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Design and application of surface PRBs for PCB remediation in the Canadian Arctic

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ABSTRACT

Over the course of three years, several surface permeable reactive barriers were designed and constructed to deal with leftover site contamination at a site located on the summit of Resolution Island, Nunavut, just southeast of Baffin Island at 61° 35′N and 60° 40′W. The site was part of a North American military defense system established in the 1950s that became heavily contaminated with polychlorinated biphenyls (PCBs) during and subsequent to, its operational years. Each of the three barrier designs has a different configuration, to meet the needs of the targeted remediation area, based on their unique contaminant histories. Modifications were made to the barrier designs based on both field observations and laboratory results. The comparison of field and laboratory results indicated that areas with higher concentrations of PCB contamination behaved differently than areas with lower concentrations of PCB contaminated soil. Previous laboratory studies only partially replicated field observations and results. It had previously been hypothesized that particle retention was the most important factor in trapping and capturing PCBs. However, rinsed filter samples from the field indicated that partitioning of PCBs between contaminated soil and granular activated carbon (GAC) filter particles were occurring at levels of 62 ± 11%, suggesting that sequestration of the PCBs from the environment should be a primary focus of the barrier. This sequestration requires both particle retention (within the granular sorptive filters) as well as maintained contact time between particles for sorption processes to proceed. This mechanism – partitioning of PCB to GAC – was more important in areas with higher PCB concentration. These results suggest that it may be possible to tailor future barrier designs to their unique site histories and locations.

1. Introduction

1.1. General introduction

Polychlorinated biphenyl (PCB) contamination in the Arctic has been documented at the Distant Early Warning (DEW) Line sites, a string of 63 military radar stations that were operated across Alaska, northern Canada and Greenland during the 1950s and early 1960s (Bright et al., 1995; Stow et al., 2005).

Source removal by soil excavation is often used for remediation of these sites. Unfortunately, much PCB contamination can be left behind during this process in the form of mobile soils. PCBs can enter the Arctic ecosystem travelling on these mobile soil particles (Poland et al., 2001). This is particularly important in the Arctic, where there is a narrow food web and PCBs bioaccumulate and biomagnify in fatty tissues (ASTDR, 1997; Fisk et al., 1998).

This paper describes how permeable reactive barriers (PRBs) can be modified from a basic funnel and gate design (Starr and Cherry, 1994) to remediate surface conditions in areas where subsurface contamination is not a concern, such as with the nature with some contaminated sites in cold regions. Site investigations have confirmed that the contamination depth is limited to primarily the top 0.3 m of soil. Given the low-volatility of the contaminant, the primary transport mechanism for PCBs in cold regions is via runoff mechanisms, with the exclusion of areas directly adjacent to the source – where downwards transport is limited by the short season in which the active layer is thawed. The application of PRBs has been investigated in cold regions such as the Arctic (Poland et al., 2001; Lindsay and Coulter, 2003) and the Antarctic (Snape et al., 2001; Woinarski et al., 2003, 2006; Gore et al., 2006; Gore, 2009). The barriers at Resolution Island, described in this paper, are the first of their kind – a novel variation of a proven technology. Each of the three barrier designs has a different configuration to meet the needs of the targeted remediation area, based on contaminant history. In all cases, particle retention must be the key parameter of the design, while ensuring permeability is maintained. The use of

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a material such as granular activated carbon (GAC) provides a granular medium for particle retention as well as a sorptive surface to remove PCBs from both water and soil. Field observations and laboratory studies of these different barriers provide insight in how to achieve an optimal barrier design.

The initial basic design incorporating of a single funnel (ponding area) and gate (Kalinovich et al., 2008a) was modified and applied in two other areas of PCB contamination. Each barrier system required unique design configurations based on their field performance – directly due to the contaminant and remediation history of the site. Laboratory column studies elucidate results as PCB contaminated particles travel in suspension through a water column with only trace amounts of dissolved PCB. Column study results reflect PCB partitioning within a multicomponent GAC/soil/water system, as seen in the field.

1.2. Site description

The military station on Resolution Island is located at the southeastern tip of Baffin Island approximately 310 km southeast of Iqaluit and at the end of Frobisher Bay (61° 35′N and 60° 40′W). The main station site is situated on a summit 360 m above sea level on Cape Warwick at the northeastern end of the island overlooking Brewer Bay.

An estimated 8000 kg of pure PCBs (predominately Aroclor 1260) was left on site at the time of abandonment (Poland et al., 2001). Three areas were targeted for PCB remediation and eventual surface barrier construction; the valley, the beach and the furniture dump (Fig. 1). Site remediation, the design, construction and modifications of the prototype valley barrier has been described previously (Kalinovich et al., 2006, 2008b). The barrier was designed to be adaptable – allowing easy, seasonal filter changes to match site conditions and increase remediation efficacy of the system. Filter materials evolved from geotextiles and geosynthetics to more permeable granular material such as gravels and GAC. Once soil excavation activities had ceased, geotextiles were re-introduced to the system. Two additional permanent surface barriers have since been constructed and monitored.

The valley region is on the southern side of the summit and encompasses the area directly adjacent and below giant troposcatter dishes, including the maintenance buildings used for the radar dishes. Large quantities of PCBs in the form of Aroclor 1260 were stored and used in the electrical equipment in these outbuildings. Over the course of the project (1996–2005) these outbuildings were torn down and the materials contaminated with PCBs removed. The valley is the site of the initial prototype surface barrier and is described in Kalinovich et al. (2008b).

The beach refers to the extension of the valley drainage pathway that resides at the bottom of a 300 m cliff (the valley above), leading into Brewer Bay (see Fig. 1). Contamination at this site came as a result of migrating PCB contaminated soils from the above valley and was delineated into 'tiers' (Poland et al., 2001). Part of the beach area (Fig. 2) is inaccessible for excavation, with slopes averaging 10% (greater than 50% in some areas). Much of the area is covered with vegetation and soils were found to be similar to the valley, but with some fines present. In this region, large deposits of soil, rock and boulders were found. The stability of the soil in this region was attributed largely to the vegetative cover. Instability of excavated soil in the beach region was a concern as several areas of contamination were inaccessible by equipment, and/or the bulk removal of soils would lead to mass erosion of PCB contaminated soils into Brewer's Bay. A stainless steel barrier system was constructed in the beach area to deal with these unstable soils and the migration of PCBs until the region stabilized.

East of the valley lies an additional area (referred to as the furniture dump) that was heavily contaminated with PCBs (Figs. 1 and 3). In 1999, fourteen transformers and miscellaneous electrical equipment were removed from this area. Soil in this area was sandy, with no vegetation present, excluding small amounts of lichen and moss. The drainage from the dump opened onto a sandy flat and continued east over a cliff to the ocean. PCB contamination for this site is shown in Fig. 3. After excavations, there was little soil left in this region (Fig. 4).

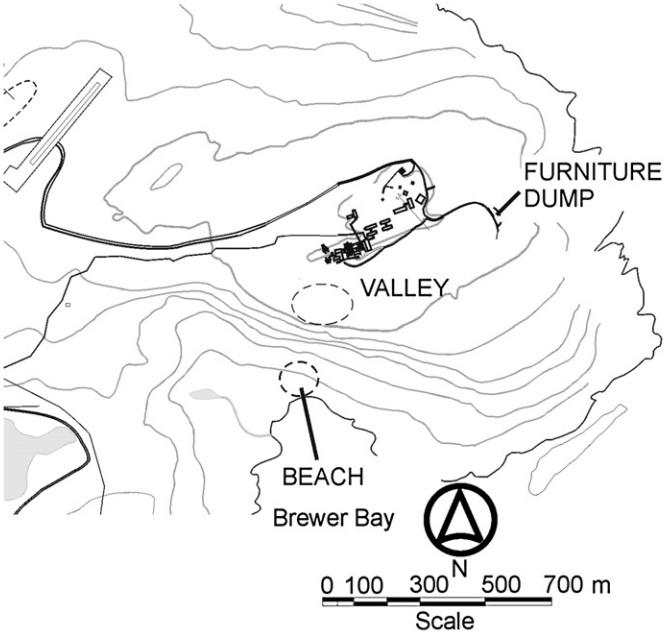

Fig. 1. Site map of Resolution Island, Nunavut.

2. Methods

2.1. Monitoring

Monitoring plans were set up at each barrier site. Prior to instalment of the barrier systems, areas were sampled and

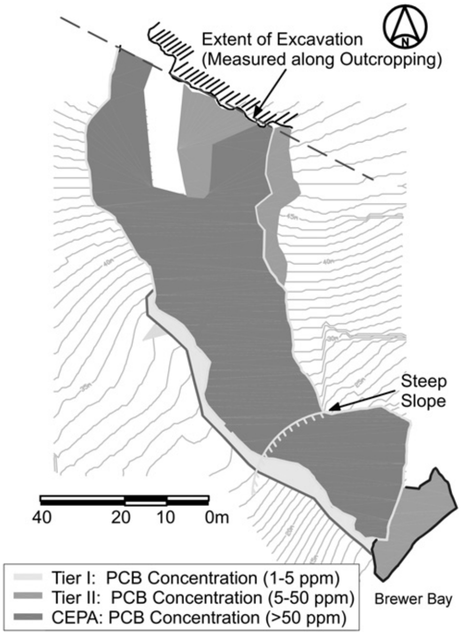

Fig. 2. Map of contamination at beach prior to excavation.

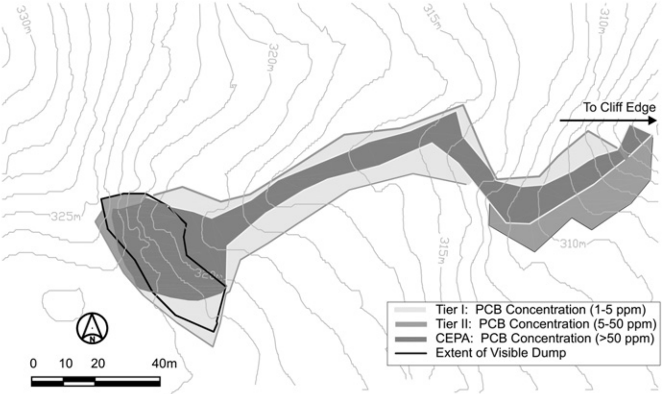

Fig. 3. Map of contamination at furniture dump prior to excavation.

analyzed to ensure a 'clean' (<1 μg/g PCB) base for construction. Upstream and downstream point samples were taken to establish known prior concentrations. Clean cells were constructed directly behind each barrier gate, in efforts to demonstrate whether contamination was breaking through the barrier system or not. Clean cells were constructed and isolated from the surrounding areas using geosynthetic clay liners filled with clean fill obtained from uncontaminated areas of the site. Monitoring schematics for the barrier systems are illustrated in Figs. 5 and 6.

2.2. Sampling and analysis

Soil, gravel and GAC samples were collected using plastic scoops and placed in WhirlPak bags. Water samples were collected in 1 L Teflon bottles. Samples were shipped by air freight to Queen's University, Kingston, Ontario, Canada for testing. The standard analytical procedure for the analysis of PCBs, namely gas chromatography with an electron capture detector (GC/ECD) was used. These analyses were performed at the Analytical Services Unit, Queen's University by the procedures described in Kalinovich et al. (2008b). Solvent extraction using dichloromethane by soxhlet apparatus or shaker for solids and liquid–liquid extraction for liquids was used. After a solvent exchange to hexanes, the eluent was flushed through a Florisil clean up column with hexanes prior

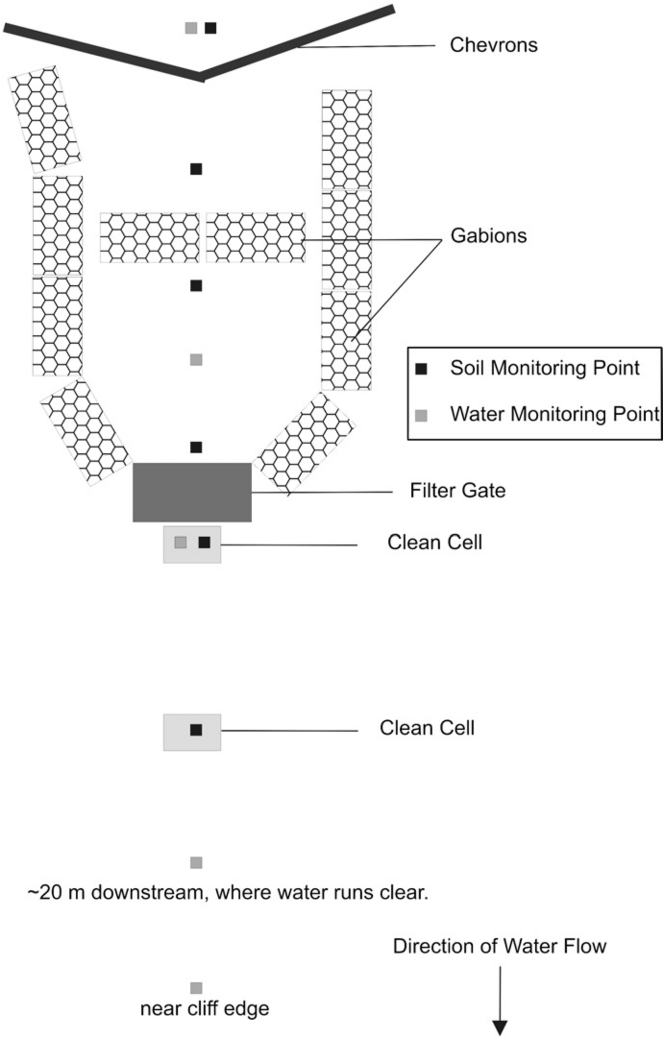

Fig. 5. Monitoring schematic illustrating monitoring points and clean cells, valley barrier.

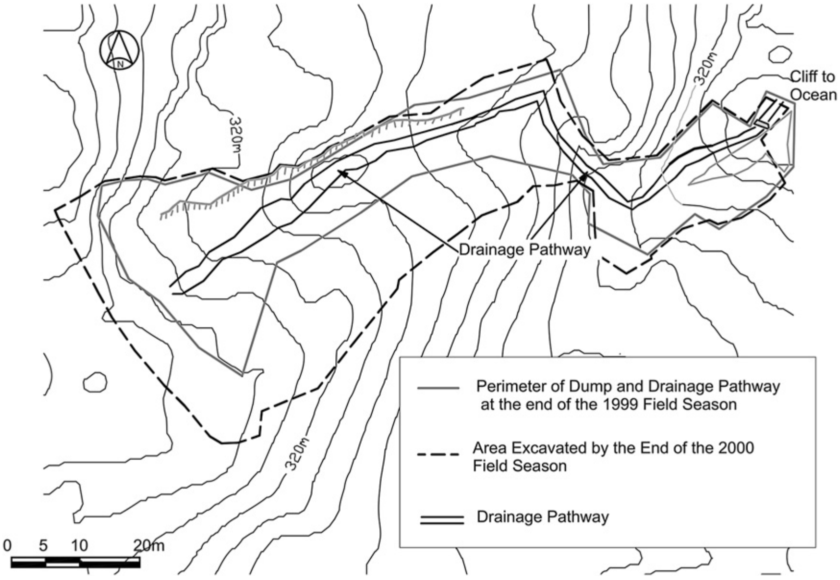

Fig. 4. Map of contamination at furniture dump after excavation.

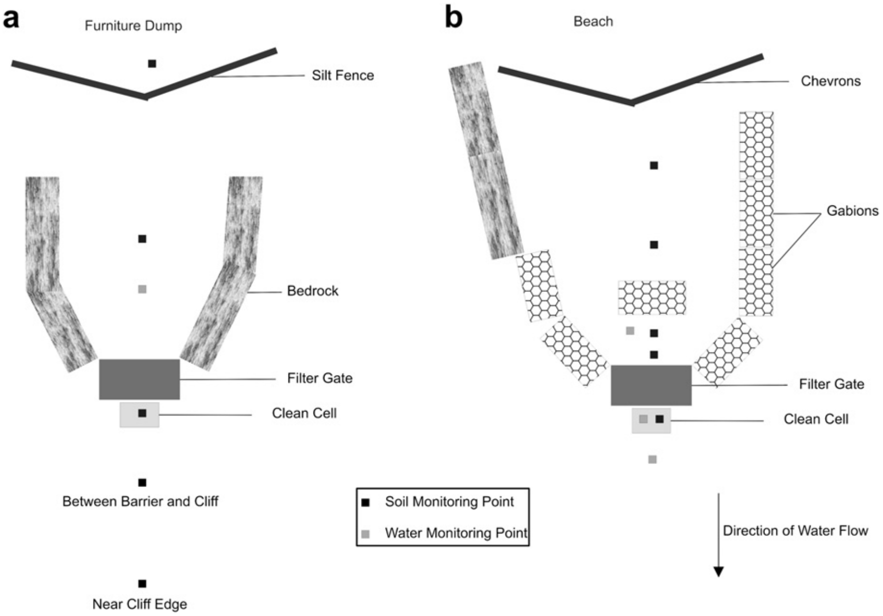

Fig. 6. Monitoring schematic illustrating monitoring points and clean cells, furniture dump (a) and beach (b) barriers.

to GC/ECD analysis. Each sample was analyzed using an HP 5890 Series II Plus gas chromatograph equipped with a Ni^{63} electron capture detector (GC/ECD), a SPB™-1 fused silica capillary column (30 m, 0.25 mm ID × 0.25 μm film thickness) and HPChem station software. A 1260 Aroclor standard was run with the samples, analytical blank, and control sample (prepared by spiking sand with a separate source standard) along with three DCBP standards, used to calculate percent recovery. A hexane blank is also run with the samples. All control samples were within 30% of the expected value. Relative standard deviations between the samples and their analytical duplicate were below 30% for all results. Sample concentrations were corrected for surrogate recovery which was between 80% and 120% for all samples. Detection limits for PCBs by liquid–liquid extraction and by soxhlet extraction were 0.02 μg/L and 0.1 μg/g respectively.

Standard methods were adopted for soil analyses of: carbonates (Allison and Moodie, 1965), Cation Exchange Capacity (Hendershot and Lalande, 2006), particle size distribution and particle density (Kroetsch and Wang, 2006) Organic Matter as determined by Loss on Ignition (McKeague, 1978) Atterberg Limits (ASTDM D4318-98). Particle size distribution of soil samples from the funnel areas of each barrier are presented in the Supplementary Materials section.

2.3. Column studies

The PCB contaminated soil used for experiments was excavated from the site and stored at 4 °C. Different PCB concentrations in the soils were combined (rough approximation of 5 μg/g and 500 μg/g) and homogenized by mechanical mixing for 2 days to create a sample of uniform soil with a PCB concentration of 75.6 ± 0.2 μg/g.

The stainless steel column apparatus (Fig. 7) was designed for interchangeable thickness of filter materials, providing for greater flexibility in testing varying filter thickness and filter combinations. In these sets of studies, the column was operated in a horizontal configuration, in order to best mimic filter field conditions. Water flow was controlled using a programmable water pump. Breakthrough was considered evident when fines exited the column

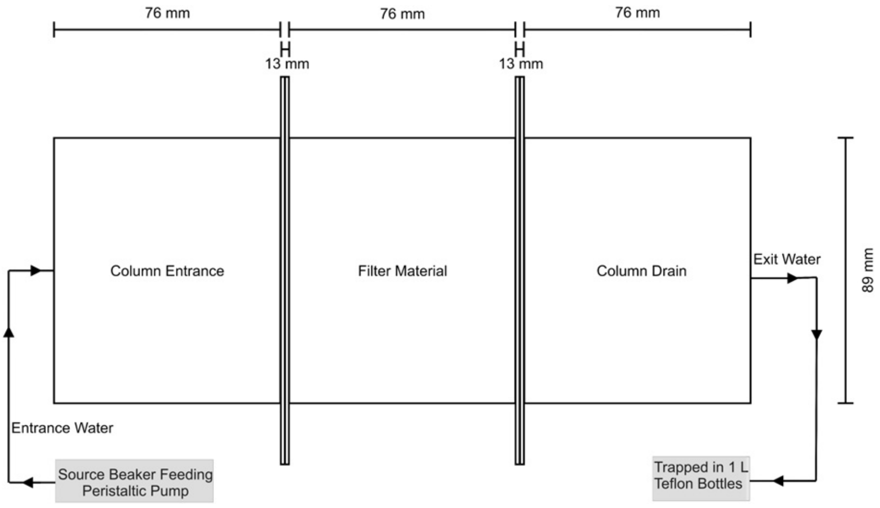

Fig. 7. Schematic of column apparatus, shown in horizontal position.

apparatus. The filter materials and water were tested periodically to ensure exiting waters were PCB free. Water was filtered through a 0.7 μm filter and the filter was analyzed for PCB content. 0.7 μm glass microfiber filters with a quantifiable amount of PCBs (>0.1 μg/g) suggested breakthrough.

A known quantity of PCB contaminated soil from the site was flushed through the column at a constant flow rate as a slurry, sourced from a glass beaker. The solution was pumped through continuously at 4 L/min for 2 min (i.e. effluent exiting from the column was re-circulated through the system).

The column was then carefully taken apart to establish the fraction of PCB contaminated soil that remained within the different sections (i.e. entrance, filter section, exit drain; see Fig. 7, configured as upwards flow). The filter portion was removed and the material was poured onto a 1 mm sieve. GAC particles range from 2 to 3.35 mm and it was possible to separate the different constituents through a wet-sieving process. This size fraction of GAC was selected due to its resistance to degradation from freeze-thaw action within the barrier system (Gore et al., 2006). The material was flushed with double de-ionized water and laid out to dry on a metal tray. Column runs were conducted in triplicate for each material used. The material was sampled for soxhlet analysis. Light Electron Microscope (magnification 0.75×, ocular 16×) photographs of the filter material were taken of the wet-sieved GAC and/or sand material from both column runs and field samples. The photographs showed that no soil grains were attached to the wet-sieved GAC filter material: all PCBs found on the GAC material could therefore be attributed to adsorption. Some column samples were sampled in triplicate to ensure homogeneity.

Site sand of similar particle shape and size to GAC (Fig. 8) was also used as a filter material. This allowed the comparison of a relatively non-sorptive material to GAC, to compare and contrast particle retention and sorption mechanisms.

3. Results and discussion

Resulting concentrations and volumes of mobile soil were unpredictable from year to year and dependent upon: the effectiveness of source removal, re-stabilization activities in the area, and to a greater degree, spring melt conditions. Initially, this required ongoing modifications over a period of several years to adapt to the onsite changing conditions. Some of these modifications are discussed with respect to the valley barrier (Fig. 9a) in Kalinovich et al. (2008b) — in particular, the move from a less permeable geosynthetic/geotextile based system to more permeable, thicker granular barrier materials. Lessons learned from these experiences can be adapted and applied for other surface barrier systems, and remediation in cold regions.

3.1. Furniture dump system

Initially, a wooden barrier consisting of a gate and one ponding area (similar to the present configuration represented by Fig. 9b) was constructed in the furniture dump and its filters were sampled in the subsequent year (Table 1). Filters chosen for this first year comprised largely of geosynthetic and geotextile materials. At this stage, in barrier system development, it was uncertain how the balance of particle retention, permeability and sorption mechanisms would be to the performance of the system in the field. Nonwoven and Woven (NW and W) geotextile filters were used upstream within the filter system for particle retention. Soil particles were intended to be trapped on the front filters. Both a geosynthetic hydrophilic sorbent and GAC were used downstream within the filter configuration to attenuate PCBs through sorption mechanisms. The barrier was constructed in a natural ponding area carved into the bedrock and the walls of the funnel are made of the bedrock lined with geosynthetics (geosynthetic clay liner overlaid with geomembrane).

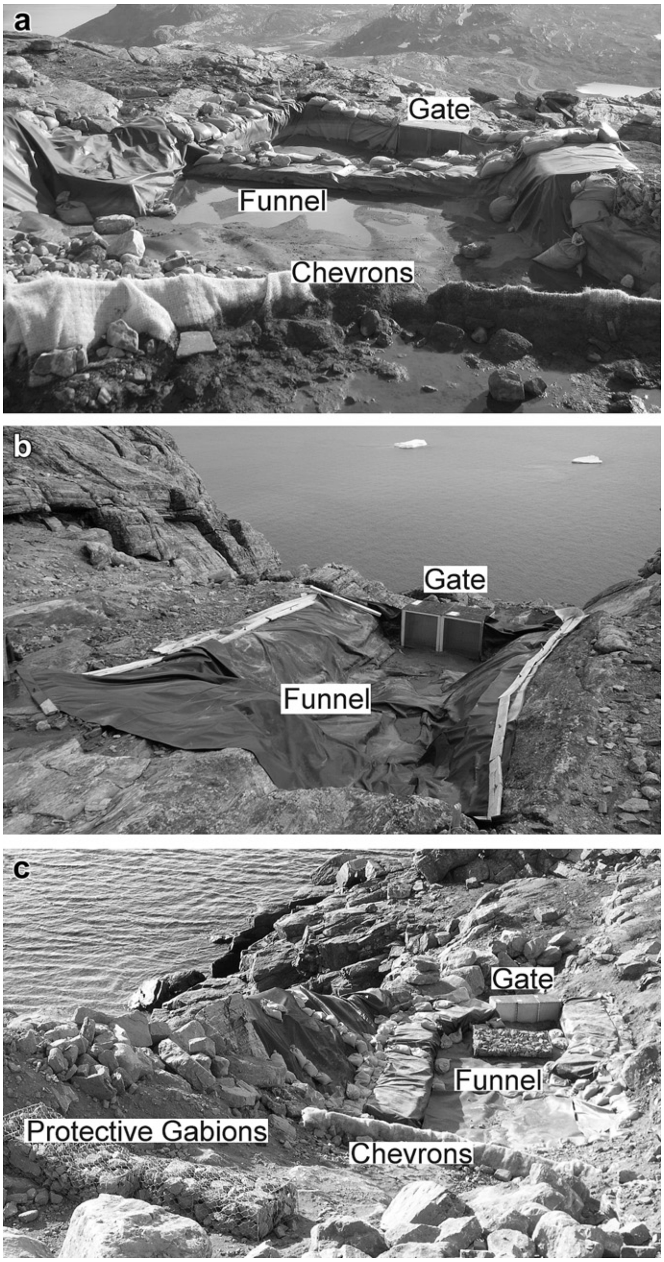

Fig. 9. Photograph of valley barrier (a), furniture dump barrier (b) and beach barrier (c) in their different design configurations.

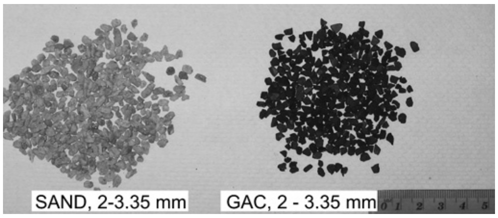

Fig. 8. Photograph of GAC and sand used for column and batch experiments.

Table 1
Mass of PCB (mg) in filters in furniture dump (FD) and valley (V) Barriers, 2004. Order of filters presented in table represents order in which water column passed through barrier system.

Filter samples	FD barrier	V barrier
W1	1.9	1.7
NW 1	21	6.5
NW 2	27	–
Hydrophobic geosorbent	16	4.8
GAC	161	360

The results from the first field season showed PCB contamination at much higher levels than expected considering the extent of source removal for this region. The wooden barrier was replaced with a permanent stainless steel gate structure and a monitoring system was implemented. Filter materials were changed to more granular, permeable materials, as it became evident that particle retention was a key attenuating mechanism in the field while maintaining the permeability of the system. Soil samples were analyzed from areas both upstream and downstream of the barrier system (Table 2). Only trace amounts of water and mobile soil particles were present in the furniture dump in subsequent years, therefore further design modifications were not necessary. The amount of contaminated soil present in the system varied from year to year, in one field season, approximately 0.3 m^3 of contaminated soil was removed from the funnel which corresponded to a PCB mass removal of 15.5 g. These high amounts of PCBs indicate that although the area was thoroughly excavated and vacuumed, small quantities of highly contaminated PCB soil remain.

The PCB concentration in the soil trapped between filter boxes was found to be 68 μg/g. This indicates that the barrier was successful in trapping highly contaminated fines, as this concentration was greater than what was being caught via sedimentation processes in the funnel and of that downstream from the barrier system.

3.2. Beach barrier system

A third barrier system was constructed at the base of the cliff at the beach site based on the success of the design of the initial prototype barrier in the valley. The footprint of the barrier system was excavated to <1 μg/g prior to installation. This barrier system design was based on the valley modified design that dealt with high volumes of mobile contaminated soil particles and water. The stainless steel gate width was increased from 1.2 m (original valley design) to 1.8 m in order to accommodate higher flow rates and sediment volume (see Fig. 9c).

The amount of PCB in the sediment trapped by the barrier was quite low: the amount of pure PCB removed from the barrier system was calculated to be 2.5 g, with soil concentrations ranging between 0.3 and 1.3 μg/g. Monitoring samples prior to construction of the barrier reinforce that these low concentrations are indicative of successful excavations in the area (PCB concentrations in soil range from 0.5 to 3.6 μg/g within the vicinity). These results indicate that the excavations and particularly stabilization in the area were highly successful and that the beach barrier system, out of the three surface barrier systems, deals with the lowest concentrations of PCB contaminated soils.

Table 2
Soil monitoring points in furniture dump barrier (2004–2007).

Location of sample	PCB concentration (μg/g)		
	2005	2006	2007
Upstream of sediment trap	<1.0, 58	24	43
In funnel	24	20	32
Between filters in gate	–	68	118
Between barrier and cliff	38	49	32
Near cliff edge	2.8	16	12

3.3. Barrier site comparisons

3.3.1. Monitoring

Monitoring points of both soil and water were constructed at each barrier location (valley and furniture dump) using a point sampling technique (see Figs. 5 and 6). PCB contaminated soil could be found downstream from both the valley and furniture dump barriers. Table 2 shows PCB concentrations for samples taken at the furniture dump barrier locations for three years. Soil monitoring results for the valley barrier can be found in Kalinovich et al. (2008b). The monitoring of these same points over the years was intended to help evaluate barrier efficacy and improve their design. Prior contamination of soils downstream from the barrier systems interfered with monitoring results. To deal with the large contaminated area of inaccessible soils in the valley-beach drainage pathway, the beach barrier was installed to trap migrating PCB soils from the valley. Although monitoring of these systems is difficult due to the presence of previous contamination, these results demonstrate that downstream contamination has not increased in subsequent years showing that mass migration of PCBs are not moving past the barrier systems themselves. However, it should be stressed that monitoring results downstream from the barrier systems are not conclusive as per the reasons explained above.

Monitoring results from the furniture dump barrier show a concentration effect of PCB contaminated soil in between the filters – indicating that coarser fines are settling out in the ponding area, and highly contaminated more mobile fines are being trapped by the filter system. The PCB concentrations in soil trapped within the filters are approximately 3.5 times greater than concentrations found in the funnel. This type of magnification of PCB contaminated levels was not seen in the other barriers – rather, the other barrier results indicated that soil concentrations trapped between filters was similar to soil concentrations found present in the ponding areas. This may have been due to the significantly smaller volumes of mobile soil in the furniture dump, compared to the beach and valley barriers.

Unfortunately, particle size characterization to quantitatively demonstrate this hypothesis was not conducted. However, visual inspection of the soils and the following set of arguments supports this hypothesis. Minimal organic material is found in the soil on Resolution Island. The furniture dump contains 2.18% organic matter (Table 5) as evaluated through a Loss on Ignition method (McKeague, 1978), indicating sorption specificity related to organic carbon is not the dominant mechanism for sorption of PCBs to soil particles. Highly hydrophobic compounds with low-solubility such as PCBs (reference solubility for Aroclor 1260 at 20 °C is 2.7 μg/L, Ruzo et al., 1974) will sorb very strongly to smaller particles rather than larger particles due to the increased surface area:volume ratio in smaller particles. The barrier system was designed to act as a settling pond with treatment filters. Larger (lower levels of PCB

Table 3
Mass of PCB (g), mass of PCBs in filter (g) and volume of soil (m^3) collected by each barrier for the years 2006–2007.

Barrier	Volume of sediment (m^3)		Mass of PCBs in sediment (g)		Mass of PCBs in filter (g)	
	2006	2007	2006	2007	2006	2007
Valley	2.2	1.0	23	9.5	0.13	0.29
Beach	2.0	1.3	0.7	1.3	0.05	0.06
FD	0.3	0.3	30	17	0.73	0.34

Table 4
Filter results from all barriers in 2005–2007. Listed in order as flow moves through barrier system. Order of filters presented in table represents order in which water column passed through barrier system.

Filter	Valley			Beach			FD		
	Mass PCB (mg)			Mass PCB (mg)			Mass PCB (mg)		
	2005	2006	2007	2005	2006	2007	2005	2006	2007
½ Gravel	149	64	–	–	14	23	–	70	37
Full gravel	65	47	17	–	15	13	33	134	42
GAC	23	20	128	–	7.2	11	48	258	121
GAC	75[a]	–	145	–	8.9	10	–	249	138
NW2	–	–	–	–	–	0.3	–	–	–

[a] This set of GAC filters was placed in the valley during the summer season and are not part of the regular filter configuration.

contamination) particles will settle out in the pond, and finer (increased levels of PCB contamination) particles will be more mobile, effectively concentrating in between and on filters. Results from Fig. 10 demonstrate that carbonaceous filter materials (such as GAC) have a much larger affinity for PCBs than the surrounding site soil particles and will be able to effectively ‘sorb’ PCBs from both the soil and water phases. These results and observations concluded that a fine, polishing step was required at the end of the granular sorptive system to retain highly contaminated fines that could ‘wash out’ from the granular system. This polishing step was introduced as a half-height nonwoven geotextile filter (NW2) and was added to all barrier systems.

Dynamic storm and spring runoff produce varying amounts of sediment and levels of contamination in the barrier systems both upstream and downstream, making monitoring of the barrier systems difficult to evaluate. In the furniture dump, PCB concentrations in soil pockets are highly heterogeneous: two samples taken within the same soil pocket (i.e. in front of the sediment trap) had respective concentrations of <1.0 μg/g and 58 μg/g.

As sediment loading in the areas decreased over time, it became possible to re-introduce geotextiles as final polishing filters in the barrier systems. To help better monitor the efficacy of the valley barrier, a second clean cell was installed further downstream from the barrier system. The area previously downstream from the valley barrier site had been delineated as 5–50 μg/g PCB contamination, and since the area was not vacuumed, pockets of 5–50 μg/g soil remain and are readily mobilized through spring melt conditions. The results in sampling downstream from the barrier give no indication to how well the barrier is truly performing due to the known previous contamination in this area.

The beach barrier system was built at the end of the drainage pathway to accommodate the PCB contaminated soils that could not be accessed for removal downstream of the valley barrier, and above the area of excavation at the beach (see Figs. 1 and 2). However, the area downstream from the beach barrier system has been shown to contain <1.0 μg/g PCB consistently in soil, both before and after barrier implementation, indicating that the barrier is retaining PCB contaminated fines, and breakthrough of these fines is not occurring at detectable levels downstream.

Table 5
Soil analysis for soils from funnels of barriers.

Barrier	pH	Atterberg limits	Density (g/cm^3)	Carbonates (mg)	Organic matter (%)	CEC
Beach	6.7, 6.8	NO PLASTICITY	1.2	2.0033	3.18	4.2
Valley	3.9	NO PLASTICITY	1.2	2.0004	2.46	1.7, 1.8
FD	3.8	NO PLASTICITY	1.3	2.0083	2.18	1.7

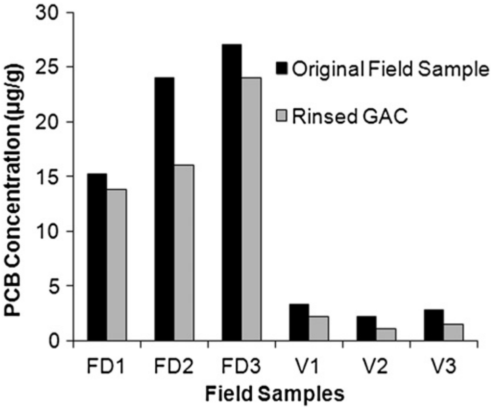

Fig. 10. Rinsed and non-rinsed field GAC filter samples. FD1-3 denotes 3 furniture dump GAC barrier field samples and V1-3 denotes 3 valley GAC barrier field samples.

3.3.2. *Sediment*

Both the volume of soil and mass of PCB collected in the furniture dump barrier can be compared to those of the valley barrier. In 2005, 7 m^3 of soil was removed from the valley barrier, with a total mass of PCB removal of 60 g. In the furniture dump, the mass removed was small (~0.8 g), however the volume of soil remaining was quite low (0.3 m^3); indicating that the soil concentration in the Furniture Dump system was 2.5 times greater than that travelling through the valley barrier. This relation between volume of soil and levels of contamination can be seen for all three barrier sites in Table 3. The results are compatible with the contaminant history of the areas. The area with a contaminant history of higher PCB concentration contaminated soils in a smaller area (furniture dump) is presently showing higher masses of PCB accompanied by a lower volume of soil as more stringent source removal techniques were exercised in areas with PCB in soil concentrations exceeding 50 μg/g. Although less soil remains in the area overall, soil that remained was highly contaminated with PCBs. In the case of the valley and beach drainage pathways, the PCB contamination was more dispersed and therefore large areas and volumes of soil were contaminated with lower concentrations of PCBs, requiring less stringent source removal protocols. As a result, greater volumes of soil remain in these areas with a relatively lower quantity of PCBs.

In a snapshot of distribution of mass of PCBs within the three barrier systems (mass in both filters and sediment and volume of sediment), it can be seen that the majority of PCBs trapped within the three barrier systems comes from the entrapment of the contaminated sediment – most importantly in trapping the relatively small amount of mobile soils in the furniture dump (Table 3).

The furniture dump also behaves differently temporally compared to the other two barriers (Table 3). The major trend for both the valley and beach barriers is that both sediment deposits and mass of PCB are decreasing – indicating that the surrounding regions may be re-stabilizing. In contrast, the furniture dump had been excavated and vacuumed to bedrock in 1999 and the area should have stabilized, given the valley barrier's behaviour. Instead, concentrations of PCB have not significantly decreased in the furniture dump (Table 2), with sediment and level of contamination varying depending on spring runoff conditions (reflected by soil volumes that were transported to the barrier systems in Table 3). Since there is very little soil remaining in this region due to the extent of its removal, site heterogeneities should be somewhat diminished except for near areas where excavation was improbable (such as near the cliff edge). These increased high-level PCB concentrations over time in the furniture dump may indicate that PCB is re-surfacing as freeze-thaw action can bring previously buried contaminants to the surface (Macdonald et al., 2005).

If the rising level of contamination (in terms of soil concentration) in the furniture dump barrier is due to this process, surface barriers may become more relevant for application in cold regions as areas that were previously in permafrost and are now experiencing freeze-thaw activity (Hugh, 2008; Grossi et al., 2007), thereby potentially releasing buried contaminants.

3.3.3. Filters

Initially in the valley, the performance of these materials was hindered as the large sediment loading was much greater than expected. This perceived need for greater particle retention led to a switch to thicker, permeable granular materials while soils in the excavated areas were highly mobile. Excavation ceased at the end of the 2005 field season and therefore the amount of soil coming through the valley barrier had decreased significantly by 2006. Filters for particle retention were constructed of gravel and placed as protective filters in front of the smaller-particle GAC filters. Initially, the gravel trapped greater amounts of PCB compared to the GAC, indicating that sedimentation and large particle retention were the chief mechanisms of PCB sequestration in the barrier system due to the large volumes of contaminated soils mobilized via runoff (Table 4). As soil bridges formed in the gravel matrix due to the large volumes, the pore throats of the permeable gravel filters became constricted, protecting the GAC filters and reducing the amount of contact between GAC filters and PCB contaminated soils, resulting in lower concentration in the GAC filters. Laboratory investigations of granular and geotextile filter design criteria are presented in Kalinovich et al. (2008a). In subsequent years, the GAC filters trapped more PCB than the gravel filters – similar to the furniture dump. These results indicate that as soil volume decreases and with time, particle retention and separation by particle size becomes a more dominant mechanism in the barrier system. As soils stabilized within the region, the particles with greater PCB concentration (fraction of soil particles that are smaller) were more readily trapped by the GAC filters. The increased concentrations accumulating in the filters indicated the presence of sequestration mechanisms in the GAC. Since PCB concentrations in GAC were not found to be greater than that in the surrounding soil, this was not a dominant mechanism for the system.

Filter samples taken in 2004 from the valley and furniture dump barriers show that with the exception of the granulated activated carbon (GAC), the furniture dump barrier retained greater amounts of PCB in its filters (Table 1). The granular filter matrix was more important in the valley system rather than the furniture dump system, likely due to the increased contaminated soil loading. In the furniture dump, even though the area was excavated thoroughly, inevitably some PCB contamination would remain in the fractured bedrock. This contamination could be present as oil and migrated slowly through the soil, which may explain why the hydrophobic geosorbent retained more PCB.

Results of the small pore-sized nonwoven geotextiles (NW1 and NW2 in Tables 1 and 5) clearly indicate that a small amount of highly contaminated fines are migrating through the furniture dump drainage pathway.

In comparing all the filter results (Table 4), it can be seen that the furniture dump captured the greatest amount of PCB and the beach the least, representative of the respective site contaminant histories at each barrier location. As described above, the protective granular barriers (larger filter particle size, larger filter pore throats) trapped more PCB than the following charcoal filters in both the valley and beach barrier systems. This was not the case with the furniture dump as concentrations increased with smaller particle size to much greater effect. The furniture dump field results indicate that either fine particle retention and/or possibly greater sorption of PCB to the GAC filter material is occurring at this location, mechanisms which are not happening to the same extent at the other two barrier sites. Whether these results are indicative of the prior excavation work and source removal of PCBs or whether these results illustrate barrier performance differences between areas of high concentration (furniture dump) and relatively lower concentrations (valley and beach barriers) is difficult to discern from the field data.

As soils in excavated areas stabilize, the amount of coarser grained material transported to the valley and beach barriers will decrease relative to the finer (greater level of PCB sorbed) material. In 2005, excavation was still proceeding which would account for the increased volume of sediment in that year. The valley and beach barriers are functioning as designed since the contaminant is being removed as water passes through the barrier system. The reintroduction of two geotextile filters to trap the finer particles as the final step is to increase the efficiency of all three barrier systems and remove the finer material being transported from the drainage area.

Differences in performance of the barriers have been iterated in previous sections: the amount of sediment deposited in the various barrier funnels, and the mass of PCB retained in each barrier system. The furniture dump behaves differently than the other two barriers – indicating one of two possibilities: Firstly, higher levels of contaminated soil behave differently than lower levels of PCB contaminated soil within this GAC system and secondly, barrier systems with less water flowing through the GAC filters adsorb PCBs more effectively.

Permeable barriers have a finite treatment capacity and the lifetime of the barrier can be limited by physical changes to the barrier, such as decreases in porosity and permeability (Blowes et al., 2000). Clogging of the barrier by particles also leads to preferential flow channels that may reduce adsorption capacity of the barrier material by reducing residence time with the reactive media (Seki et al., 2006). Over the 2003–2007, design modifications had been made specific to the individual barrier systems to accommodate these factors. These design modifications were partially made possible through better understanding of the behaviour of the barrier materials in controlled, laboratory experiments. These laboratory experiments are described below.

3.4. Laboratory studies

Initial column tests compared GAC to a sand with similar particle size and shape in order to evaluate whether particle retention (a function of the filter matrix, independent of filter material) or sorption to the filter material (a mechanism dependent upon the filter material) was a more important factor. The column tests demonstrated that particle retention was the most important factor in trapping PCB contamination -there was no significant difference ($t = 0.3564$, $p > 0.05$) found between the sand (0.2 ± 0.3%) and GAC (0.4 ± 0.3%) materials for adsorption during column runs. Sorption percentages were calculated using total mass of PCBs deployed for column experiments was used to compare and illustrate differences between the two filter materials.

It was seen from field samples at the furniture dump that although very little soil was present in the filter matrix, high concentrations of PCBs were evident. Laboratory studies were undertaken to evaluate whether the PCB in the filter was attached to the soil, or adsorbed onto the GAC. Several filter samples from the furniture dump barrier (FD1, FD2 and FD3) and the valley (V1, V2 and V3) with higher PCB concentrations were selected for analysis. These samples were rinsed with distilled water to remove all soil particles from the GAC and left to dry prior to soxhlet extraction and GC/ECD analysis. These samples, like the rinsed column samples, were also subjected to LEM analysis to ensure all soil particles were removed from the GAC material. PCB sorption to GAC in field samples was found to be 35 ± 2% (valley) and 62 ± 11% (furniture dump). Results of initial and final partitioned concentrations are shown in Fig. 10.

Samples of filter matrix from the column were obtained and analyzed for total mass of PCBs alongside rinsed filter samples, (a sampling process that mimics field sampling and sorption calculations). The amount of PCBs sorbed to GAC at $t = 72$ h was found to be 18.5 ± 3.4%, a value similar to field results, considering the retention time of a particle in the laboratory compared to the field, where retention times of a PCB contaminated particle can range from 1 day up to 1 year. There are three significant differences which can be observed in the field that affect adsorption in the barrier/column systems, three of which are mentioned here: flow rate, retention time and soil concentration. Temperature can also play a role in adsorption mechanisms (Arora et al., 2011), but as field concentrations (colder temperatures, approximately 4 °C) proved to be higher than column concentrations (warmer temperature, 21 °C), temperature effects were not evaluated. There is also a noted difference between how the different sites are behaving; sorption clearly plays a much more integral role in the furniture dump barrier system. The soil characteristics of these two sites are similar (see Table 5). The flow regime through the barrier systems are different; the valley (and beach) barrier experiences greater volumes of both water and soil – which indicates why the column studies results were more comparable with the valley rather than the furniture dump.

Adsorption in field sample results (particularly the furniture dump results) could not be fully explained by the current column studies conducted. This may be due to long contact time in the field or increased particle-to-particle (soil-to-GAC) contact (Werner et al., 2005). This occurs from spring run-off, when PCB-contaminated soils are mobilized and subsequently trapped within the granular filter matrix. The majority of mobilization occurs during spring run-off and infrequent storm events over the course of the summer (June–September) where large volumes of fast-moving water can mobilize the contaminated soils. As the water flow decreases, soil particles become trapped within the granular filter matrix for periods ranging from several months up until 1 year. Column tests indicated that particle retention is important for retaining PCBs, and this logic follows in the field – particle retention is required prior to mass transfer sorption. Mass transfer processes occur between soil particles and GAC in the filter matrix as a combination of two mechanisms: the first being an increased affinity for the PCB molecule to be attracted to GAC sorption sites over the soil particle, and the second due to the highly hydrophobic, low-solubility nature of PCBs. The required particle retention combined with partitioning behaviour for hydrophobic contaminants such as PCBs provides an interesting twist to design criteria that is seldom considered for sorptive, activated carbon barriers (Erto et al., 2010).

Over time, granular filter materials can be washed out (Locke et al., 2001). To ensure the granular filter design was thick enough to prevent this mechanism, the column was flushed with an increased volume of water (100 L) and compared to a lesser volume (8 L). PCBs were not removed from the filter system by the increased volume of water flushing through the system, respective system mass loss of PCB was found to be 6.1 ± 0.4% with 8 L and 3.8 ± 2.0% with 100 L.

The valley field system design was based on spring run-off conditions to trap approximately 70% of the soil settling out via sedimentation processes under worst-case flow scenario conditions (Kalinovich et al., 2008b). Retention of contaminated particles cannot be sacrificed to improve the permeability of the filter system. Therefore, the permeability of the system is dependent upon the success of the sedimentation processes upstream in order to treat the finer, more contaminated particles flowing through the system. The total volume of the valley barrier system is 5773 times larger than the column and should exceed the worst case scenario clogging conditions by the same order of magnitude in terms of mass of soil. In order to mimic the field system, scaled ratios of mass: volume must be replicated in the column system.

Impacts from diurnal freezing and thawing, and the permeability of a half-frozen system were explored in the laboratory, as the barrier system in was likely to be exposed to these conditions in the field. Gore et al. (2006) found that GAC with particle sizes ~750 μm (screened 1 mm × 4 mm) did not experience mechanical breakdown during freeze-thaw cycles. Permeability conditions that would mimic spring conditions (half-frozen filters from the bottom) were recreated in a controlled, laboratory setting. Column studies were conducted in triplicate with half-frozen filters to evaluate permeability during this formation. Results indicated that permeability of the filter system was adequate – over 4 kg of soil added to a system with two 7.56 cm gravel filters followed by two 7.56 cm GAC filters. Initially, representations of soil mass to volume of filter systems between column and field appear poor: the mass of soil to volume of the column filter system is 1632 kg/m^3 and the mass to volume of the field barrier system is 81 390 kg/m^3. This corresponds to 82 times more filter system volume in the field than in the column, with 3150 times more soil in the field than in the column apparatus. These results are important to understanding the design of these types of barrier systems in cold regions. This 4 kg loading translates to roughly 1630 kg/m^3 mass of soil/system volume to clog the column system when half-frozen. In comparison to the 2005 valley field season (the largest volume of soil loading for the system), a mass of 12 600 kg of soil was captured for the entire valley field barrier system. In comparing total system volume, a comparable mass/volume ratio is gained: a ratio of 890 kg/m^3 is found in the field where water still flowed through the barrier system, a value that is less than 1630 kg/m^{3}in the column filter system required to clog the system under half-frozen filter conditions. These results indicate that the column apparatus is giving meaningful, scaled results and that the barrier system design, incorporating sedimentation processes, compensates for worst case scenarios that could impair gate permeability. In the field, these results were applied through modifications to the beach barrier by increasing the volume of the beach barrier filter system to improve remediation efficacy.

4. Conclusions

The surface barrier systems that were originally installed in 2003 and 2005 have proven to be successful in trapping PCB contaminated soil. The monitoring plans have adapted over the years to accommodate changes in design and efficiency of monitoring the barrier systems themselves. Changing patterns in previously contaminated areas downstream of the barrier confounds monitoring points that are taken in these locations. It is difficult to tell whether the contamination comes via breakthrough of the barrier systems or whether it is from contamination already present in the area shifting to a new pocket or gully. As soil pockets stabilize over time, less sediment at lower concentrations will pass through the barrier systems and the performance of a monitoring strategy will improve. Conversely, the furniture dump system behaves differently than the other two barrier systems: as time goes on greater contamination seems to flow through the barrier system. The cause for this is unknown. Increased freeze-thaw action may be bringing previous contamination to the surface. However, the barrier is effectively concentrating and trapping highly contaminated fines as can be seen in the filter results.

Laboratory studies indicated that particle retention was the most important factor in retaining PCBs and that mass transfer mechanisms were occurring in the short duration studied. Rinsed field samples demonstrated that sorption plays a larger role than had been simulated in the laboratory – particularly for areas with highly PCB contaminated soils, as with the furniture dump barrier system. The investigation of half-frozen filters and the stressed importance on sedimentation processes are important design challenges that must be considered for surface remediation in cold regions. Based on these preliminary results, design criteria for adsorptive barrier systems should consider particle retention mechanisms for hydrophobic contaminants that are unlikely to be transported via conventional advective–dispersive solute mechanisms. If retention time criterion takes into account adequate time for contaminant mass transfer between soil particle to GAC particle, the contaminant will remain adsorbed to the GAC filter matrix and clean soil particles may exit the system. This sequestration can be incorporated into the design for both surface and subsurface barriers, by designing the retention time of particles within the filter to be equal to that of the time needed for partitioning. These findings are applicable to design criterion for all sorptive barrier systems dealing with hydrophobic contaminants.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jenvman.2011.12.037.

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