

INVESTIGATING THE DESIGN AND APPLICATION OF A FUNNEL AND GATE BARRIER FOR PCB REMEDIATION IN THE CANADIAN ARCTIC

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ABSTRACT

The application of geosynthetics as filters and sorbents in a funnel and gate barrier system is being investigated for use at Resolution Island, Nunavut. This site, which is located southeast of Baffin Island, was part of the U.S. military's radar system in the 1950s and was heavily contaminated with PCBs. A funnel-and-gate-barrier system has been proposed as a long-term remediation action plan. Initial results from a field trial will be reported. One of the initial concerns in designing this system is how the geosynthetics will perform in the harsh arctic conditions. Changes in permittivity in geosynthetics that have been exposed to UV and freeze-thaw conditions and the sorption kinetics of the various geosynthetics have been investigated under laboratory conditions.

RÉSUMÉ

Un système de filtres et de tampons a été façonné d'un tissu géosynthétique afin de servir d'entonnoir et de barrière. Le tout est en place sur l'île de Résolution à Nunavut où on l'étudie à présent. Situé au sud-ouest de l'île du Baffin, l'île de Résolution faisait partie d'un système de radar appartenant à l'armée américaine durant les années 50. En conséquence, le site est devenu sévèrement contaminé de BPC. Un système d'entonnoir et de barrière a été suggéré comme moyen à long-terme de réclamer le site. Le premier obstacle dans la conception du projet sera de déterminer la résistance du tissu géosynthétique aux conditions climatiques extrêmes de l'Arctique. À cette fin, plusieurs tissus géosynthétiques furent testés dans le laboratoire avec des données obtenues lors de tests semblables sur tissus ayant été exposés aux rayons UV et aux conditions de dégel pour obtenir les résultats cinétiques d'absorption.

1. INTRODUCTION

1.1 Site: Resolution Island, Nunavut

Resolution Island, Nunavut is a former military base in the Canadian Arctic, part of the Pulevaul Line system of radar stations that connected the Distant Early Warning (DEW) Line to southern defence headquarters in the United States (Poland *et al.*, 2001). In 1985, an agreement was reached between the United States and Canada to replace the DEW Line with a new satellite-based system and to remediate the former military base sites. This site was assessed and is being cleaned up according to Canadian regulations and guidelines (Poland *et al.*, 2001).

Much of the remediation work at the site has been due to the presence of polychlorinated biphenyls (PCBs). There are three pathways in which PCBs can migrate in an environment: leaching from soil, becoming mobilized via runoff and dispersed as an aerosol into the atmosphere. PCBs do not readily volatilize and it is generally accepted that even when traveling atmospherically, they are attached to water or soil particles. PCBs are a high priority for remediation. They bioaccumulate in fatty tissues, are toxic in high levels, and are suspected carcinogens.

PCB contamination in the arctic is generally confined to the top 30 cm of soil. This means that most of the PCB contaminated soil can be excavated. There were over 8000 kg of pure PCBs (Aroclor 1260) in various matrices (soil, oil, concrete) left at the site in Resolution Island when it was abandoned in 1974. In 1994, the Analytical Services Unit (ASU) at Queen's University instigated a remediation plan of the area. Excavation of the soil with PCB concentrations greater than 1 ppm is expected to be completed by 2005. However, it is impractical to assume that all soil containing PCB will be removed from the island. Some of the soil is trapped in the fractured bedrock and some soil cannot be accessed because it is on very steep terrain that cannot be accessed for logistical and safety reasons. Excavation of the contaminated areas has loosened soil structure, allowing soil that is contaminated to be freely mobilized by groundwater flows to the ocean. This can be expected to occur during summer rainstorms, and at the end of annual spring melts.

A long-term remediation action plan was required to prevent migrating contaminated soil from entering the drainage pathways of the island, and flowing into the ocean.

1.2 Barrier

The remediation technique chosen for this particular site was an *in situ* permeable reactive barrier (PRB), following the funnel and gate design originally investigated by Starr and Cherry at the University of Waterloo (Starr and Cherry, 1994). The function of the PRB is to capture contamination so that clean water exits the treatment area, without altering drainage pathways. Due to permafrost there is essentially no groundwater and the barrier is constructed to treat surface water.

In situ treatment curtains have been increasingly applied towards remediation of PCB-contaminated sites. (Magar, 2003). However, the technology has not yet been applied to arctic sites. The southern *in situ* treatments tend to use zero-valent iron as a reactive material to help dechlorinate the organic compound. Under the cold conditions in the arctic, this reaction will occur far too slowly for this particular design to be adequately effective (Yak *et al.*, 1999, Su and Puls, 1998). Granulated Activated Carbon, (GAC) has been used in many PRBs (Lorbeer *et al.*, 2002, Birke *et al.*, 2003, Tri-Agency Permeable Reactive Barrier Initiative, 2002) and is a suitable sorption material for PCB remediation (Durfee *et al.*, 1976, Ghosh *et al.*, 2003). In 1988, PCB contamination from St.-Basile-Le-Grand Fire in Quebec was remediated using a geosynthetic (Paquin *et al.*, 1997). Materials used in the barrier must be able to withstand the harsh Arctic.

The portion of soil with the highest PCB contamination is also the fraction with the smallest particle size (ASU, 2002). The barrier was designed to filter fine particles of soil and to treat runoff water containing PCBs. Contaminated drainage water would first flow through gabions and over a mat in order to trap particulate matter. Water and entrained particulate matter would then be contained by the "funnel" and forced to pass through the filter box or "gate". The box consists of four pairs of slots into which filters or cassettes containing absorbing material can be placed. The steel boxes were built using 1.6mm stainless steel panels.

In addition to the field trials on Resolution Island, testing has been conducted in the laboratory on the various filter and absorbent materials used on site. Batch tests have been carried out on GAC and the geosynthetic absorbent boom, in order to see if an isotherm can be established and used to evaluate sorption kinetics (Crittenden, *et al.*, 1985). The geotextiles were also tested for permittivity and permeability after being subjected to freeze-thaw and UV stresses to simulate the harsh conditions in the arctic environment.

2. METHODS

2.1 Field Trial

The barrier was installed in August 2003 on site with the following materials. The first filter was a woven geotextile, Terrafix 200W or 400W. The second filter was a

needle punched nonwoven geotextile, Terratrack 800R or 1200R. In both types of filters, the higher model number indicates a tighter weave of fabric. The third filter contained either granulated active carbon (GAC) or Matasorb as the sorption agent in a 25mm thick cassette constructed of polypropylene. The final filter contained four 3M absorbent booms (1 m long with a diameter of 12 cm) in a 75mm thick cassette. Filters from the steel barrier were removed at the end of the 2003 field season and taken back to the laboratory for PCB analysis.

2.2 Filter Analysis

The geotextiles (200W, 400W, 800R) were sampled by cutting out three 7 cm by 7 cm squares cut across the top, the middle and the bottom of the filter. This was done so that the values in each area could be averaged, and applied to give an appropriate value for each section of filter (top, middle, bottom) as well as averaged for the whole filter. The Matasorb shredded material was sampled in two rows down the sides of the filter from top to bottom, totalling six samples with two samples taken from the top, two from the middle region and two from the bottom region of the filter box. Because the granules of the activated carbon (GAC) shifted during transport back to the laboratory, the granulated carbon was poured into several large containers and thoroughly mixed. In total, nine samples were taken for extraction and the results were averaged. In the case of the absorbent booms, there were four booms in each filter box. Four samples were taken from these filter boxes, one per boom. The booms were divided into the following categories: top, top middle, bottom middle and bottom; the results for the two middle booms were pooled. The samples were then analyzed for PCBs using Soxhlet extraction and GC/ECD analysis.

2.3 PCB by Soxhlet

All dried, pre-weighed samples were placed in a glass thimble and spiked with a 100 μ L aliquot of DCBP, a surrogate standard. Following Soxhlet extraction, the sample is analysed by gas chromatography (GC) using electron capture detection (ECD). Extracts were concentrated using a rotoevaporator and the solvent was exchanged to hexane before cleanup of the sample, accomplished by flushing the hexane containing PCBs through a Florisil silica column, making up to volume with hexanes to 10 mL.

2.4 GC/ECD Analysis

Approximately 1.5 mL of sample is transferred from the 10mL volumetric into a labelled GC vial and sealed.

Each sample was analyzed using an HP 5890 Series II Plus gas chromatograph equipped with a ^{63}Ni electron capture detector (GC/ECD), a SPBTM-1 fused silica capillary column (30 m, 0.25 mm ID x 0.25 μ m film thickness) and the HPChem station software. The chromatographic conditions were as follows: Sample volume - 2 μ L, splitless injection, initial temperature - 100 °C for 2 min; ramp - 10 °C/min to 150 °C, 5°C/min to 300

°C; final time 5 minutes. Carrier gas used was helium with a flow rate of 2 mL/min. Nitrogen was used as a makeup gas for the ECD.

A 10 ppm 1260 Aroclor standard is run with the samples, blank and spike along with three DCBP standards, used to calculate percent recovery. A hexane blank is also run with the samples.

2.5 Batch Testing

All samples were air dried prior to testing.

1260 Aroclor concentrations were determined using gas chromatography (HP 5890 Series II Plus) with electron capture detector (ECD), as described above. Each adsorption medium was evaluated in duplicate. Each sample series consisted of 1.0000 ± 0.0005 g of sample, with various adsorbate concentrations, plus one blank and one with a 1260 Aroclor spike.

Samples were mixed for varying times on a rotating apparatus to ensure the reactions went to equilibrium. The PCB on the adsorbent and in the water were both analyzed and the corresponding adsorption efficiencies were determined (Crittenden *et al.*, 1985)

800 mL of distilled, deionized water was added to a 1 L Teflon bottle. To the water, a spike of 1000 µg/mL of 1260 Aroclor was added, in varying concentrations. This solution was allowed to tumble in a revolving box, at a rate of 30 ± 2 rpm, as per Ontario Leachate Testing Regulations 558/00.

After one hour of tumbling (to allow some time for the solution to mix), the bottles were removed and 1.0000 g (± 0.0005) of pre-measured sample was added to the bottle. Once the sample was added to the bottle, the mixture of 1260 Aroclor, water and geosynthetic were allowed to tumble for various periods of time: 12 hours, one day, three days and one week.

At the end of the period of time, the samples were then filtered through pre-weighed Q8 Fisher Filter paper into separatory funnels, upon which a PCB analysis in water was performed, as outlined in Section 2.6. The bottles were rinsed and the rinsate poured through the funnels, to ensure that all material has been retrieved. The samples were then allowed to dry so that they can undergo Soxhlet extraction, as outlined in section 2.3.

2.6 PCB in Water

PCBs in water are analyzed through liquid-liquid extraction using separatory funnels.

Once all the sample has been filtered through into the 1 L separatory funnel, 100 µL of decachlorobiphenyl (DCBP) is added to the water as a surrogate standard. 25 mL of dichloromethane (DCM) is added to the separatory funnel. The funnel is then agitated for 1 minute, with periodic venting. Upon settling, it is possible to separate out the

bottom organic layer through a filter filled with sodium sulphate into a round bottom flask. The sodium sulphate is rinsed with DCM using a Pasteur pipette to ensure better recovery. This is repeated three times, to ensure acceptable recovery.

A solvent exchange is then performed on the DCM in the round bottom with hexanes using a rotoevaporator. The hexane solution is filtered through a Florisil clean-up column of silica and made up to 10 mL in hexanes. A 2.5 mL aliquot is used for analysis in a gas chromatograph (GC) using an electron capture detector (ECD), as described above in Section 2.3.

2.7 Permittivity Testing

Four different geotextiles were tested for their permittivity and permeability, including woven 200W and 400W and nonwoven 800R and 1200R.

A second set of these geotextiles was exposed to many freeze-thaw cycles to mimic the Arctic environment. This procedure ran for 150 days. Each morning the filters were submerged in water and placed in a freezer. At night (after 10 approximately hours) the filters were removed and allowed to thaw at room temperature (24-29°C). These steps were repeated every 1-2 days for a total of 100 continuous freeze-thaw cycles. Another set of these same geosynthetics was exposed to ultra-violet light for five months during spring and summer. The materials were secured to a wooden board and placed on the roof of the Biosciences building at Queen's University, Kingston, Ontario, Canada. The filters were monitored and continually exposed to the elements.

After completing exposure conditions, the geosynthetics were tested using an ASTM standard procedure, the ASTM D-4491 standard "Test Method for Water Permeability of Geotextiles by Permittivity,," (ASTM, 1991) Modeling of permeability and permittivity was performed using apparatus at the Royal Military College (RMC) in Kingston, Ontario, Canada. The flow rates through the woven and nonwoven filters were recorded along with the water pressures on either side of the geotextiles.

3. RESULTS AND DISCUSSION

3.1 Field Trial

3.1.1 Geotextiles (200W, 400W, 800R)

The 200W and 400W geotextile filters were soil stained along the bottom half. The nonwoven geotextile (800R) was soil-stained completely, indicative of high water levels and clogging.

Samples were analyzed for PCBs as described and the results indicate that the filters were successful in trapping PCBs. The results shown below in Figure 1 were obtained from averaging and multiplying the concentration of the sample squares by the density and area of the

section in question (top, middle, bottom). This yields total μg of PCB trapped by the filter and allows direct comparison of the filters.

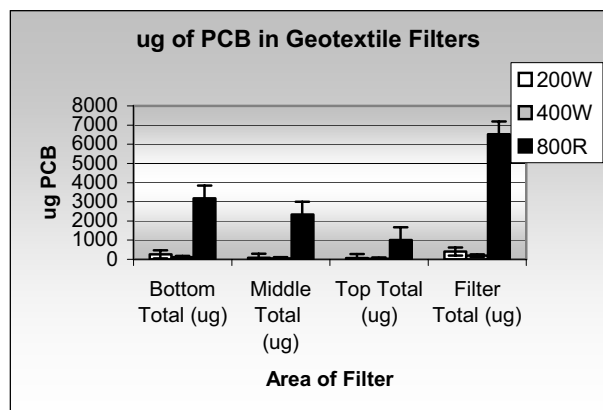


Figure 1: Values of μg PCB in subdivided filter areas (top, middle and bottom) and total μg PCB per geotextile filter ($n = 3$, error bars = 1 s.d.).

From these results it can be seen that there is a vertical gradient in concentration with more PCBs trapped at the bottom of the filters than at the top. This gradient is likely due to the fact that most of the soil stayed in the bottom half of the flowing water column. These results confirm that most of the PCBs are sorbed onto fine soil particles. Pore opening sizes must be chosen carefully to prevent clogging. The 800R was most successful in trapping PCBs. However, due to clogging it is no longer being used as a filter.

The barrier was designed to filter out fine particles of contaminated soil, these initial field trials indicate that the geotextiles were successful in this task. The total amount of PCBs trapped by the geotextiles was 7.1 mg in the 6-week trial.

3.1.2 Geosynthetic Sorbents

The results for the hydrophilic and hydrophobic geosynthetic sorbent booms and GAC are shown below in Table 1. The results for the hydrophilic sorbents are an average between the two filter boxes, which were placed side by side in the field.

Table 1: Values of μg PCB in subdivided filter areas (top, middle and bottom) and total μg PCB per geotextile filter.

Filter	Bottom Total (μg)	Middle Total (μg)	Top Total (μg)	Filter Total (μg)
Hydrophobic Sorbent				
GAC	1700	770	220	2700
	-	-	-	360000
Hydrophilic Sorbent				
	2200	1500	270	4000

The hydrophilic booms were further investigated by analysis of the outer casing of the boom (which was covered in soil particles) and of the center of the boom (which would have adsorbed PCB from the groundwater). The outer casing for the sample taken was found to contain 36 $\mu\text{g/g}$ PCB while the inner sorbent material was found to contain <0.5 $\mu\text{g/g}$ PCB.

GAC was used as a filter material since it has been shown to have been a promising reagent for the adsorptive removal of highly persistent chlorinated hydrocarbons such as PCBs (Birke *et al.*, 2003).

It was impossible to get a vertical or horizontal distribution of PCBs for the GAC filter, since the granules shifted during transport. The GAC was therefore thoroughly mixed before analysis and discrimination between the filter sections was not possible. In total, nine samples were taken for Soxhlet extraction and the results were averaged. The granulated activated carbon retained the highest amount of PCBs during the field trial.

The total amount of PCBs trapped by the geosynthetics and reactive materials was 370 mg.

3.1.4 Comparison of All Filter Materials

The sorbent materials trapped more PCB than the geotextiles. This is likely due to the fact that the smallest soil particles contain the highest concentration of PCBs. Also, the filter cartridges for the sorbent materials were thicker than the geotextiles, thereby providing a longer flow path.

From the results in Table 1, one may be tempted to conclude that GAC was a more effective adsorbent than both the hydrophobic and hydrophilic sorbents. However, many PCB-contaminated fines and silt could have been trapped in the GAC filter. These results will be compared to results obtained from batch tests below to assess whether the amount of fines trapped by the GAC was a significant contributor to its high amount of PCB retention.

3.2 Permeability Testing

Permittivity and permeability tests were performed on the materials to help establish if they were appropriate for the barrier system. It was necessary to investigate whether the materials and structure would be able to survive harsh winter conditions.

Permittivity tests were carried out to assess the flow capacity of each geosynthetic (ASTM, 1991). The pressure differences across the geosynthetics were recorded when different flow rates were applied. The values for all four geosynthetic filters and the medium they were exposed to are presented in Table 2.

Table 2: Permittivity and permeability values obtained for each geosynthetic filter.

Geotextiles	Permittivity	Standard Deviation	Permeability	Standard Deviation
800R				
Literature	0.58	-	0.23	-
flow test: control	0.62	0.08	0.25	0.03
flow test: freeze/thaw	0.45	0.14	0.19	0.05
flow test: UV-light	0.75	0.27	0.30	0.12
1200R				
Literature	0.25	-	0.15	-
flow test: control	0.19	0.07	0.11	0.04
flow test: freeze/thaw	0.38	0.10	0.23	0.06
flow test: UV-light	0.28	0.08	0.17	0.05
200W				
literature	0.17	-	0.03	-
flow test: control	0.37	0.08	0.07	0.03
flow test: freeze/thaw	0.34	0.12	0.07	0.03
flow test: UV-light	0.73	0.39	0.15	0.08

Literature values in Table 2 are taken from manufacturer values (Terrafix, 1997). Exposure to UV-light and freeze/thaw cycles did significantly (95% Student's t-test) affect the flow through the geotextile. Specifically the 200W was affected by UV, the 800R by freeze thaw and the 1200R by both UV and freeze thaw. In some cases the material was stretched, which allowed greater permittivity and permeability values. In other cases the pores of the materials were damaged and collapsed, giving lower flow rates, hence lower permittivity and permeability values.

3.3 Batch Test Results

The geosynthetic sorbent was tumbled for three periods of time: 12 hours, 24 hours and 1 week, with varying concentrations (25 to 1000 ppb in water) of PCBs. PCB analysis indicated that the sorbent was very effective at absorbing the PCBs. For all concentrations and tumbling times the PCBs were recovered only in the sorbent. Recovery of the PCBs in the sorbent was averaged over 39 samples and found to be $96\% \pm 13\%$. In all cases, the amount of PCB detected in the water was below detection levels (< 3 ppb). PCBs, especially 1260 Aroclor, which is made up primarily of hexa- and septa-chlorobiphenyls, which have very low solubilities in water (Hutzinger et al., 1983).

It was noted that there was no significant difference between 12 hours, 24 hours and 1 week of tumbling,

which indicates that the reaction comes to equilibrium by 12 hours.

GAC was tumbled for two different time periods, 12 hours and 24 hours at varying concentrations (25 to 1000 ppb in water). There was no detectable PCB in the water and recovery for GAC ($92\% \pm 6\%$, $n=14$) demonstrates that GAC is as effective a sorbent as the geosynthetic boom at under the prior mentioned conditions.

Sorption capacities in excess of 800 $\mu\text{g/g}$ were deemed to exceed the amount required in the field, as apparent from field data and therefore were not pursued. Sorption capacities may become more important upon retrieval of future field data.

In the field the GAC absorbed significantly more PCBs than the two other sorbents. This suggests that in the field the GAC not only absorbed PCBs, but it also acted as an effective fine particle granular filter. Alternatively, the sorption kinetics of GAC maybe more suited for non-equilibrium field applications than the hydrophilic geosynthetic sorbent.

Column tests are needed to determine whether the adsorption of PCB unto the sorbents is instantaneous.

4. CONCLUSION

The field installation trial of the PRB funnel and gate barrier system currently on site in Resolution Island, Nunavut is working as expected. The barrier system is functioning to trap PCBs in a short period of time, as confirmed by batch tests which showed that GAC and the geosynthetic boom are excellent adsorbents of PCBs. Permeability of the barrier materials however, seem to be effected by freeze-thaw and UV effects. Column tests are needed to mimic both non-equilibrium and arctic conditions to determine whether these initial lab results are indeed promising.

5. ACKNOWLEDGEMENTS

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