APPLICATION OF SOLVENT EXTRACTION TECHNOLOGY TO PCB CONTAMINATED SOIL AND CHEMICAL/BIOASSAY MONITORING

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Introduction

Unlawful dumping of capacitors of polychlorinated biphenyl (PCB) use found in Kobe, Japan in 2001 left about 60 m^3 of soil contaminated with PCBs. Solvent extraction process [1] has remedied 68 m^3 (92 ton) of the relevant soil at the site during 2002 – 2003. This paper describes the situation of soil contamination, summary of solvent extraction treatment applied and monitoring results (chemical analysis and bioassay) during this remediation.

PCB contamination at the site

The contamination site was grassland in the mountains of Kobe, Japan. Totally 19 capacitors were put on the bed of an abandoned truck and PCB oil spill from two broken capacitors were observed. The PCB spill amount was estimated at approximately 6.6 kg by actual PCB oil loss. The specified PCB was a mixture of Kanechlor-300 and Kanechlor-400. In order to obtain a detailed horizontal/vertical distribution of PCB concentrations, soil samples were taken according to the procedure of Ministry of the Environment of Japan [2]. Figure 1 denotes the contamination area where PCB was detected (above the Japanese environmental limit value). The relevant mass of contaminated soil was 68 m^3 (about 6.4 m x 6.2 m in surface area and 2.0 m in depth at maximum). Soil from this area was excavated and treated by the solvent extraction.

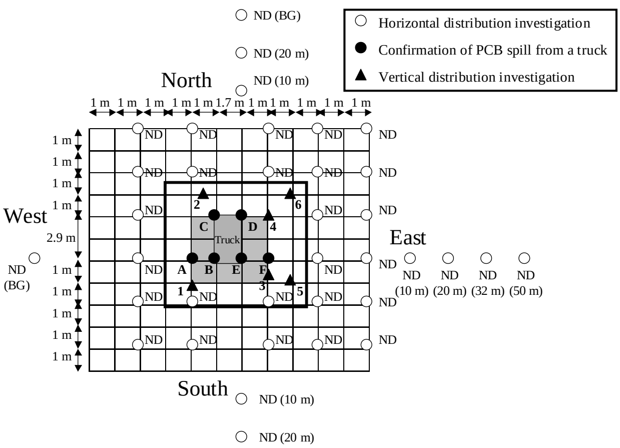


Figure 1. PCB contamination and excavation area (surrounded by a thick line)

Soils consist of a mixture of clay and Masa soil that is derived from weathering of granite. Two samples of the site soil have following characteristics: density: 2.6 g/cm^3, 50% grain size: 3.4 – 7.1 mm, grain size > 75 mm (gravel): 0.7 - 0.8%, 2-75 mm (gravel and sand): 60 - 68%, 75 µm – 2 mm (sand): 18 – 23%, 5 – 75 µm (silt): 7 – 8%, < 5 µm (clay): 7 – 9%. For the soil samples, 80% of PCBs was contained in the fraction of 0.1 – 2 mm grain size.

Solvent extraction technology

Solvent extraction technology was adopted to treat soils contaminated with PCBs on site. Prior to a full-scale treatment, an initial treatability study was conducted to determine the technology's applicability to PCB removal from the soil of the site. A schematic diagram of this full-scale process is shown in Fig. 2. The major components consist of solvent extraction container, vacuum extraction system and solvent purification system. When operating a treatment, soil was treated in a container that held about 1.5 m^3 of soil. Solvent (isopropanol) was pumped into the container. With the container covered and sealed to prevent contaminant and solvent loss, the isopropanol solvent mobilized PCBs. The solvent remained in contact with the soil for about two hours at ambient temperatures and pressures. After the extraction, the majority of solvent was drained and residual solvent was removed from soil using vacuum extraction. The collected extracted solvent was introduced to the solvent purification system to remove PCBs from the solvent; the solvent purification system consisted of two unit operations: filtration and PCB removal, and the purified solvent was then pumped to the clean solvent storage tank. Extraction cycles were repeated until the PCB concentrations in the soil are less than the Japanese environmental limit value (not detected (< 0.0005 mg/L) in a leaching test as measured by GC-ECD).

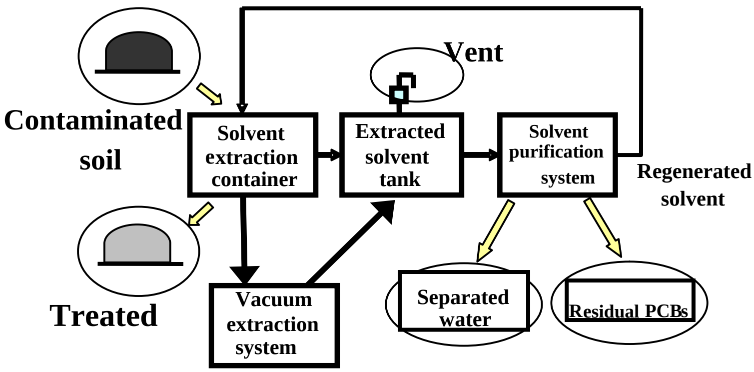


Figure 2. Solvent extraction process description

Demonstration results

Totally 47 batch treatments were conducted for the PCB contaminated soil. Samples of untreated and final treated soils (collected as composite samples to ensure homogeneity) corresponding to each batch were analyzed for PCBs by GC-MS. It took 8.4 cycles on average to reduce PCB concentrations to the required level throughout all the batch treatments. When treating soils of deep part with high clay fractions, addition of extraction cycles was needed to achieve the PCB reduction to targeting concentrations. PCB analysis indicated that the average PCB concentration in the untreated soil was 88 µg/g-dry (the median concentration was 47 µg/g-dry) and that in the treated soil was 1.2 µg/g-dry (the median concentration was 0.71 µg/g-dry). The average PCB removal efficiency was about 99% (Fig. 3).

PCB and dioxin congener/homologue analysis results for untreated and treated soils in one representative treatment batch were indicated in Fig. 4. Two to three orders of magnitude in reduction was observed for TriCBs and TetraCBs with high occurrence and more highly chlorinated PCBs. Compared to those PCB homologues, relatively lower removal (one to two orders of magnitude) was observed for MCBs and DiCBs. As for dioxins, reduction for PCDFs was about 90% on the whole, which was relatively higher than that for PCDDs. TEQ levels for untreated and treated soils in five batches were shown in Fig. 5. Untreated soils with about 100 µg PCB/g-dry contained around 1,000 pg-TEQ/g-dry equal to the Japanese environmental limit value for soil. However, due to the removal of contributing congeners (e.g., PCB #126, 105 and 118) during treatment, TEQs were reduced by two orders of magnitude (6.1 – 36 pg-TEQ/g-dry in the five treated soils).

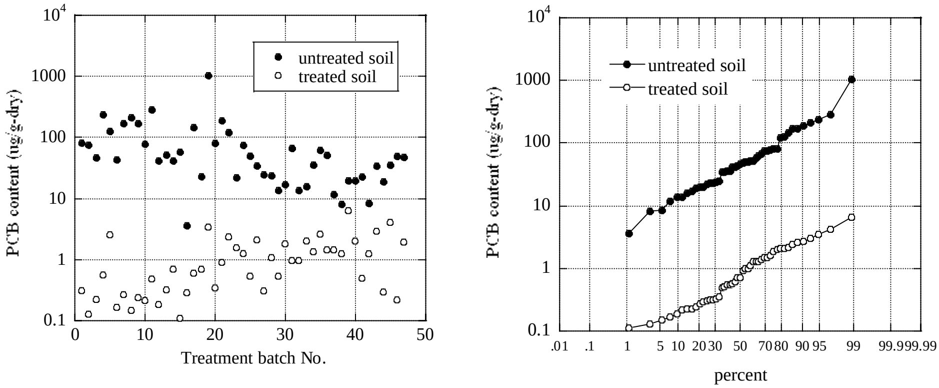


Figure 3. PCB concentrations in untreated and treated soils. (Left) Distribution plotted in order of the treatment batch. (Right) Cumulative distribution curve.

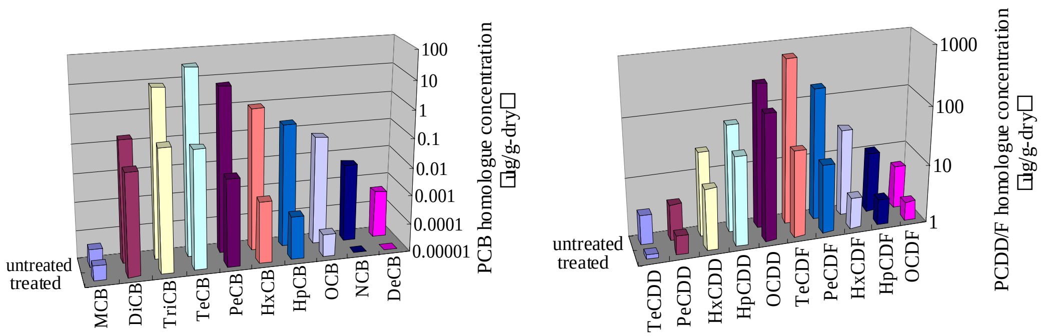


Figure 4. PCB and PCDD/F homologue concentrations in untreated and treated soils for one treatment batch (Lot No. 6).

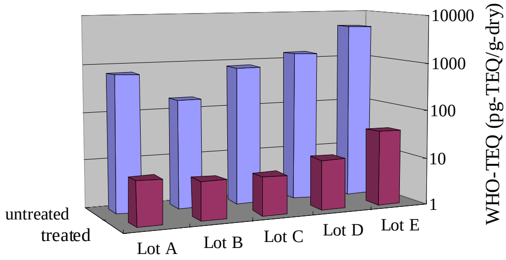
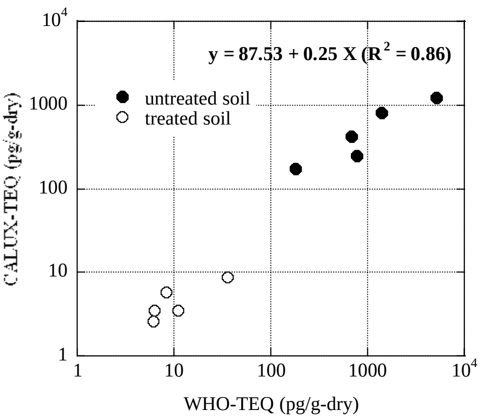


Figure 5. TEQ concentrations in untreated and treated soils for five treatment batches.

Bioassay monitoring results

In vitro bioassay monitoring study during treatment allows screening of dioxin-like potency and toxicological risk assessment using the DR-CALUX® AhR reporter gene bioassay [3] (BDS, the Netherlands) and screening and estimation of PCB content using the ELISA adopting anti-PCB #118 antibody [4] (EnBioTec Laboratories, Japan). By simplifying and optimizing the sample pre-treatment methods, these two bioassays were applied to the soil samples before and after the extraction treatment. For the DR-CALUX measurement of the acid-stable fractions (*i.e.*, *n*-hexane-soxhlet-extract from soil was processed by concrete sulphuric acid treatment on a small scale), the CALUX-TEQs were in good agreement with WHO-TEQs (Fig. 6). On the other hand, the PCB-ELISA results well-correlated with PCB sum using *n*-hexane-soxhlet-extract from soil for the ELISA (Fig. 6). If the sources of PCB contamination of soil are clarified and the contamination is well-characterized (*e.g.*, not complicated), the bioassays can be a powerful analytical tool to be replaced with costly instrumental methods and can serve to give reliable results in the validated case framework.



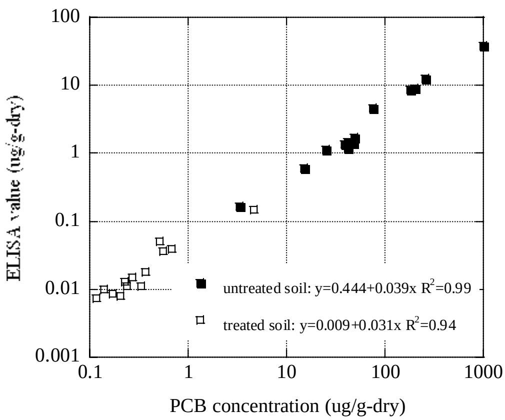


Figure 6. Bioassay results of untreated and treated soils. (Left) DR-CALUX. (Right) PCB-ELISA.

Mass balance of PCBs and compliance with regulatory requirements

After the entire completion of solvent extraction treatment, recovery distribution of PCBs was found to be 6,300 g as concentrated PCBs separated in the solvent purification unit, 8 g as PCBs absorbed in filter and activated carbon used for the separated water treatment process in the solvent purification system. The recovered PCB amount was approximately consistent with the estimated PCB spill amount (6.6 kg).

It was confirmed by regular monitoring that the applied technology met Japanese environmental, health and safety and other regulations related to the operation concerning storage, treatment, transportation and disposal of contaminated soils and treatment residues (details not shown here).

Conclusions

Application results of the solvent extraction technology to PCB-contaminated soil actually found in Kobe, Japan were abstracted in this paper. This technology is available to on-site soil remediation, and can employ appropriate solvents depending on targeting contaminants and soil characteristics, while subsequent destruction of extracted contaminants is an important issue to be tackled on. Bioassays (DR-CALUX and PCB-ELISA) dealt in this study can make it a valuable contribution to monitoring study.

Acknowledgements

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