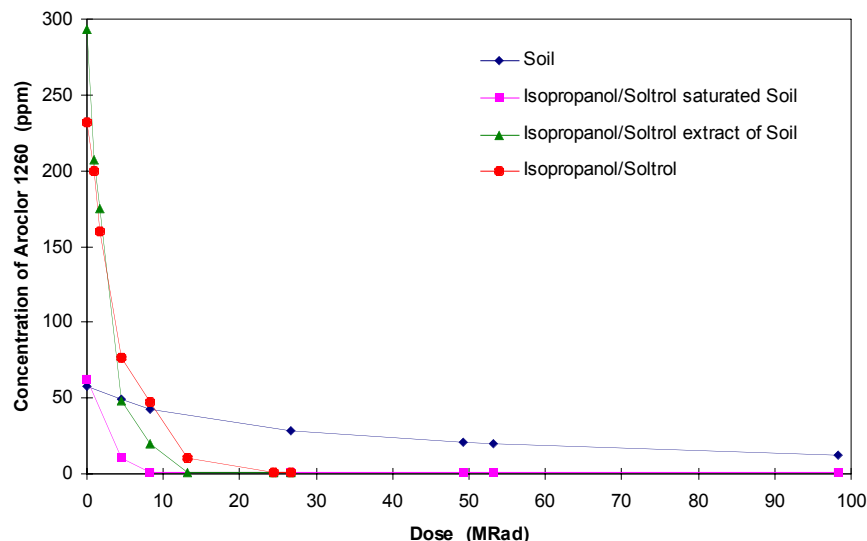


Figure 2. Radiolytic degradation of Aroclor 1260 in different matrix

The chromatographic analysis of degraded PCB mixtures indicated that the γ -ray induced degradation proceeds through a reductive dechlorination process leading to the PCBs with successively lower numbers of chlorines. These observations were confirmed by irradiating solutions containing known concentrations of individual PCBs congeners. The irradiated samples were analyzed with the capillary gas chromatography–mass spectrometry system. The identity of radiolytic products detected in the chromatograms was confirmed with mass spectra. The major radiolysis products of PCB #180 were hexachloro biphenyl congeners, PCB #167-(2,3,4,4', 5,5'), PCB #153-(2,2', 4,4', 5,5') and PCB #141-(2,2', 3,4,5,5'). Formation of these congeners indicates that the γ -ray induced dechlorination occurs preferentially at the meta position. Higher doses led to formation of pentachlorobiphenyls and other PCBs with lower chlorine substitutions.

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References

1. 40 CFR 761, US EPA Regulatory Guidelines.
2. Tumiatti, W., S. Dallo, P. Aglietti, G. Camino and S. Kapila; Proceedings of EPRI 1995 PCB Seminar, August 29-31, 1995; Boston, Massachusetts.
3. Tumiatti, W., SEA Marconi, European Patent Appl. N. PCT/EP93/03609, 1993.
4. Singh, A., W. Kremers, P. Smalley, and G.S. Bennett, *Radiat. Phys. Chem.* 25, 11, 1985.
5. Mincher, B.J., R.E. Arbon, W.B. Knighton and D.H. Meikrantz, *Appl. Radiat. Isot.*, 45 (8), 879-887, 1994.
6. Kapila, S., and W. Tumiatti, SEA Marconi, European Patent Appl. 1997.