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Solvent extraction and tandem dechlorination for decontamination of soil

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Abstract

The United States Environmental Protection Agency (US EPA) guidelines allow removal of polychlorinated biphenyls (PCBs) from soils via solvent extraction. This option holds promise for removal of other recalcitrant organic contaminants as well. A study was undertaken to evaluate the effectiveness of solvent extraction with two tandem degradation techniques. The degradation techniques were chemical dehalogenation with immobilized reagents and γ-ray irradiation. The integrated approach was evaluated with contaminated 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 a contaminated site. Binary solvent mixture of alkanes and alcohols yielded the highest extraction efficiencies. Extraction efficiencies in excess of 90% were obtained for PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polynuclear aromatic hydrocarbons (PAHs). Extracted PCBs were rapidly degraded through chemical dehalogenation or with high doses of the γ-ray irradiation. The residual organics in the solvent mixture were removed with activated carbon, and the solvent was recycled for subsequent soil extractions. Contaminants adsorbed on the activated carbon were destroyed with a counter flow oxidation process.

Keywords: Dehalogenation; Chemical treatment; Irradiation; Pollutants; PCBs

1. Introduction

The presence of recalcitrant organic contaminants in soil continues to be a cause of concern. Chlorinated aromatic compounds, as a class, are some of the most persistent organic pollutants. The members of the class include polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), chlorinated phenols, and polyhalogenated alkyl benzenes, to name just a few. During the past two decades, several methods for removal and disposal of these compounds from varied environmental matrices have been proposed and implemented on a commercial scale. These include incineration, UV–Vis photolysis, radiation, chemical dehalogenation, and deposition in secured landfills. Due to low penetration of light and the presence of reactive chemicals, degradation of chlorinated contaminants in soil through direct photolysis or chemical dechlorination has not been successful. As a result, high-temperature incineration continues to be the treatment of choice for highly contaminated soils and other solid matrices (Hunt and Wolf, 1984; Skinner and desRosiers, 1989). High-temperature incineration is highly effective for destruction of PCDDs and PCBs. The technique has been successfully used at contaminated sites, such as Times Beach, Missouri. Due to its

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high cost, the application of this technology is primarily limited to destruction of Askarel, mineral oils with high concentrations of PCBs, and PCDD-laden soils.

Recent (US Environmental Protection Agency) regulatory guidelines permit soil extraction with innocuous solvents for removal of PCBs from contaminated soils. Solvent extraction technologies offer a more 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 (Tumiatti, 1993; Tumiatti et al., 1995), and radiolysis involving γ-ray irradiation (Singh et al., 1985; Mincher et al., 1994) for the destruction of PCBs.

2. Laboratory experiments

2.1. Selection of extraction solvents

These 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. On the basis of these criteria, mixtures of alkanes and low molecular weight alcohols were deemed acceptable. These solvents possess low toxicity, low extinction coefficient, and do not react with alkali metal glycolate based dechlorination reagents. To arrive at the acceptable solvent mixture, partition experiments were carried out. Soils with known concentrations of contaminants were equilibrated with enough solvent to achieve near saturation. 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.

2.2. 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. This reagent eliminates the safety and reaction rate problems encountered with the alkali metal or alkali metal oxide–polyethylene glycol based reagents. A number of non-alkali metals were used as dehalogenation accelerators. Polyalkyleneglycols of different molecular weights were evaluated as phase transfer catalysts. The dechlorination experiments were conducted in a batch mode or in a continuous mode.

For continuous mode, reagents were immobilized on a suitable adsorbent and packed into thermostated columns. A variety of adsorbents were evaluated for the purpose. To optimize the process, the mole ratios of polyglycol or Nixolens® and hydroxide or alcoholate 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). To ascertain the dehalogenation efficiency of the process, aliquots of contaminated matrices were sampled and analyzed with a gas chromatograph with an electron capture detector at the start of the treatment and at set time periods thereafter.

2.3. γ-ray irradiation experiments

These experiments were carried out with ^{60}Co γ-ray sources at the University of Missouri Research Reactor (MURR). Aliquots of PCB-contaminated materials (soil, dialectric 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 ^{60}Co 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 irra-

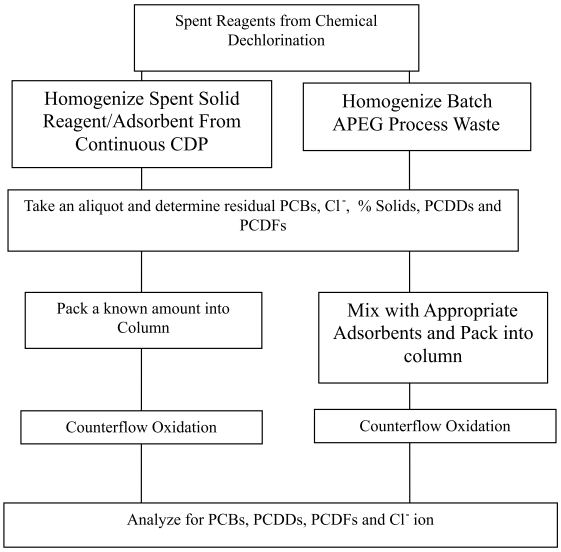

Fig. 1. Flow schematic of counterflow oxidation experiments.

diated. 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.

2.4. Counterflow oxidation

The objective of these experiments was to evaluate the efficacy of counterflow oxidation for the destruction of PCBs adsorbed on carbonaceous adsorbents and the spent dechlorination reagents. The experimental protocol for the experiments is given in Fig. 1.

2.5. Field trials

Field trials to evaluate the applicability of solvent extraction for the removal of PCDDs and PAHs were conducted at a contaminated wood treatment site in the San Joaquin Valley, California. Experiments were carried out in batch mode with eight stainless steel treatment bins, each capable of holding 500 kg of contaminated soils. The contaminated soils were excavated at the site during an exploratory drilling operation to assess the extent of contamination. Soils were homogenized in large batches and packed into the treatment bins to a depth of 90 cm. Aliquots of soil were analyzed to ascertain the concentration of contaminated mixture in soil. 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. Residual solvents were removed from the soil by pumping water from the bottom of the soil bed.

2.6. Quantitative determination of PCBs, PCDDs, and PAHs

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 analytical methodologies used for these determinations are outlined in the flow schematics in Fig. 2. The gas chromatographic separations of PCB congeners were carried out with a 30 m × 0.25 mm (I.D.) fused silica capillary coated with methyl:phenyl (95:5) polysiloxane stationary phase. Prepurified helium was used as the carrier gas, and its flow rate was maintained at 1 ml 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.

3. Results and discussion

3.1. Solvent selection

One of the most important criteria for selection of solvents was the equilibration period needed to extract the contaminant soil. Short equilibrium periods are

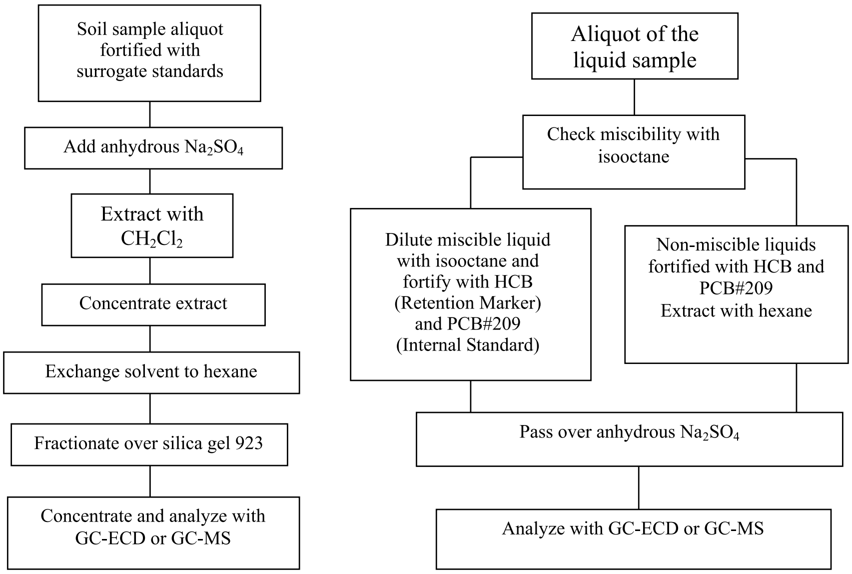

Fig. 2. Flow schematic of analytical methodologies for determination of PCBs and other contaminants.

desirable for high throughput. It was found that the equilibration period increased with the increased fluid viscosity. Thus, higher alkane homologs required longer equilibration periods. Alkanes with chain length longer than C_{12} were found to be unsuitable because of excessively long equilibration period. Results showed that greater than 90% of the contaminants could be readily desorbed into decane and lower hydrocarbons. The addition of small amounts of alcohols yielded higher extraction efficiencies. The best results were obtained with 5:1 alkane–alcohol mixture. The analysis of soils from the field treatment bins showed that 90–95% of PCDDs and PAHs were removed from the soils.

3.2. Chemical dechlorination

Efficiency of the chemical dechlorination process (CDP) was evaluated with liquids such as transformer oils and alkane alcohol mixtures contaminated with PCBs. The PCB concentration in these matrices ranged from 10–30,000 parts per million (ppm). In one experiment, hydrocarbon transformer oil with a PCB concentration of approximately 700 ppm was treated with CDP by vigorously mixing reagents at 100°C. The concentration of PCBs was monitored over time periods ranging from 2–120 min. The results showed that PCB concentration was reduced rapidly to 2 ppm in less than 20 min. The PCB concentration was lowered further to 0.2 ppm in 30 min. The gas chromatographic profiles of PCB residues remaining after different treatment periods are shown in Fig. 3. It was observed that the dechlorination efficiencies were enhanced significantly with the application of ultrasound (20 kHz, intensity 50 W/cm^2). 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 min. In other experiments, concentration of PCBs in transformer oil was reduced from 8765 to 20 ppm in less than 30 min. The most effective reagent was found to consist of a suitable polyalkyleneglycol or an alkene oxide copolymer (molecular weight $\geqslant 6000$) 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 is particularly suitable for on-site decontamination of dielectric oil and

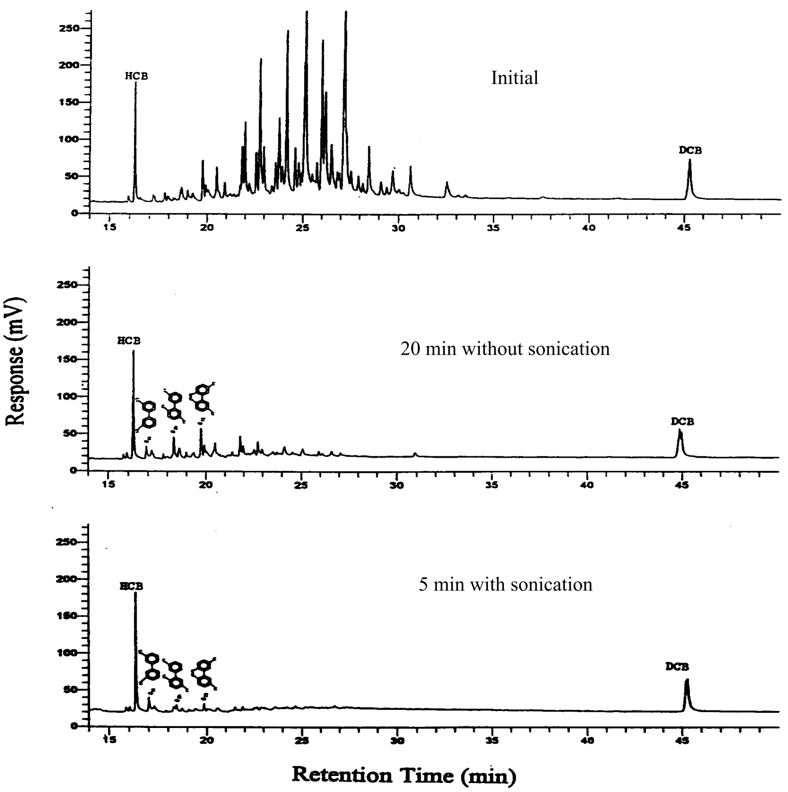

Fig. 3. Chromatograms of PCB residues in solvent extract after chemical dechlorination.

soil–solvent extracts since it permits treatment in a continuous operation.

3.3. 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 resulting chromatograms are shown in Fig. 4. The chromatograms depict the concentrations of residual PCBs extracted in soils after different doses of γ-ray irradiation. The results show that the PCB concentrations decreased with an increased γ-ray dose. However, large doses in the megarad 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 Mrad were needed to degrade PCBs from 300 ppm down to 1 ppm in solvent saturated soil. A comparison of radiolytic degradation of PCBs in different matrices is shown in Fig. 5.

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 congers. 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 chromatographic data for non-irradiated and irradiated solutions of PCB#180 (2,2′, 3,4,4′, and 5,5′-heptachlorobiphenyl) are shown in Fig. 6. 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.

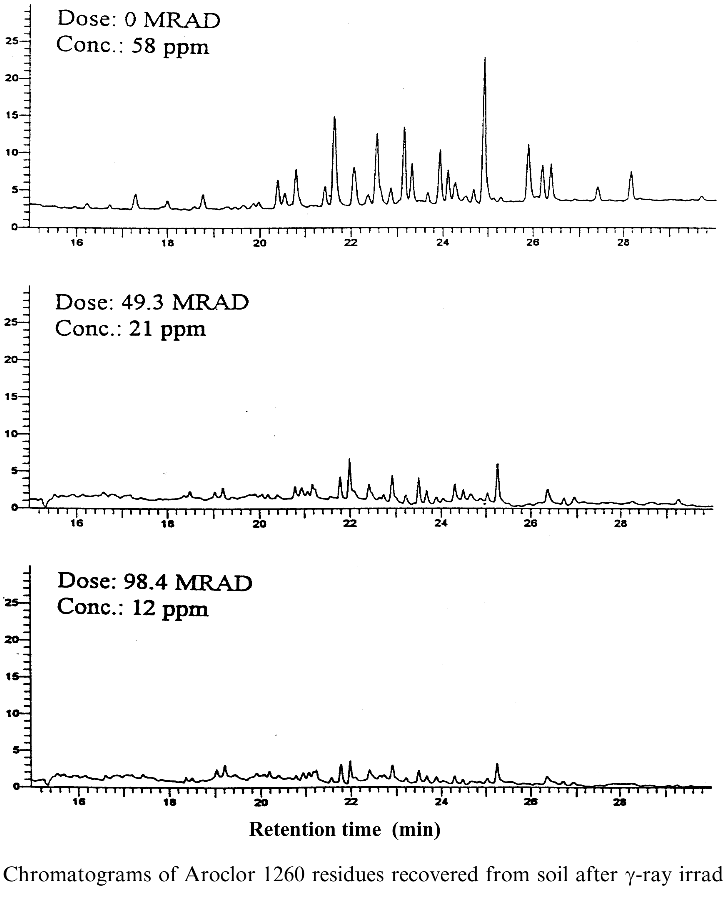

Fig. 4. Chromatograms of Aroclor 1260 residues recovered from soil after γ-ray irradiation.

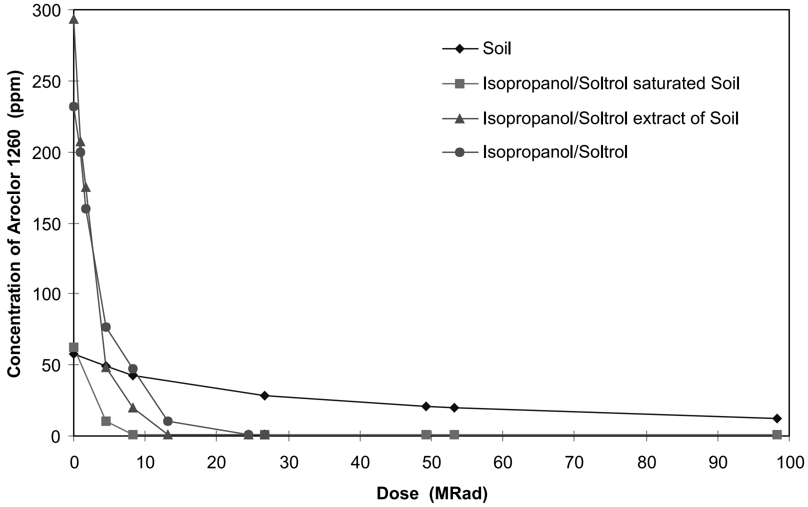

Fig. 5. Radiolytic degradation of Aroclor 1260 in different matrices.

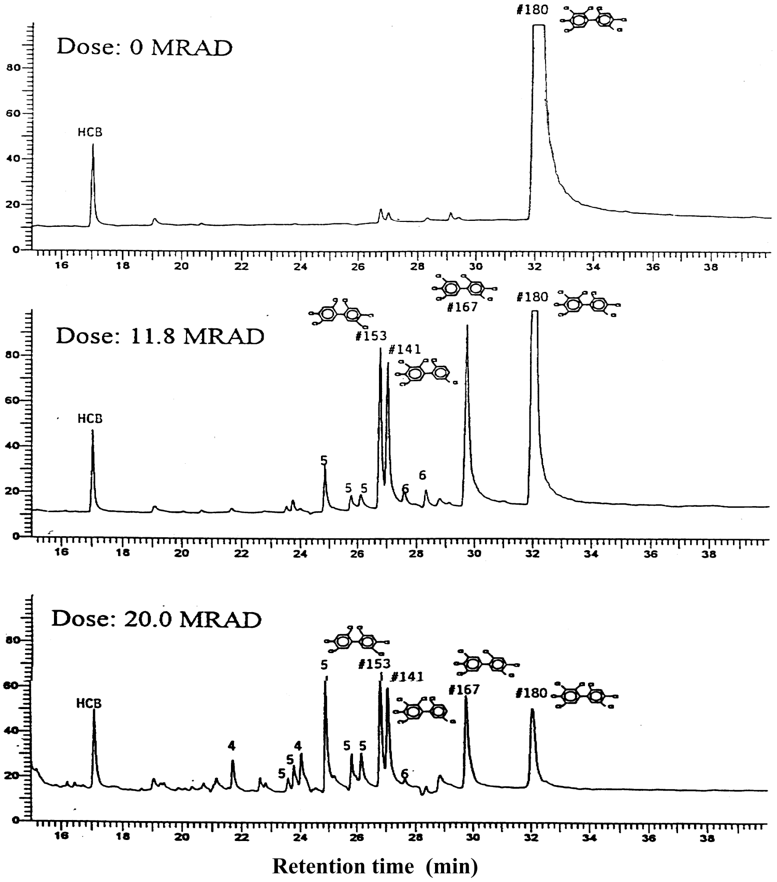

Fig. 6. Chromatograms of a PCB#180 solution before and after γ-ray irradiation.

3.4. Counter flow oxidation

The residual contaminants in the solvents were removed with activated carbon that was, in turn, regenerated with a controlled oxidation process termed "counterflow oxidation". The details of the process have been provided elsewhere (Kapila and Tumiatti, 1997). Results show that the process is highly effective in degrading PCBs adsorbed on carbonaceous adsorbents. Degradation efficiencies better than 99.99% were achieved with PCB-containing liquid and solid matrices. It should be pointed out that experiments conducted earlier in our laboratory had shown that the process did not affect the surface area and the absorptive capacity of the adsorbent, thus permitting its repeated utilization.

4. Conclusions

The results of the study indicate that a solvent extraction in tandem with 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 combination with the CDP process should prove to be cost effective. The radiolytic degradation of PCBs is effective only in solvent impregnated soils at high doses and is not likely to be of practical use.

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References

Hunt, G.T., Wolf, P., 1984. Incineration of PCBs. Environ. Sci. Technol. 18, 171–179.

Kapila, S., Tumiatti, W., 1997. SEA Marconi, Inc., European Patent Appl..

Mincher, B.J., Arbon, R.E., Knighton, W.B., Meikrantz, D.H., 1994. Gamma-ray induced degradation of PCBs in neutral isopropanol using spent reactor fuel. Appl. Radiat. Isot. 45 (8), 879–887.

Singh, A., Kremers, W., Smalley, P., Bennett, G.S., 1985. Radiolytic dechlorination of polychlorinated biphenyls. Radiat. Phys. Chem. 25, 11.

Skinner, J.H., desRosiers, P.E., 1989. Advances in dioxin risk management control technologies. Chemosphere 18 (1–6), 41–55.

Tumiatti, W., 1993. SEA Marconi, Inc., European Patent Appl. # PCT/EP 9310360, 1997.

Tumiatti, W., Dallo, S., Aglietti, P., Camino, G., Kapila, S., 1995. CDP process: a new technology for continuous dehalogenation of PCBs in oil. In: Proceedings of Electric Power Research Institure (EPRI) PCB Seminar, Boston, Massachusetts, 29–31 August, 1995.

US Environmental Protection Agency, US EPA Regulatory Guidelines. 40 CFR 761.