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# Removal of Aroclor 1016 from contaminated soil by Solvent Extraction Soil Agglomeration Process<sup>1</sup>

A. Majid, S. Argue, and B.D. Sparks

**Abstract:** This communication reports the results of a study to assess the suitability of the National Research Council of Canada's Solvent Extraction Soil Remediation (SESR) process to effectively remediate soils contaminated with PCBs. A series of small-scale batch extraction tests were carried out using a loamy clay soil sample spiked with Aroclor 1016. The variables examined included the effects of solvent type, water addition, agglomerate size, and extraction additives. Aroclor 1016 recovery rates for the SESR process were higher than those found for high shear agitation of soil slurries without agglomeration and Soxhlet extraction ( $93.9 \pm 1.9$ ,  $90.6 \pm 1.5$  and  $82.7 \pm 0.9\%$  respectively). A two-stage extraction process, with a series of three wash steps incorporated into the solid-liquid separation operation, produced a treated soil with an average Aroclor 1016 concentration of  $49 \pm 8$  mg/kg on a dry weight basis ( $95.4 \pm 2.4\%$  removed).

*Key words:* PCBs, soil remediation, agglomeration, solvent extraction.

**Résumé:** Cet article cite les résultats d'une étude visant à évaluer la pertinence du procédé de restauration des sols par extraction au solvant (SESR) du Conseil national de recherches du Canada pour restaurer efficacement les sols contaminés aux BPC. Une série de tests d'extraction par lots à petite échelle a été effectuée en utilisant un échantillon sol loameux additionné d'Aroclor 1016. Les variables étudiées comprenaient les effets du type de solvant, l'ajout d'eau, la dimension de l'agglomérat et les additifs d'extraction. Les taux de récupération d'Aroclor 1016 par le procédé SESR ont été supérieurs à ceux retrouvés par de l'agitation à cisaillement élevé de boues de sols sans agglomération et par l'extraction au Soxhlet ( $93,9 \pm 1,9$ ,  $90,6 \pm 1,5$  et  $82,7 \pm 0,9$  % respectivement). Un procédé d'extraction en deux étapes, avec une série de trois étapes de lavage incorporée dans l'opération de séparation solide-liquide a produit un sol traité contenant une concentration moyenne d'Aroclor 1016 de  $49 \pm 8$  mg/kg de poids sec ( $95,4 \pm 2,4$  % retiré).

*Mots clés:* BPC, restauration des sols, agglomération, extraction au solvant.

[Traduit par la Rédaction]

## Introduction

Polychlorinated biphenyls (PCBs) were used in a wide range of industrial applications and became widely distributed prior to the recognition that they were a persistent environmental hazard. Since PCBs exhibit a high degree of chemical and biological stability and also lipid solubility, they tend to accumulate in the food chains and have been detected in human tissues (Biros et al. 1970). Extremely hydrophobic in nature, PCBs bind strongly to soil and resist biodegradation. Remediation of PCBs and PCB-contaminated soils is a challenging environmental problem.

Existing technologies for the cleanup of PCB-contaminated soil are poorly suited for treating fine textured soils. Most techniques for the removal of PCBs involve solvent extraction – washing and for fine-textured-high-clay soils these techniques tend to produce emulsions. Other soil cleaning technologies, such as high temperature thermal desorption, are also not suitable for treating fine textured topsoils because of adverse effects on soil mineralogy or associated humic matter. In such cases, the treated soil may have to be landfilled or used as subsoil because of impaired soil fertility. The chemical methods for the destruction of PCBs are also said to be impractical for remediation of PCB-contaminated materials (Yang and Pittman 1996).

At the National Research Council of Canada, liquid phase agglomeration techniques, in combination with solvent extraction, have been used successfully for the remediation of fine textured contaminated soils (Majid et al. 1999).<sup>3</sup> Agglomeration binds fine and coarse particles into larger granules, thereby greatly

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**Table 1.** Soil characteristics.

Parameter	Value
Sand content (50–2000 $\mu\text{m}$ ), w/w%	39
Silt content (2–50 $\mu\text{m}$ ), w/w%	27
Clay content (< 2 $\mu\text{m}$ ), w/w%	34
Texture	Silty clay loam
pH	7.9
Cation exchange capacity (meq/100g)	16.9
Electrical conductivity (mS/cm)	26.8
Organic matter, w/w%	4.6

improving the efficiency of the extraction required to achieve effective treatment. Typically, only a few extraction stages are required.

Recently the solvent washing – extraction method has been accepted as an alternative PCB remediation method, provided it is integrated with dechlorination technologies (Curry et al. 1998; EPA 1990). The objective of this investigation was to evaluate the suitability of NRC's Solvent Extraction Soil Remediation process (SESR) for the removal of PCBs from contaminated soil using commercial PCB mixture Aroclor 1016.

## Experimental

Detailed physical and chemical characteristics of soil sample used for this study are given in Table 1. The soil sample was spiked with 800–1200 mg/kg of Aroclor 1016 dissolved in acetone. The spiked sample was mixed for 15 min in a Waring Blendor, and then allowed to air dry for 24 h. Spiking was carried out for each sample used in individual tests instead of preparing a bulk spiked sample and then taking sub-sampling for testing. This approach provided an excellent mass balance for the recovery of Aroclor 1016 of  $95.7 \pm 3.7\%$ .

All substrates and reagents were commercially available unless otherwise noted. Aroclor 1016 was purchased from Crescent Chemical Co., Inc., New York. All other reagents were obtained from Aldrich Chemical Company, Milwaukee.

## Test procedure

A typical test involved mixing samples (100 g) of the PCB contaminated soil with 300 mL of solvent using a Waring Blendor with variable speed control. The supernatant solution was carefully decanted onto a glass filter paper and the filtrate collected in a 500-mL glass-measuring flask. The agglomerates were surface washed using fresh solvent and the washings added to the solution after filtering. After a routine sample preparation, the PCB concentration in the filtrate was determined by gas chromatography. The process was repeated one more time, using fresh solvent, with the incorporation of two further washing steps for the drained agglomerates at the end.

Details of all other procedures used in these tests have been reported previously (Majid et al. 1999).<sup>3</sup> All experiments were carried out in triplicate unless otherwise stated.

## Analytical procedure for the determination of Aroclor 1016

Determination of Aroclor 1016 in the extracts was based on a gas chromatographic procedure developed in-house. The gas chromatograph (GC) used was a Hewlett Packard model 6890 with a flame ionization detector and a 30 m  $\times$  0.53 mm (i.d.) DB-5 capillary column. Chromatographic conditions comprised an initial oven temperature of 30°C for 0.5 min, followed by an increase in temperature of 20°C/min to 210°C. Injection and detector temperatures were kept at 300°C. Quantitation was based on the area count obtained for the merged peaks with the observed retention time of 10.7 min. The area obtained for this peak in the chromatograms of the extracts was compared to the standard and calibration curve to quantify the total PCB 1016 present.

## Results and discussion

Batch laboratory tests have been carried out to evaluate the efficiency of NRC's solvent extraction solids agglomeration process for the removal of Aroclor 1016 from contaminated soils. This was a collaborative project with ALTECH to study the feasibility of using this process for the remediation of PCB-contaminated soil at Ontario Hydro sites. Initially a black Chernozem soil with relatively high clay content and a silty loam sample were used for testing. However, the silty loam sample did not respond very well in terms of solids agglomeration and was discarded in subsequent tests. The following parameters were examined for their effect on degree of Aroclor 1016 removal: solvent type, mode of extraction, mixing, state of aggregation, and additives.

The results from all tests have been summarized in Table 2.

### Effect of solvent type and the mode of extraction

Oil extraction efficiency is known to be affected by solvent type (Walker et al. 1975). PCBs are known to have a higher solubility in modestly polar solvents (Erickson 1991). However, highly polar solvents, being miscible with the needed water as a binder, do not provide a suitable medium for the agglomeration of solids.<sup>3</sup> A mixture of hexane with 5% acetone was tested for its suitability to extract Aroclor 1016 from soil while acting as a non-miscible medium for the aggregation of soil particles by water. The data, presented in Table 2, summarize the results obtained using various solvents under similar experimental conditions, which might not have been completely optimized. The data obtained using Soxhlet method (Yeong et al. 1994) are also included for comparison.

A comparison of the data in Table 2 suggests that, compared to hexane alone, a mixture of acetone and hexane extracts approximately 20–30% more Aroclor 1016 from soil. The degree of PCB dissolution was the highest for the mixtures compared to hexane alone under all modes of extraction. This is consistent with the amounts of residual Aroclor 1016 determined for each test.

**Table 2.** Summary results for Aroclor 1016 extraction from contaminated soil.<sup>a</sup>

Test No.	Solvent	Additive (% of solids)	Water (% of solids)	Size of agglomerates (mm)	Amount of Aroclor 1016 in solution (% of total)	Aroclor 1016 recovery efficiency		Amount of unextractable Aroclor 1016 (mg/kg)
						% of total <sup>b</sup>	% of dissolved <sup>c</sup>	
1	Hexane	—	—	—	61.8	50.2	81.2	384.5
2	Hexane	—	10	1–2	74.9	62.8	83.3	273.9
3	Hexane	Na <sub>3</sub> PO <sub>4</sub> ; (0.5)	10	1–2	74.9	67.3	89.9	286.6
4	5% acetone in hexane <sup>d</sup>	—	—	—	83 ± 1	82.7 ± 0.9	99.6	169.5 ± 8.9
5	As above	—	—	—	92.1	89.4	97.4	76.3
6	As above	Na <sub>3</sub> PO <sub>4</sub> ; (0.5)	—	—	91.3	87.5	99.7	89.5
7	As above	Ca(OH) <sub>2</sub> ; (1.0)	—	—	83.9	83	99	166
8	As above	—	10	0.1–1.0	92.6	91.5	99	68.7
9	As above	—	15	1–2	95.5 ± 1.2 (7) <sup>e</sup>	93.9 ± 1.9	98.5 ± 1.4	63.5 ± 15.8
10	As above	Na <sub>3</sub> PO <sub>4</sub> ; (0.1)	15	1–2	94.6	92.2	97.5	52.1
11	As above	Na <sub>3</sub> PO <sub>4</sub> ; (0.25)	15	1–2	92.8	92.3	99.3	68.9
12	As above	Na <sub>3</sub> PO <sub>4</sub> ; (1.0)	15	1–2	88.4	87.7	99.2	110
13	As above	—	20	2–3 plus sticky mass	95.9 ± 1 (5) <sup>e</sup>	89.6 ± 3.2	94.1 ± 5	37.8 ± 8.3
14	As above	Na <sub>3</sub> PO <sub>4</sub> ; (0.5)	20	As above	94.5 ± 2.4 (5) <sup>e</sup>	86.3 ± 5.0	91.2 ± 3.0	46.5 ± 20.8
15	10% acetone in hexane	—	—	—	93.4	92.1	98.6	64.2
16	As above	Na <sub>3</sub> PO <sub>4</sub> ; (0.5)	—	—	93.9	89.7	95.7	50.5
17	As above	—	15	1–2	95.9	91.3	95.2	41.2
18	As above	Na <sub>3</sub> PO <sub>4</sub> ; (0.5)	15	1–2	85.2	84.5	99.2	142.4

<sup>a</sup>Concentration of Aroclor 1016 in soil ranged from 800 to 1200 mg/kg; solvent to soil ratio: 2:1 (w/w basis).

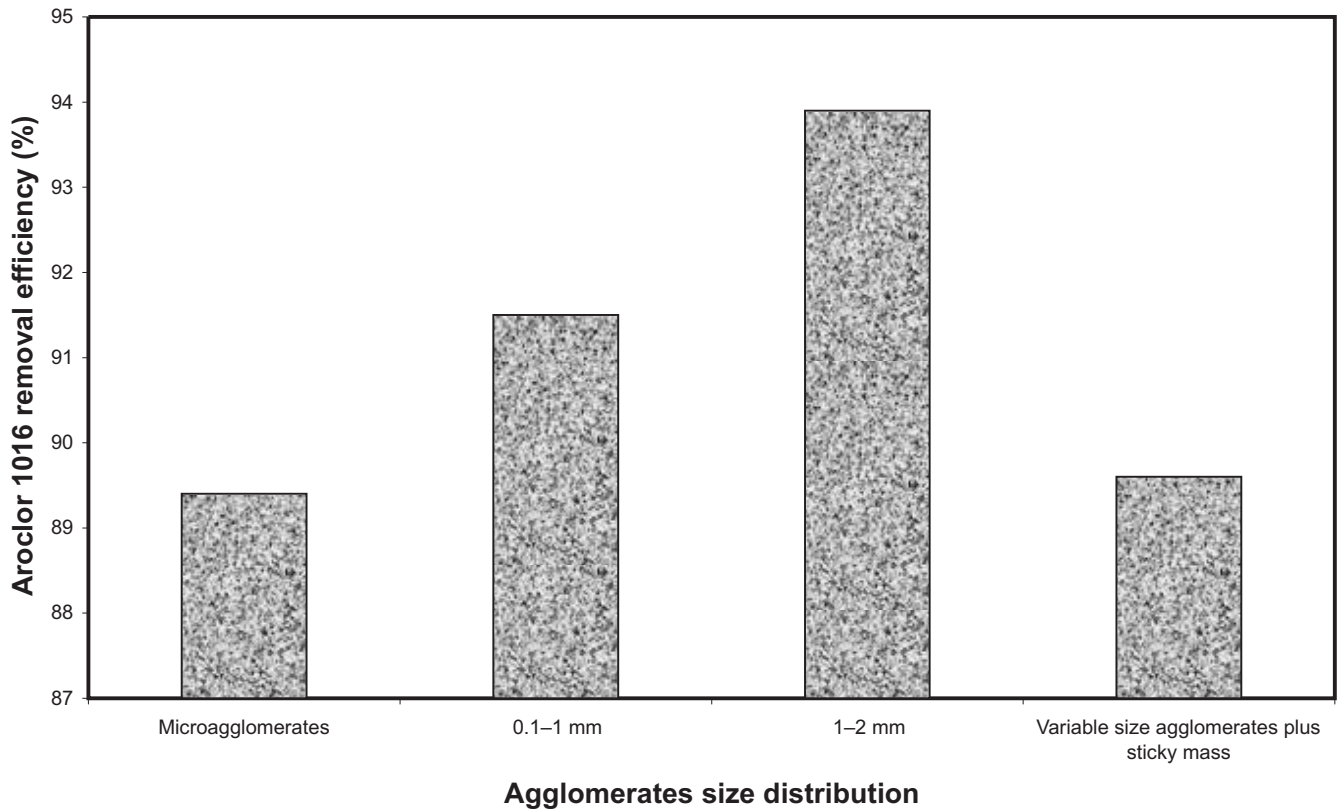
<sup>b</sup>Total amount of Aroclor 1016 added initially.

<sup>c</sup>Calculated as: (Amount recovered/Solubility factor × Total amount of Aroclor 1016 added initially) × 100.

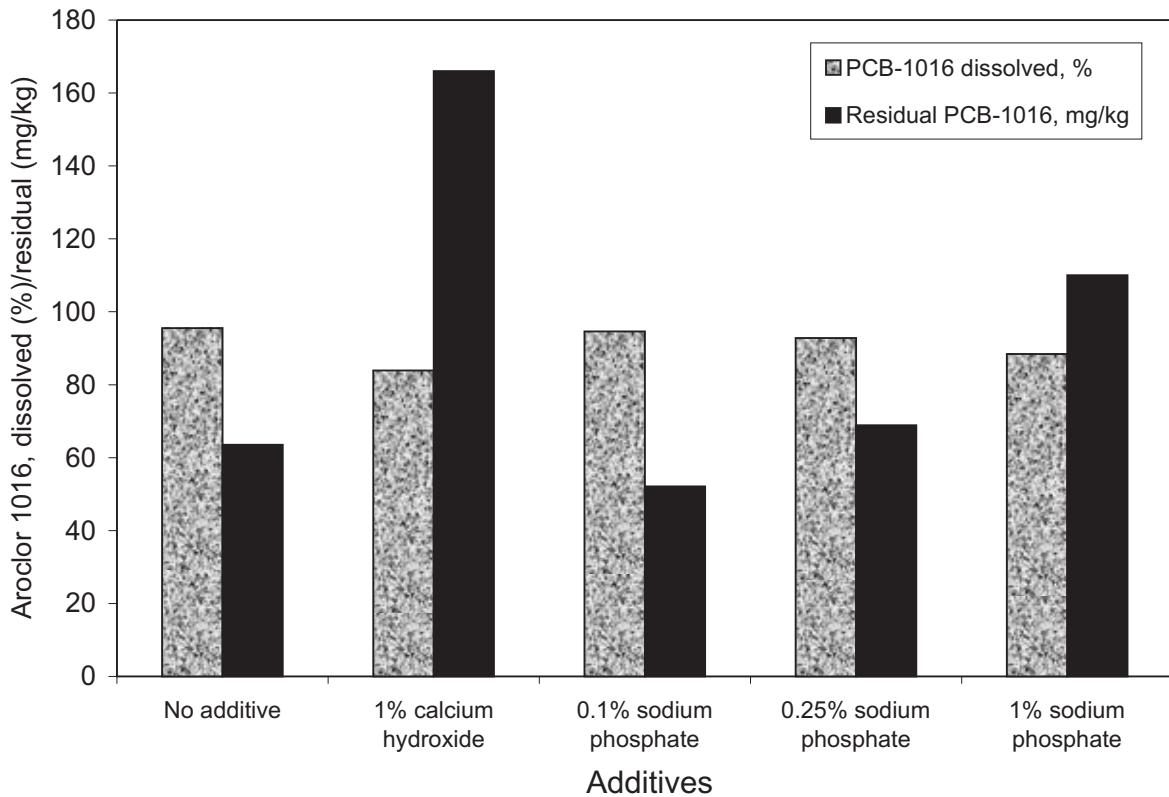
<sup>d</sup>Soxhlet extraction, 20 h.

<sup>e</sup>Values in parenthesis represent the number of tests carried out. All other values are average of three tests.

**Fig. 1.** The effect of mixing and state of aggregation.



**Fig. 2.** The effect of additives on the solubility of Aroclor 1016.



**Table 3.** The effect of mixing and state of aggregation on the Aroclor 1016 removal efficiency.

Solids state of aggregation	Aroclor 1016 removal efficiency (% of total)	Residual (mg/kg solids) Aroclor 1016	
		Extractable	Unextractable
Fine particles	89.4	22.4	76.3
0.1–1-mm sized agglomerates	91.5	8.7	68.7
1–2-mm, sized agglomerates	93.9 ± 1.2 (7)*	35.6 ± 23.8	63.5 ± 15.8
Mixture of agglomerates plus sticky mass	89.6 ± 3.2 (5)*	27.8 ± 15.3	37.8 ± 8.3

\*Values in parenthesis represent the number of tests carried out. All other values are average of three tests.

A comparison of the theoretical and measured Aroclor 1016 concentration for extracts in each test suggested that a small amount of Aroclor 1016 remained insoluble. The difference between the theoretical and experimentally determined amounts of Aroclor 1016 was designated as unextractable residual Aroclor 1016. This difference was presumed to be due to the fraction of Aroclor 1016 that was strongly adsorbed on the soil surface that remained unextractable under the experimental conditions used for this testing. Measured Aroclor 1016 concentrations represented the available fraction of Aroclor 1016. Extraction efficiencies are based on the amount of dissolved Aroclor 1016.

Overall recoveries of dissolved Aroclor 1016 were also poor for hexane compared with a mixture of acetone and hexane. The latter resulted in an almost complete recovery of the dissolved Aroclor 1016 compared with approximately 80% recovery of the dissolved Aroclor 1016 with hexane alone. The Aroclor 1016 recovery data for 5% acetone in hexane was almost identical to the recovery data for 10% acetone in hexane. However, the agglomeration of solids in 5% acetone in hexane was more easily achieved than in a mixture of 10% acetone in hexane. Hence, the subsequent tests were carried out in a mixture of 5% acetone in hexane.

The data given in Table 2 also demonstrate the effect of the mode of extraction on the Aroclor 1016 recovery efficiency. Of the three modes of extraction the best Aroclor 1016 recoveries, with the least amount of residual Aroclor 1016, were obtained using high shear agitation with solids aggregation (93.9 ± 1.9%). The Soxhlet method gave the poorest recoveries with the highest residual Aroclor 1016 remaining with the solids after extraction (82.7 ± 0.9%). This is consistent with our previous work on the removal of organic contaminants from solid matrices (Majid and Sparks 1997). Compared to the Soxhlet extraction method, SESR involves attrition mixing that appears to be beneficial in the release of contaminants from solid surfaces. This is further supported by the fact that Aroclor 1016 extraction in a Waring Blender even without solids agglomeration was also higher than that achieved with the Soxhlet method (90.6 ± 1.5% and 82.7 ± 0.9%, respectively).

### The effect of mixing and aggregation state

Data shown in Table 3 demonstrate the effect of mixing and state of aggregation on the removal efficiency of Aroclor 1016. Two major process control parameters for SESR are the amount

of bridging liquid and the degree of agitation (Meadus et al. 1994). Optimization of these two parameters leads to the formation of dense, spheroidal agglomerates where the suspending medium is virtually eliminated from the internal pore volume. Figure 1 shows the data for the recovery of Aroclor 1016 as a function of the aggregate size of the treated soil. Maximum recovery was achieved for the agglomerates in the size range of 1–2 mm with a recovery of 93.9 ± 1.9%. However, the minimum contaminant solution retention in the agglomerate pores was obtained in the size range, 0.1–1 mm, as suggested from the amount of extractable residual Aroclor 1016 from the treated soil agglomerates.

### The effect of additives

In our previous work we have found that the addition of a small amount of sodium phosphate, gypsum, or calcium hydroxide to the solids–solvent slurry during the mixing stage of SESR enhanced contaminant removal efficiency (Majid et al. 1999).<sup>3</sup> The effect of these reagents on the removal of Aroclor 1016 from contaminated soil was also investigated (Fig. 2). The effect of calcium hydroxide was more pronounced compared to sodium phosphate. Compared to the blank tests, the addition of calcium hydroxide resulted in a reduction of the solubility of PCB and an increase in amount of unextractable residual PCB. The addition of sodium phosphate did not effect the solubility of PCB; however, the amount of unextractable residual Aroclor 1016 appears to be correlated with the concentration of sodium phosphate. Smaller amounts (0.1%) resulted in the lowest residual Aroclor 1016 levels compared with greater amounts that gave higher residual Aroclor 1016 levels. The smaller amount of sodium phosphate may act as a surfactant, facilitating the removal of PCB 1016 from solid surfaces.

One of the beneficial effects of the presence of sodium phosphate was the production of relatively dry agglomerates. Under similar conditions of agitation and amount of bridging liquid, presence of sodium phosphate produced nonsticky individual agglomerates.

### Conclusions

The suitability of the SESR process, in which solvent extraction of contaminant is combined with solids agglomeration, has been tested for the remediation of a soil sample contaminated

with Aroclor 1016. The recovery rates for extraction of Aroclor 1016 by SESR were  $93.9 \pm 1.9\%$  compared to  $90.6 \pm 1.5\%$  for high shear agitation without solids agglomeration and  $82.7 \pm 0.9\%$  for the Soxhlet method. These results suggest that SESR has a potential to effectively remediate PCB-contaminated fine textured soils provided the latter can be released from the solid surface into solution.

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