CSTARS Center for Spatial Technologies and Remote Sensing

The Suitability of a Variety of Particulate Sorbents as Spill Response Tools

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The University of California, Davis

Executive Summary

The Suitability of a Variety of Particulate Sorbents as Spill Response Tools

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As part of the Department of Fish and Game, Oil Spill Prevention and Recovery (OSPR) Scientific Study and Evaluation Program (SSEP) intent for research 1.A: Investigation and evaluation of applied spill prevention and response programs and technologies, this study compared ten oil sorbent products made of peat moss, agricultural cellulose, recycle material cellulose, mineral dust, and polymer plastic for the ability to adsorb and/or absorb Alaska North Slope oil and reduce the immediate and longer term potential of oiling feather and fur bearing animals, and minimize contamination of shore vegetation.

In the summer of 2009, two trials measured the effectiveness of ten sorbents and duplicate sorbent to decrease the stickiness of crude oil on two substrates using natural wiper materials. The tested substrates from the coastal environment were marsh vegetation *Salicornia virginica* (pickleweed) and open fresh water. After oil application to individual tank compartments, the vegetation and water surfaces were treated with loose particulate sorbents. One tank in each trial was left untreated as the control measurement. Two wiper materials were used to simulate bird and animal coats, goose feathers and lamb sheering pads. The change in weight (WC) of the wipers measured the adherence (stickiness) of oil and sorbent; clean dry wipers were weighed before, and then after wiping the substrate. The wiper measurement began immediately after treatment application, then daily for the first week, weekly for the remaining first month, and then at a two month interval. WC mean and variance were compared among the sorbents and control, and the sorbent was deemed effective if it differ from the control sample at the 95 % significant difference level.

This investigation successfully evaluated three hypotheses:

a) *Applying a particulate sorbent material to petroleum-contaminated marsh vegetation and water will immediately render it less sticky to fur and feathers.*

The sorbents selected for this study nearly eliminated oil adherence to feathers and fur in the water substrate, and significantly reduced the amount of oil stuck to the wipers from pickleweed. Within the first four days, the low density petroleum molecules, such as kerosene, substantially contributed to oil absorption from the control, although it diminished over the first 7 days. The sorbents reduced oil adsorption immediately with the first measurements after the treatment application.

b) *The adherence of crude oil to wildlife feathers and fur can be evaluated by wiping with feathers and wool pads on oil treated vegetation and water surfaces.*

Both feather and fur wiper types demonstrated the effectiveness of the sorbents could be measured. In pickleweed, five significantly separate groups of sorbents were identified in both feathers and fur; and in water, seven in feather and five groups were significantly different. Feathers and fur wiper types satisfactorily simulated water fowl and mammals by their strong oil absorption and water repelling characteristics.

c) *Different particulate sorbents likely vary in their effectiveness to absorb spilled oil on marsh vegetation and water, and in the ability to reduce the adherence of oil to feathers and fur.*

In pickleweed substrate and feather wipers, the ground agricultural crop residues Kenaf and Dri-Zorb; and peat moss dust products Sphag Sorb and Cansorb were the only sorbents effective in reducing oil stickiness. In pickleweed substrate and fur wipers, these four sorbents plus a recycled cellulose dust NatureSorb were the only sorbents effective in reducing oil stickiness. While others sorbents had somewhat lower WC means for feathers and fur than the control, the difference was not significant.

In water substrate, nearly all sorbents were effective in reducing the stickiness compared to untreated oiled substrate, and nearly equivalent to the pre-oil and pre-treatment measurements. The organic sorbents were hydrophobic, preferring oil to water, and as such aggregated the oil into floating patches. Mineral sorbent absorbed the oil it contacted on the surface with dusting and remained for a short time, or without contacting oil sank rapidly. Wipers were ran through the oily sorbent patches, and then rinsed in the adjacent clear water changed weight only slightly.

The suitability of these organic and mineral dust or particles sorbents to prevent adherence of oil on feather and fur was successful demonstrated. Further research is needed to determine toxicity of the combinations of oil and sorbent to animal. While some of these materials are all ready advertised for oil clean-up, further research in others is needed. The application timing and method of these materials is an additional research area needed for effective use of the sorbents.

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1.0 INTRODUCTION

1.1 Sorbent Materials to Reduce Oil Spill Impacts on Wildlife

This project evaluates a strategy for petroleum spill containment based on application of biodegradable and mineral absorbing material to reduce exposure to plants and animals. Rapid absorption/adsorption and containment materials or dispersants are the principal methods of reducing spill expansion and facilitating oil recovery (EPA 1999). Application of loose particulate sorbents immediately after a spill may reduce the potential oiling of feather and fur bearing wildlife, and inhibit damage to shore vegetation. The 2007 local spill of bunker oil from the *Cosco Busan* in San Francisco Bay, and the present disaster in the Gulf of Mexico from the explosion and sinking the British Petroleum deep sea platform encourage continued investigations less toxic means of containing the oil and inhibiting contamination of water fowl and mammals.

This 2009 project follows the 2007 preliminary investigation to demonstrate a measurement method and sensitivity for evaluating sorbent effectiveness in reducing the amount of oil adhering to feather and fur (Ustin 2007). In this earlier study, a single organic sorbent of peat moss dust Sphag Sorb successfully reduced Prudhoe Bay crude (PBC) oil contamination of feather and fur. The light oil fraction facilitated absorbing all oil fractions immediately and for a few days after the oil and sorbent were applied to water and pickleweed substrates. For the present study, nine additional sorbents were chosen for evaluation and comparison.

The simulated spill environment was partitioned into two substrates for oil contamination: vegetation and open fresh water. The marsh vegetation used in this study, *Salicornia virginica* (pickleweed), was selected for its dominance in saline marshes of the San Francisco Bay estuary and generally, similar wetlands of the continental U.S. Rosso et al. (2004) showed that *Salicornia* sp. is sensitive to crude petroleum, as did our previous study (Ustin 2007). Open water is probably the most critical substrate creating the greatest exposure of oil contamination to water birds, water mammals, fish, and other wildlife.

1.2 Study Hypotheses

This study addresses Department of Fish and Game, Oil Spill Prevention and Recovery (OSPR) Scientific Study and Evaluation Program (SSEP) intent for research 1.A: Investigation and evaluation of applied spill prevention and response programs and technologies.

a) Applying a particulate sorbent material to petroleum-contaminated marsh vegetation and water will immediately render it less sticky to fur and feathers.

b) The adherence of crude oil to wildlife feathers and fur can be evaluated by wiping with feathers and wool pads on oil treated vegetation and water surfaces.

c) Different particulate sorbents likely vary in their effectiveness to absorb spilled oil on marsh vegetation and water, and in the ability to reduce the adherence of oil to feather and fur.

Table 1. List of sorbents evaluated with descriptions and trial number.

Trial	Material Description	Sorbent	Manufacturer
1 & 2	Peat, sphagnum moss (fine particles)	Sphag Sorb	Earth Care Products, Edmonton, Alberta, Canada
1	Cellulose, agricultural, cotton (dust, plant particles)	Oil Gator	Product Services Co., Jackson, MS
1	Cellulose, agricultural, Kenaf (fine particles)	Kenaf Organic Absorbent	Kengro Corp., Charleston, MS
1	Cellulose, agricultural, corn cob (particles)	Dri-Zorb	The Andersons, Inc., Maumee OH
1 (water only)	Cellulose, recycle paper with kaolin clay (large compressed paper chunks)	CheetahSorb	CEP, Houston, TX
1	Mineral, diatomaceous earth plus volcanic ash (fine particles)	Pozzolan	Western Pozzolan Corp., Doyle, CA
2	Peat, sphagnum moss (fine particles)	Cansorb	Annapolis Valley Peat Moss Co. Ltd. Nova Scotia, Canada
2	Cellulose, mixture of recycled with a blend of nutrients and micro-organisms (fine particles)	NatureSorb	Ram Energy Limited, Sunderland, UK
2	Mineral, expanded amorphous alumina silicate (fine particles)	Stardust Super Absorbent	Paradigm International, Inc., Santa Ana, CA
2 (water only)	Styrene-butadiene polymer (3 mm extruded particles)	HiSorb 1151	Dyneon LLC (3M), Oakdale, MN

2.0 METHODS

To compare the effectiveness of various oil sorbents in reducing oil stickiness to fur and feathers, two environmental substrates vegetation and water were sprayed with oil then treated immediately with sorbents. To handle the large number of samples, two trials were run during 2009, beginning in July and beginning the first week of September. One tank of substrate in each trial was oiled but not treated with sorbent as the control. In one tank in each trial, the sorbent was Sphag Sorb to provide a comparison between trials and the pilot trial in 2007. Both the treated and untreated substrates were wiped with feather plumes and fur patches. The variation in increased weight change (WC) from before to after wiping provided a relative measure among sorbents and control (no sorbent) of stickiness and remaining transferable contamination after treatment. Unlike the 2007 trial, one oil was used, Alaska North Slope (ANS) crude. Open tanks held the substrates and were maintained exposed to the weather outside at a University of California, Davis greenhouse facility to provide realistic weather conditions for each two month trial period. Vegetated tanks were aerated and sub-irrigated to maintain plant health and water levels throughout the trial period.

2.1 Sorbents Evaluated

Ten sorbents were evaluated in this project: two peat moss products, two recycle and three agricultural cellulose materials, two mineral dusts and one synthetic polymer plastic product (see Table 1). Each material structure and particle size has inherent advantages and disadvantage on vegetation and water substrates. Table 1 lists the trial number, base material, product name, and manufacturer. Short descriptions, photographs, and the Material Safety Data Sheet (MSDS) of the sorbents are in the Appendix.

2.2 Substrate Tanks and Plant Growth

2.2.1 Vegetation substrate:

Pickleweed was grown in four large tanks, approximately 0.25 m (10 in) by 1.2 m (4 ft) by 3.7 m (12 ft) of wood sides and flooring lined with 6 mil plastic sheeting. Plant medium, sub-irrigation, and root aeration were the same method as the 2007 trial. Perlite, a thermally treated volcanic glass plant growth media (http://www.perlite.org) was added to the tanks and saturated with low salinity water for several days before transplanting. The root and water were aerated using drip-emitter hose looped on the tank bottoms and fed a consistent air pressure of approximately 2 psi from a vane pump (Fig. 1.). Optimum water level was maintained with float valves (Fig. 2 a. and b.) at 7.5 to 10 cm (3 to 4 in) deep.

August 9, 2008, approximately 680 pickleweed plants from North Coast Native Plant Nursery (Petaluma, California) were transplanted into the moist Perlite base from 20 cm (8 in) Leach Tube pots in prepared galvanized tanks used in the 2007 trial. These plants were transplanted late, and insufficient growth was obtained to conduct the first trial during that summer. On October 15, 2008, these smaller tanks were moved to a greenhouse before the first frost. The plants grew slowly until late winter when higher temperatures accelerated growth to nearly maximum canopy. March 9, 2009, these plants were transplanted into the Perlite in the large wood tanks outside. Over the next four months the plants re-established a full canopy and were ready for oil and sorbent applications of the first trial in July. An additional 700 plants from the nursery were transplanted directly to the two remaining large wood tanks on April 14, 2009. These plants grew to full canopy through the summer and were ready for the September trial.

Our experience in growing *Salicornia* sp. found that commercially available aquarium sea water salt mixture provides a consistent and easysalinity control (Pearcy and Ustin

Fig. 1. Large vegetated tanks with overhead lines to supply air to subsurface aeration hoses from van pump, and water to float valves.

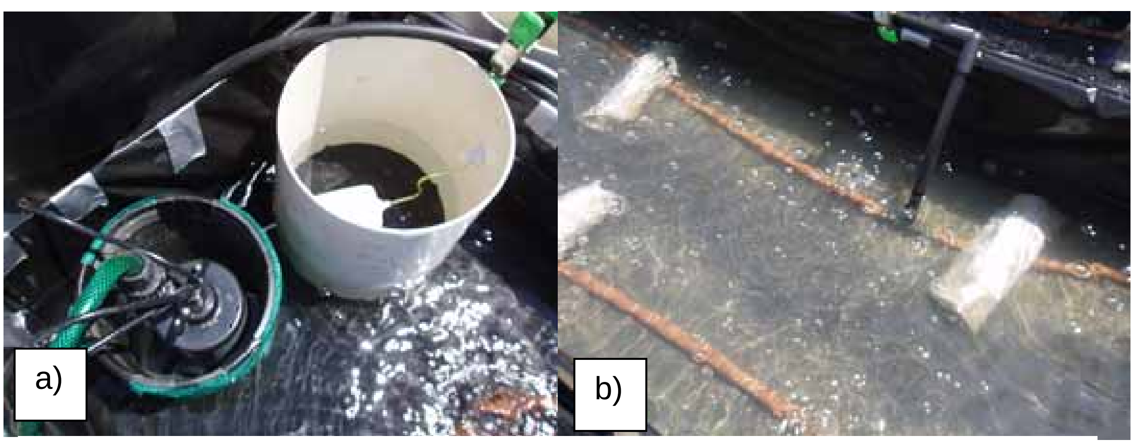

Fig. 2. a) Still wells with sump pump and float valve to maintain water conditions, and b) drip irrigation hose used to aerate the water under the plants.

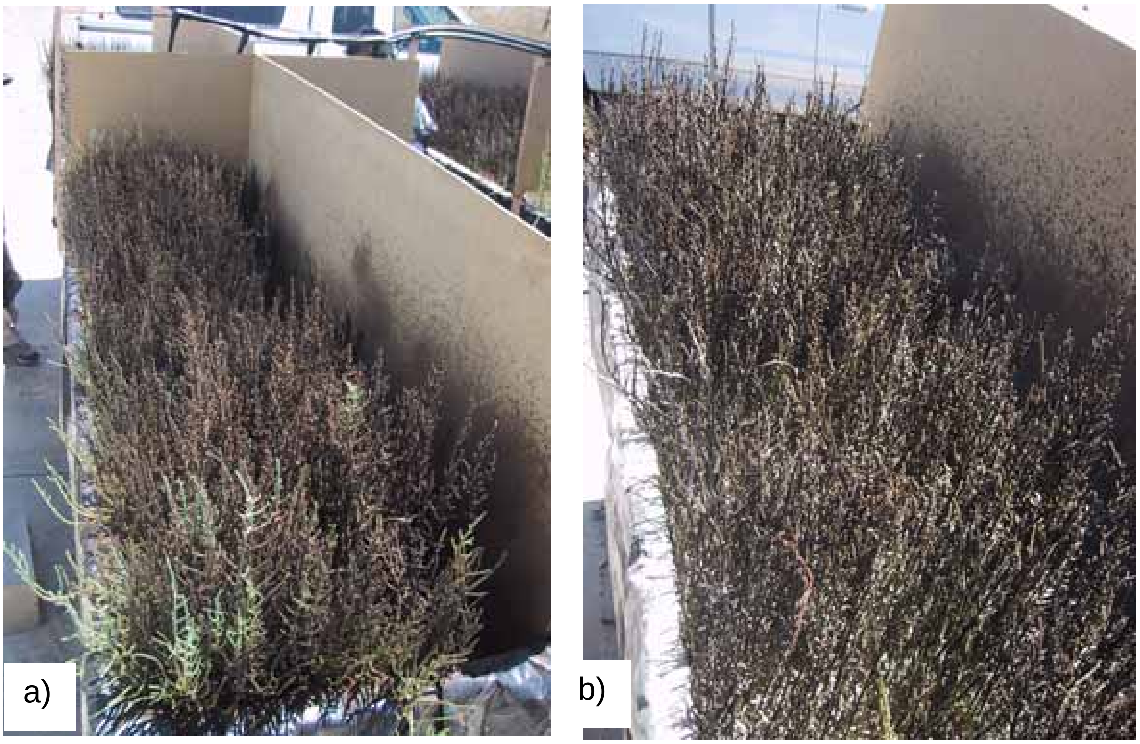

Fig. 3 Pickleweed, oiled, a) treated with Sphag Sorb, and b) treated with Pozzolan sorbents.

1984; Ustin 1984; Rosso et al. 2004). The status of the hydroponic salt and nutrient mixture was monitored with hydrometer (specific gravity) and nutrient test kit measurements. Sea water salinity ranges from 34.6 to 34.8 parts per thousand (ppt, grams of salt per kilogram of water). The Perlite was saturated with 14.0 to 20.5 ppt (specific gravity of 1.014 to 1.016). After transplanting, the specific gravity was kept 1.008 to 1.010 with water and fertilizer additions. Nutrient fertilizers were added monthly through the growing period by draining all but the last 2 cm from each tank into a mixing tank. After adding dissolvable fertilizer and balancing the salinity, the water was returned to the tanks. The fertilizer (15-30-15) was added to maintain the nitrate (NO_3) level between 400 to 600 ppm. After dilution the nitrate content was measured using the Hach Saltwater Master Test Kit #2068600, www.hach.com).

Before each trial, the pickleweed substrate tanks were divided into four chambers before spraying with equal amounts of oil and applying the various sorbent treatments. The dividers were 60 cm (2 ft) wide hardboard (Masonite) panels to prevent cross contamination of sorbents between adjacent tanks. For the water substrate, panels were held in-place temporally while applying the sorbent.

2.2.2 Water substrate: For the water substrate, sheet metal tanks approximately 0.6 m (24 in) by 3 m (10 ft) were lined with two layers of 6 mil heavy black plastic and filled with 15 cm (6 in) fresh water before each trial. These tanks were used in the 2007 trial for pickleweed and water.

2.3 Substrate Treatments and Sampling

2.3.1 Oil application: A four gallon sample of Alaska North Slope crude oil (ANS) was contributed by the Valero Refining Company in Benicia, California. No chemical constituent characterization was provided or determined for this sample.

The substrates were uniformly coated with ANS using a garden pump sprayer to the drip point on vegetation and to a thickness of approximately 0.1 mm (0.004 in) on the water (as calculated by the tank surface and amount applied).

2.3.2 Sorbent trials: Two trials began on July 6, 2009 (July trial) and August 31, 2009 (September trial). Splitting the sorbents into two trials was necessary to reduce the weightings to reasonable number within each work day. In pickleweed, eight sorbent treatments were applied, including the repeated Sphag Sorb. The water substrate tanks were treated with 10 sorbents including the repeated Sphag Sorb. Two additional sorbents, HiSorb and CheetahSorb, could be only used on water due to large particle size. The controls within both trials were oiled substrates that were not treated with sorbent. After oil application, the sorbents were applied by sieving handfuls of material until the canopy was fully dusted. The sorbents were liberally applied to thoroughly cover the pickleweed canopy and water surface to assure sufficient oil absorption and reduce sampling error. Figures 3 a. and b. illustrate the dust applied to pickleweed with Sphag Sorb and Pozzolan treatments.

2.3.3 Trial sample measurements: Measurements involved daily and weekly wiping the vegetation and water substrates following oil and sorbent applications. The sample of each tank for the day consisted of five wipers (observations) of feather and fur. Before the oil application (t00), both substrates were wiped to estimate the error due to measurement alone. The substrates were wiped to test oil adherence immediately after sorbent treatment on day 1 (t01); then daily on days 2 (t02), 3 (t03), 4 (t04), 5 (t05), 6 (t06), 7 (t07), 8 (t08); weekly on day 15 (t09), 22 (t10), 29 (t11); and monthly on day 61 (t12). The water trials continued for only two weeks until t09. The water tanks were not restocked as the water evaporated in the mid summer heat of the Sacramento Valley. Measurements stopped when tanks contained only oil and sorbents.

The ability of the sorbent to reduce oil stickiness was measured by the weight change (WC) of the wiper before and after wiping the substrate. Less oil and sorbent stuck to the wiper indicates a relative reduction of contamination on feathers and fur. Two wiper materials were used: 1) goose feathers, 7.5 cm (3 in) long bunches similar in appearance to deep-sea fishing jigs, and 2) sheepskin sheering pad, 0.6 cm (1/4 in) pile, 3.8 cm (1-1/2 in) squares. For vegetation, feathers were superior wipers by the fine, flexible main stem reaching between branches and at nodes where oil accumulated (Fig. 4.). Oily sorbents were shaken off from feathers with two hits on the tank side just as a bird or animal would to remove any loose sorbent and oil. Feathers were also far superior by instantaneously saturating with oil preferentially over water; the bane of all birds caught in an oil spill.

The wipers were prepared in individually labeled resealable sandwich bags and weighed. After wiping the substrate surfaces until no additional oil or sorbent would attach

Fig. 4. Wiping technique shown with crude oil on pickleweed.

(Fig. 4.), the wiper was returned to the plastic bag, dried if necessary, and re-weighed. The sampling sequence started with the first wipers for all tanks, then the second wiper for all tanks. This sequence was repeated for all five wipers, and for each type of wiper. The wet wipers were dried at low heat (40 ºC, 104 ºF) for at least 24 h, and plants samples for more at least one week in a shed used for drying grain and plant samples.

To overcome any bias in sorbent application and sampling, plants or areas of water were arbitrarily selected for wiping within the tanks. Individual plants were harvested for each wipe sample to assure no multiple wipes of the vegetation and to measure the plant biomass. These plant samples were collected in pre-labeled paper lunch bags, and dried for biomass weight.

2.3.4 Statistical analysis: Statistical analysis and graphics of the WC of wiper observations were created with S-Plus statistical software (ver. 6.2, Insightful Corp., Seattle, WA) using analysis of variance (ANOVA) and regression modeling. In Figures 5 through 10, box-whisker plots of WC portray the ANOVA statistics for treated and untreated combinations of substrates, wiper types, and sorbents by sample dates. In these whisker-box plots, the upper and lower extents of the boxes represent the interquartile distance between the 25th to 75th percentiles of WC observation within each measurement sample (Insight 2001). Due to the imprecision of the measurement method, whiskers were chosen to show the 10 % and 90 % sample measurement range. Values exceeding 1.5 times the interquartile distance were considered outliers and removed (Devore & Peck 2001). All portrayal of significant difference and confidence intervals, such as line hatching in the plots, were determined at 95 % level from ANOVA. Overlapping cross hatching of control and sorbent measurements indicates an insignificant difference between sample measurements.

3.0 RESULTS

3.1 Observations and Sorbent Effectiveness within Pickleweed Trials

3.1.1 Pickleweed substrate: The method prescribed wiping until no additional oil and sorbent would attach to the wiper, instead of wiping the plant material clean. If plant material and oily sorbent were not in excess, the possibility existed that the WC would be limited or related to amount of pickleweed harvested. To validate that no such relationship existed, wiped plant samples were individually bagged, dried and weighed to determine biomass (including a small error due to residual oil and sorbent). There was no correlation between biomass and WC in either feather or fur wiper values over all sorbents and control (r = 0.0047 and r = 0.00075, Pearson's product moment correlation coefficient). The harvested plant biomass weights were somewhat consistent. For the 670 pickleweed sprigs harvested for feather wipers, the biomass mean weight was 3.68 g (+/- 3.56 to 3.79 g without removing outliers). For same number of pickleweed sprigs wiped with fur, the mean weight was 3.83 (+/- 3.72 to 3.95 g without removing outliers). In the 2007 pilot trial, similar consistency among plant weight and lack of correlation to WC were found. Also, attempts to normalize wiper WC by biomass added greater variance within samples.

3.1.2 Untreated vegetation measurements (control): The box-whisker plots in Figures 5 through 6 show the high variability in WC from pickleweed not treated with sorbent (control) at first sampling (t01). This is likely due to the rapid evaporation of highly volatile components in oil over the several hours of the sampling process. Later samples from controls show more consistent measurements, and narrower confidence internals. We observed immediately after spraying the plants that the oil was very thin, light brown in color and readily adsorbed on everything that brushed against the plants. After four or five days, the stickiness in the control was nearly gone, as seen in the rate of decline in the WC means in these Figures.

3.1.3 All sorbent types: A comparison of WC mean and significant difference between feathers and fur wipers on all sorbents for pickleweed are shown in box-whisker plots of Figures 5 a. and 6 a. The effectiveness of each type of sorbent is evident in separation of the means, and significant differences can be seen within the first four days in both feathers and fur wipers. Cellulose and peat moss type sorbent wipers gained significantly less WC than those from the control, roughly 1/10 to 1/2 of the control wipers WC. The mineral products were not effective as a type, and show no difference from the control. Variation within each sorbent type is discussed below.

3.1.4 Peat sorbents: The two evaluated peat moss sorbents Sphag Sorb and Cansorb were nearly identical in particle size and other apparent characteristics. These two products also absorbed oil from the pickleweed nearly the same (Fig. 5 b.and 6 b). Both feather and fur wipers WC for Sphag Sorb and Cansorb were not significantly different from each other. As a sorbent type, they are significantly different from the control, however the Cansorb was within the variation of the control for t01.

As the first week proceeded the differences narrow, and by day four (t04) the means are very similar to control. These measurements indicate Sphag Sorb and Cansorb would not be as effective as many of the cellulose products in reducing contamination of feathers and fur when oil is directly applied to vegetation.

This result is consistent for fur wipers in the 2007 Sphag Sorb-PBC trial where there was no significant difference in any of the daily or weekly measurements. For feathers, this is contrary to 2007 Sphag Sorb trial where the difference between the peat moss and control were

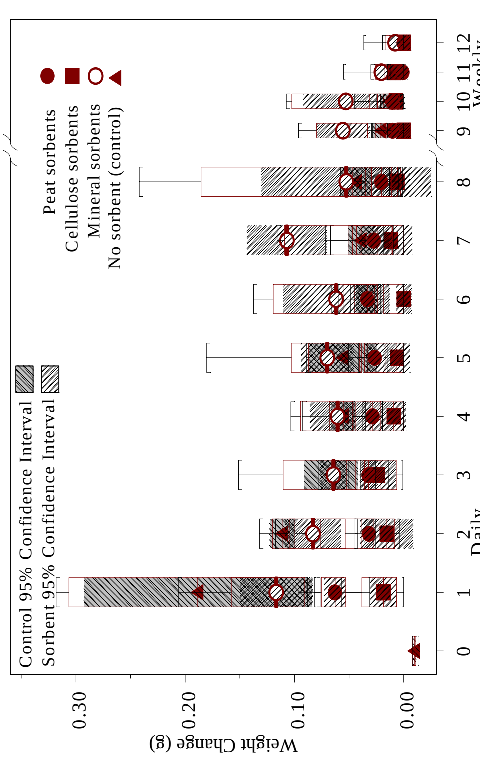

Fig. 5 a. Pickleweed, feathers, all sorbents, and control.

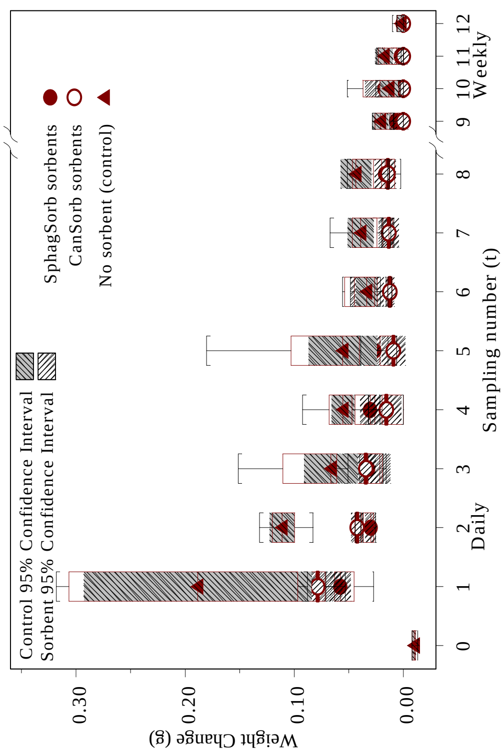

Fig. 5 b. Pickleweed, feathers, peat moss sorbents, and control.

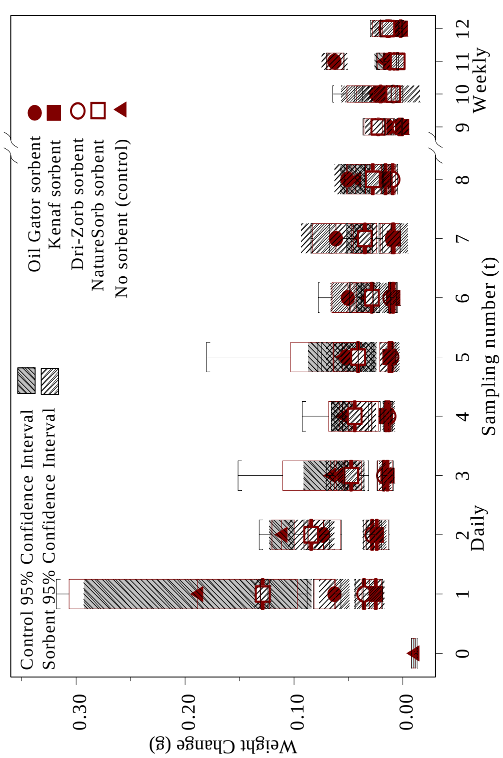

Fig. 5 c. Pickleweed, feathers, cellulose products, and control.

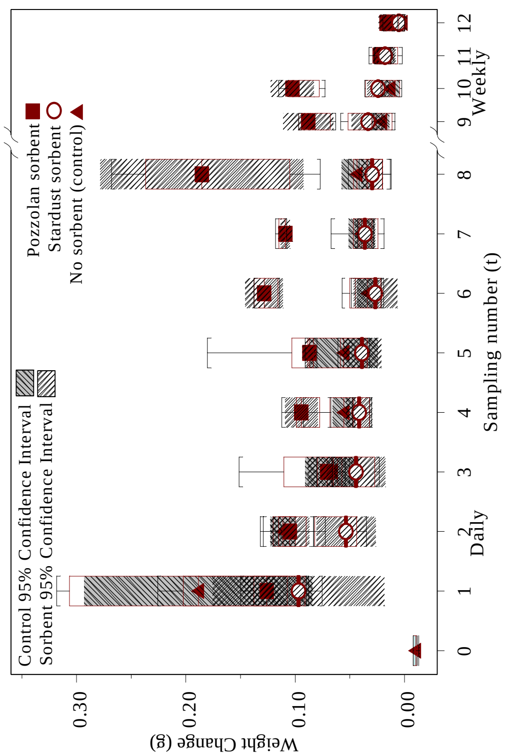

Fig. 5 d. Pickleweed, feathers, mineral products, and control.

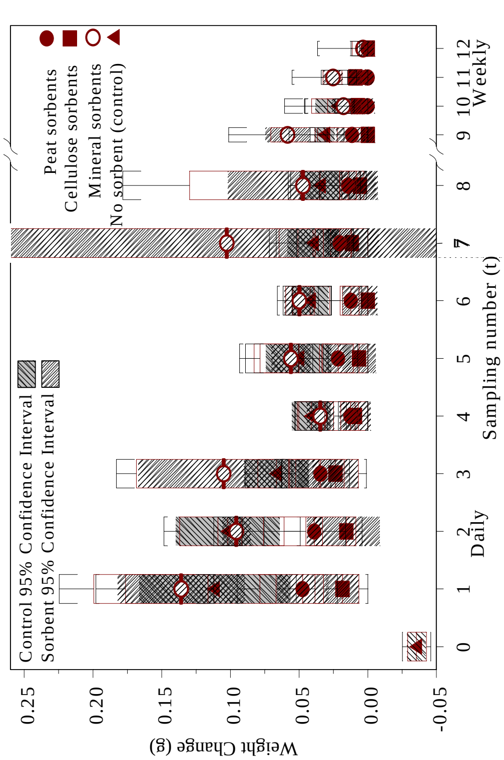

Fig. 6 a. Pickleweed, fur, all sorbents, and control.

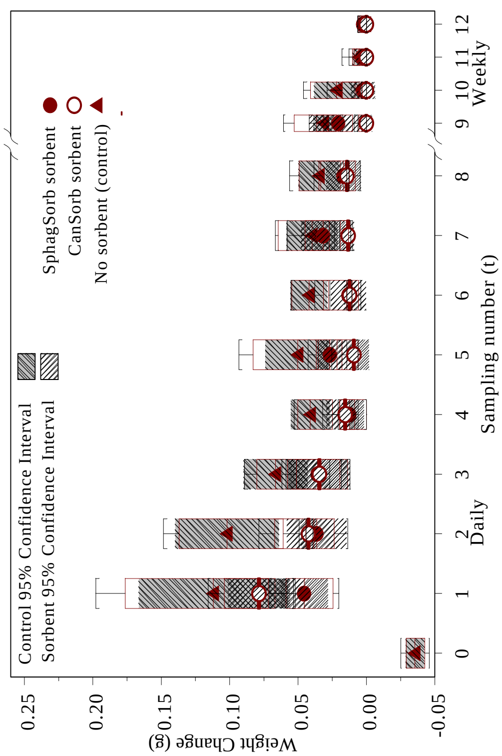

Fig. 6 b. Pickleweed, fur, peat moss products, and control.

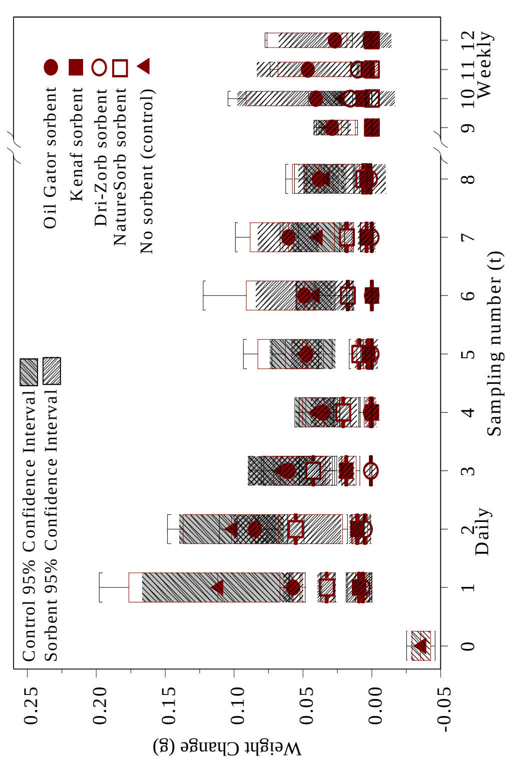

Fig. 6 c. Pickleweed, fur, cellulose products, and control.

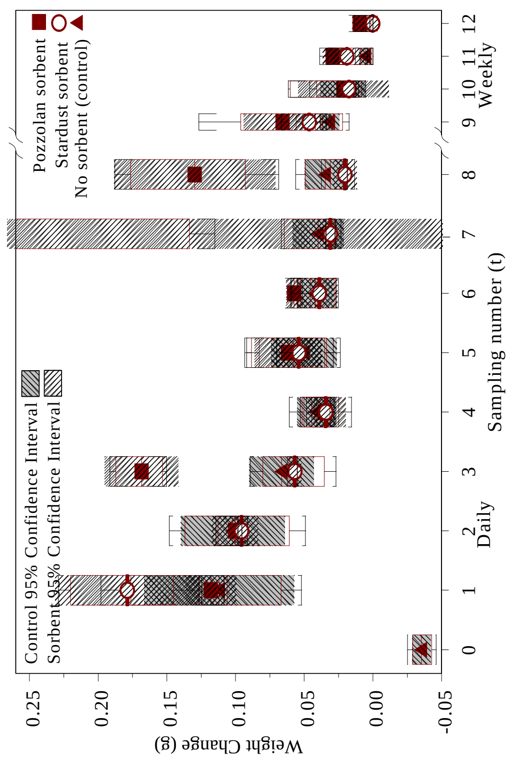

Fig. 6 d. Pickleweed, fur, mineral products, and control.

significantly different for the first day and until the third or fourth sample day. Just for this concern Sphag Sorb sorbent was repeated in each trial to provide an indicator of the variability between trials due to environmental and other factors. In Figure 7 a., the feather wiper WC for the two 2009 trials have generally similar means that are significantly different from the for 2007 trial. The 2007 WC means for feathers wipers is also the same or even greater than the control for 2009 after t03. In Figure 7 b., the fur measurement means for the four trials were mixed, and generally not significantly different from the control. Among these three trials the different WC measurements with feather and fur on sorbent treated pickleweed indicates there is influence by air temperatures, oil viscosity, technician skills, and other factors on determining the relative effectiveness.

3.1.5 Cellulose sorbents: In the pickleweed substrate for both feathers and fur, two of the four evaluated cellulose absorbents produced significant results compared to the control through t05 with feathers and t07 with fur (Fig. 5 c. and 6 c.). The WC for ground Kenaf and corn cob Dri-Zorb products was significantly lower than that for the control and other cellulose sorbents. These two sorbents were also significantly more effective than the peat moss products on pickleweed. The cotton residue Oil Gator and recycled cellulose NatureSorb products were similar to each other and to the control beginning from t02.

3.1.6 Mineral sorbents: Of the two evaluated mineral products on pickleweed, Pozzolan and Stardust, WC means were not significantly separated from the control for either wiper, as seen in Fig. 5 d. and 6 d. In a few measurements, these WC mean values were equal or more than the control.

The higher density of mineral material in feathers and fur may have contributed to inferred lower effectiveness compared to low density peat moss and cellulose products. In Figures 5 a and 6 a, note that all feather tests in pickleweed are shown with same y-axis, and similarly, all fur measurements in pickleweed are shown with the same y-axis. The same amount of oil may have been adsorbed by per unit of sorbent, but the greater sorbent density was enough to increase combined weight towards the control weight. However, we did observe a greater amount of oily sorbent on the feather and fur wipers.

3.2 Observations and Sorbent Effectiveness within Water Trials

3.2.1 Water substrate: The water trial demonstrated the effectiveness of the sorbents immediately after application. Enough oil was applied to cover the entire water surface. Effective sorbents would "pool" the oil into islands of oily sorbent, surrounded by clear water. For all sorbents, the procedure of brushing the wipers first through the oily sorbent islands then the surrounding clear water, if any, allowed the wipers to be rinsed or remain contaminated.

3.2.2 Untreated water measurements (control): The box-whisker plots in the series of Figures 8 and 9 show greater consistency within water WC in control sample values compared to pickleweed control. We observed untreated oil surface instantly saturated the wipers with oil. Fresh oil acted as a surfactant on

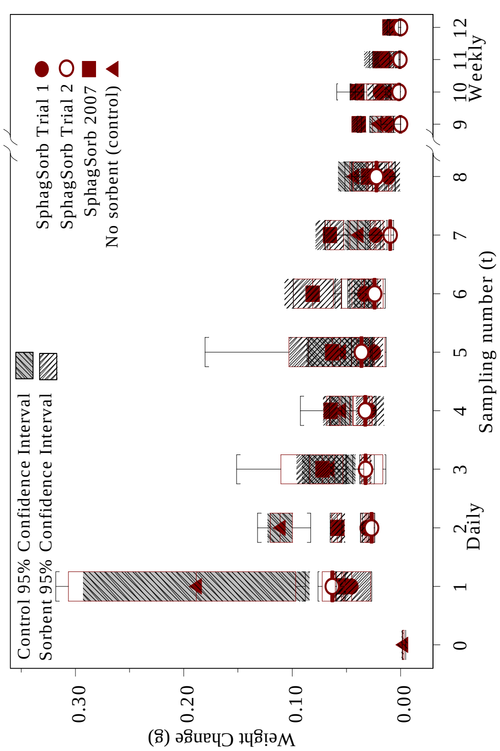

Fig. 7 a. All trials of Sphag Sorb for pickleweed and feather.

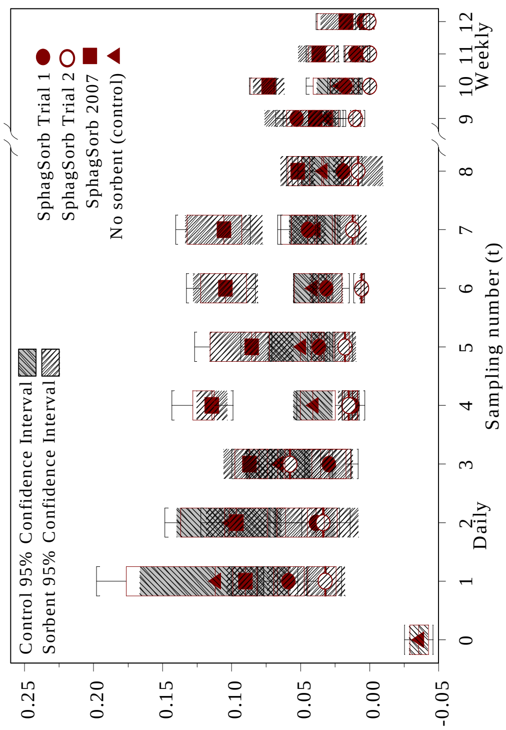

Fig. 7 b. All of Sphag Sorb sorbent for pickleweed and fur.

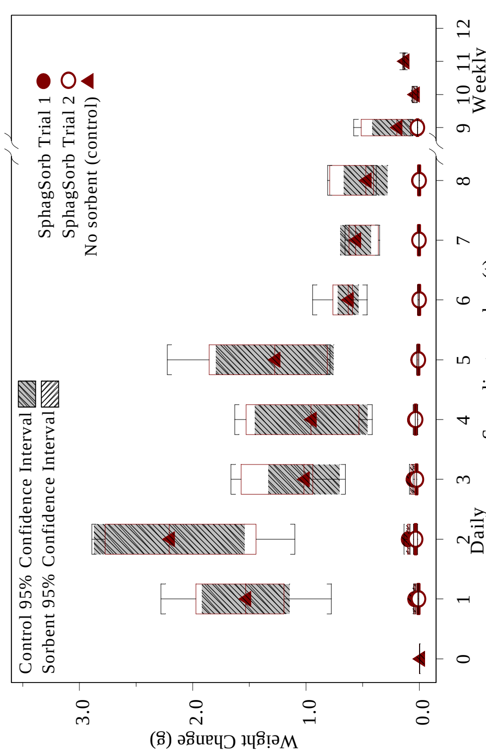

Fig. 7 c. 2009 trials of Sphag Sorb sorbent for water and feather.

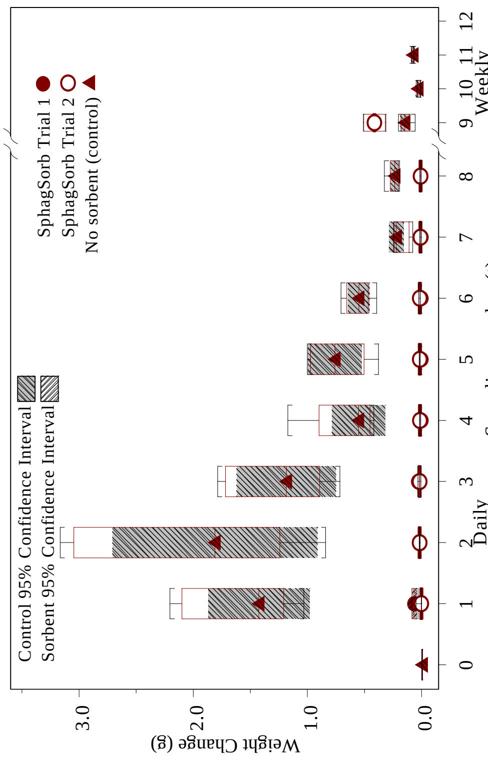

Fig. 7 d. 2009 trials of Sphag Sorb sorbent for water and fur.

feathers and fur wipers by destroying the hydrophobicity and rapidly permeating the wiper with oil. This total saturation is also evident in the water WC values which are in multiple grams, unlike the tenths of grams for WC of pickleweed wipers.

3.2.3 All sorbent types: In the box-whisker plots of water feather and fur wipers WC (Figures 8 a and 9 a) where all sorbent types were very effective in absorbing oil from the water surface and preventing oil adsorption by the wipers, with the exception of Stardust mineral sorbent. The wipers came away wet, but not oily, even though the wipers were brushed through the oily sorbent patches on the water. The wet wipers were dried before re-weighing. One of the two mineral products was effective, but other mineral sorbent extended the confidence limit for the mineral type, thus reducing the difference from the control.

3.2.4 Peat sorbents: Sphag Sorb and Cansorb peat moss were also nearly identical in the water trials, and absolutely effective in absorbing and aggregating the oil from the surface (Figures 8 b and 9 b). For both feathers and fur, the low WC was similar, though significantly different, to the pre-treatment (t00) within the critical first week. There was one exceptional fur sample on t04 (Figures 9 b.).

In the 2007 trial on water, WC values for Sphag Sorb for the first two days (t01 and t02) were as effective. There were only two water measurements with sorbents during this trial due to laboratory sampling collected nearly all sorbent and oil from the surface. The remaining surface was only clear water, as it was in 2009. In Figure 7 c., the WC values for both wipers were pooled, and show the variation in Sphag Sorb WC was insignificant between trials for 2009.

3.2.5 Cellulose sorbents: The five evaluated cellulose products for water included two additional sorbents with large particle size that had physically inhibited absorbing oil from the pickleweed surfaces. For both feather and fur wipers, Oil Gator, Kenaf, and Dri-Sorb cellulose products from agricultural residues were nearly equally effective in absorbing oil (Figures 8 c. and 9 c.), although significantly different from one another. The oiled surface was cleaned of oil so that there was no visible difference from the pre-treatment (t00) wipers; however we measured a significant difference in the WC values. In the recycled cellulose materials, CheetahSorb was as effective, and nearly equal the agricultural celluloses and pre-treatment (t00) WC samples. However, the otherrecycled cellulose NatureSorb did not adsorb the oil as cleanly as the other cellulose sorbent. It was significantly different with half or less the amount of oil on the wipers from the control water tank (Fig. 8 c and 9 c).

3.2.6 Mineral sorbents: The two mineral products are distinctly different. In water, the Pozzolan is nearly the same WC as the pre-treatment (t00) and other sorbent WC measurements for both feathers and fur (Fig. 8 d. and 9 d.). Where the Pozzolan dusted oil on the surface, the oil was absorbed and bound so the wipers which rinsed cleanly in the water. Where Pozzolan was not intercepted by oil on the surface, it immediately precipitated to the

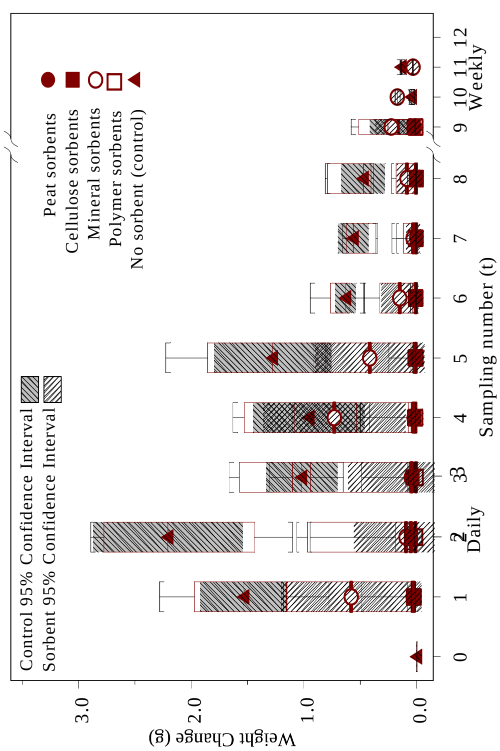

Fig. 8 a. Water, feathers, all sorbents, and control.

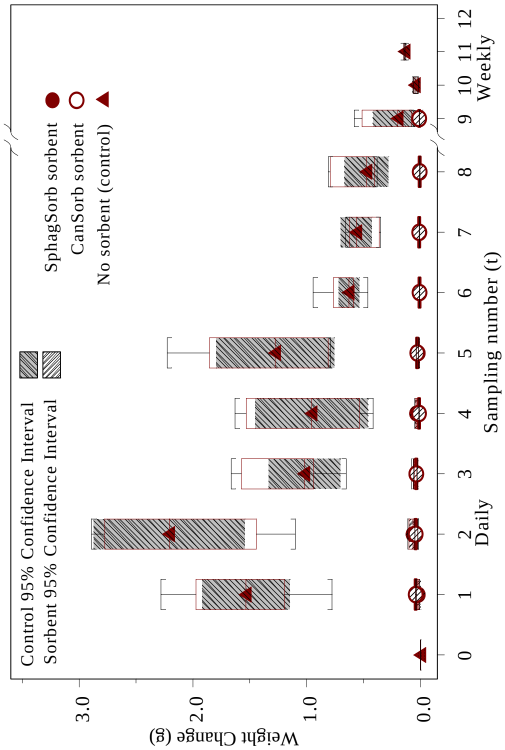

Fig. 8 b. Water, feathers, peat moss, and control.

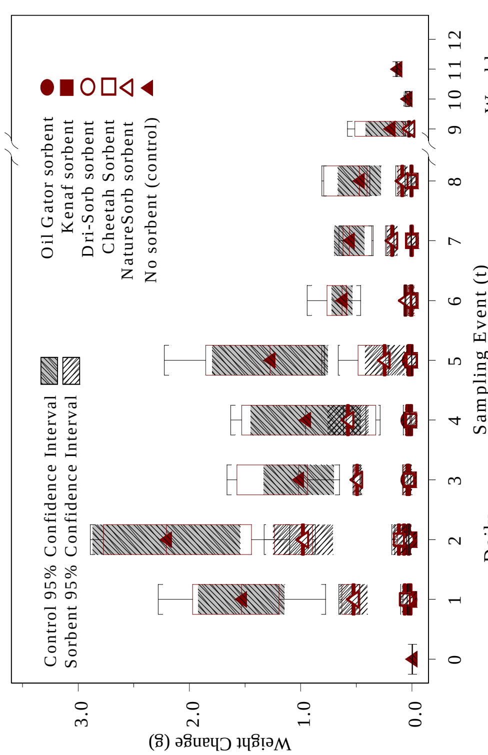

Fig. 8 c. Water, feathers, cellulose sorbents, and control.

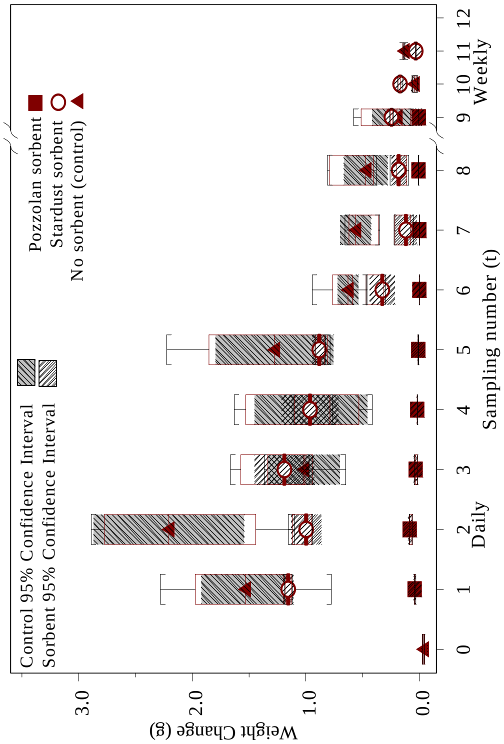

Fig. 8 d. Water, feathers, mineral products, and control.

bottom of the tank, as did the oil-mineral mixture within a few days. With Stardust, there is no significant difference from the control except for the second sample (t02) with feathers (Fig. 8 d) and with fur which had greater WC than the control in the first samples (Fig. 9 d). It absorbed oil poorly, and most sank to the bottom.

3.2.7 Polymer sorbents: The one plastic polymer HiSorb were 4mm (1/6 in) by 4 mm (1/6 in) size tubular pellets and could be evaluated only in water. It was similar in effectiveness to the peat moss, cellulose, and Pozzolan. For comparison with other sorbents, it is charted with the "best of" sorbents for the water trials (see Fig. 10 c). After spreading HiSorb on less than half of the oily surface, it remained floating. HiSorb moved easily around the water surface with air movement, absorbing surrounding oil, and cleaning the entire surface. As with the peat moss and others, the wipers did not draw oil off the sorbent, and were rinsed in the clear water.

4.0 DISCUSSION

4.1 Sampling Design

From the 2007 trial we determined the number of repeated wipers necessary to infer a significant difference between treatments. The mean difference for feather wiper WC in that two-tail test was 0.068 g between treatments immediately after application (t01). The calculated sample size for the necessary power to separate treatments suggested that even two wipers would provide the required level of significance. However, if the difference between sorbent WC is half as much, 0.037 g, five wipers are required. The design for this 2009 trial used the greater number of replicated wipers for each sample, anticipating a smaller difference among the several sorbents. The greater number of replicates also allowed discarding 1 or 2 outliers due to method imprecision.

The differences seen in the mean and variance for WC among Sphag Sorb treatments for the three trials during 2007 and 2009 support continuing the practice of including a "reference" sorbent in all trials. From this information we can attribute some variability among sorbent means was due to factors other than the effectiveness of the sorbents, such as oil evaporation rates, wiping skills, and other measurement errors.

4.2 Loss of Stickiness with Time

The data collected daily within the first week demonstrated this is a critical measurement period due to the rapid loss of volatile components and increasing oil density towards less sticky tar. The statistical graphic for both untreated substrates exhibit this declining rate of stickiness. Also apparent in measurements of the control treatments, if left untreated the oil on vegetation and water evaporated all volatiles to the tar constituents, and the oil did not stick to the wipers. In Davis, the high summer temperature and dry air ensure this happened quickly. The average daily high temperature during the first week of each 2009 trial was 31 and 32 ºC (88 and 90 ºF), respectively, for the July and September trials (CIMIS 2010). In comparison, the average daily high temperatures at Point San Pedro, California, on the San Francisco Bay during the same periods were 25 and 26 ºC (77 and 79 ºF) (CIMIS 2010). The differences in temperature and humidity between the inland valley and bay will

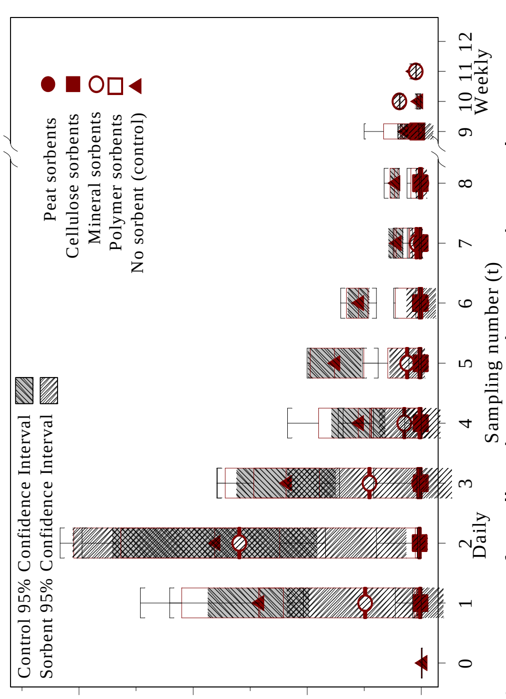

Fig. 9 a. Water, fur, all sorbent products, and control.

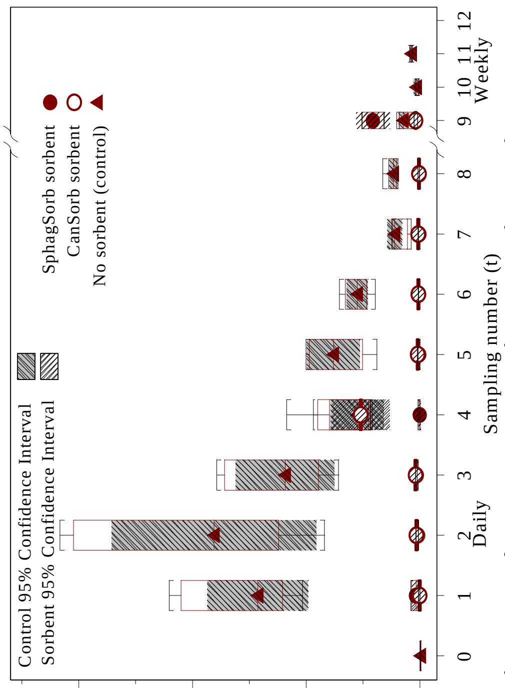

Fig. 9 b. Water, fur, peat moss sorbents, and control.

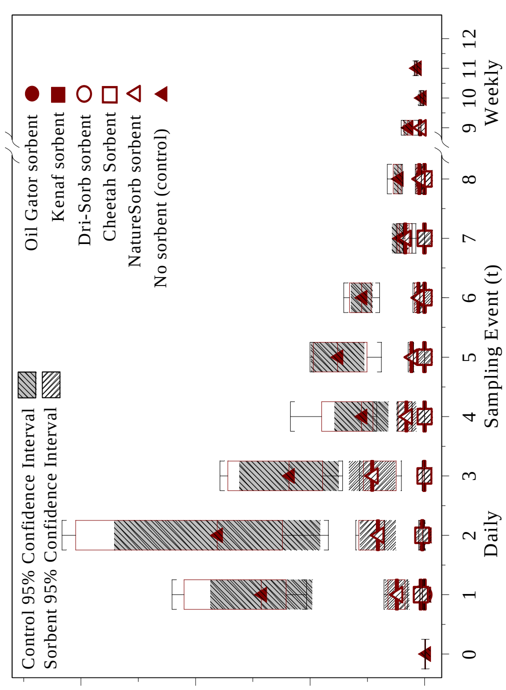

Fig. 9 c. Water, fur, cellulose sorbents, and control.

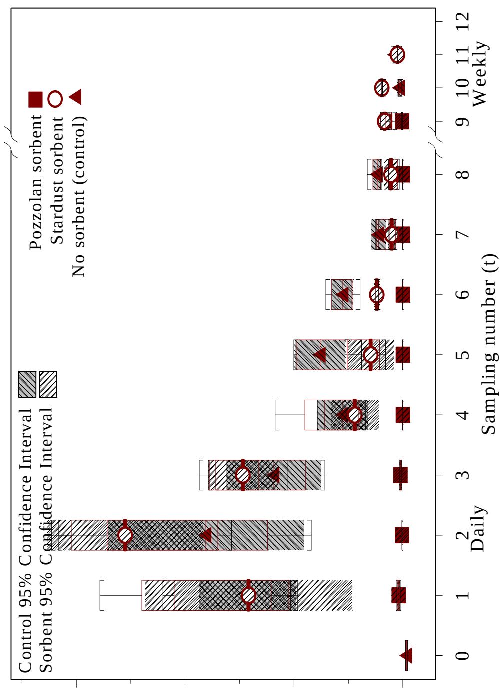

Fig. 9 d. Water, fur, mineral sorbents, and control.

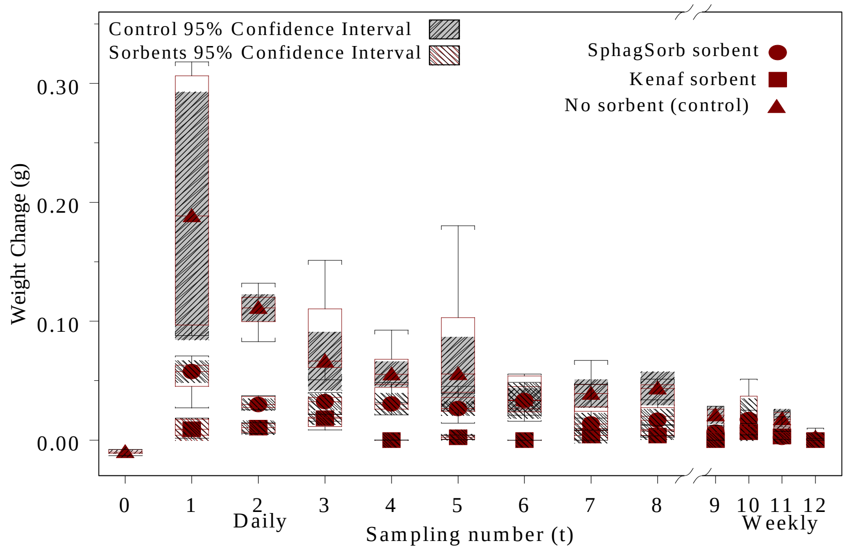

Fig. 10 a. Pickleweed and feather wipers and sorbents significantly different from control and lowest WC within their types.

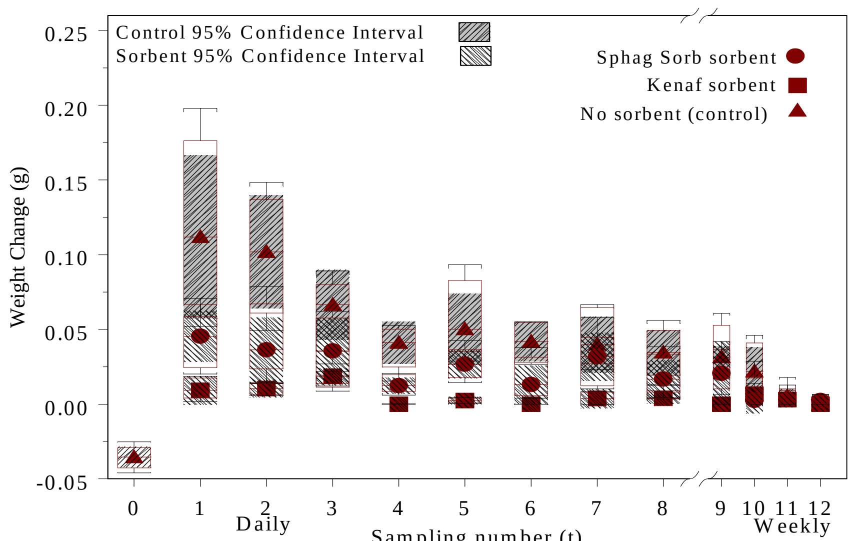

Fig. 10 b. Pickleweed and fur wipers and sorbents significantly different from control and lowest WC within their types.

have a significant effect on the rate volatilization, and length of time the birds and mammals are exposed to contamination.

4.3 Addressing Study Hypotheses.

4.3.1 Hypothesis: a) Applying a particulate sorbent material to petroleum-contaminated marsh vegetation and water will immediately render it less sticky to fur and feathers.

In this study some of the various peat moss, cellulose, and mineral sorbents evaluated with both pickleweed vegetation and on water surfaces were effective in completely eliminating oil sticking to feather and fur wipers, while other sorbents were only partially effective. The sorbent with the lowest

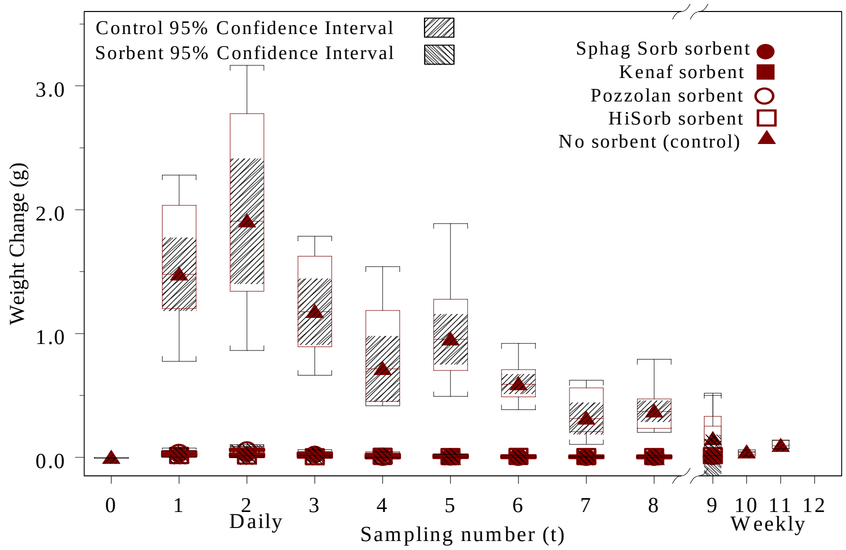

Fig. 10 c. Water, feathers and fur wipers, and sorbents significantly different from control and lowest WC within their types.

WC within each type of sorbent are shown in Figures 10 a and b for pickleweed and Figure 10 c for water. While the same sorbents were different in WC for feather and fur wipers in pickleweed, the best sorbents were in distinguishable in WC for the wipe types and shown in one plot.

b) The adherence of crude oil to wildlife feathers and fur can be evaluated by wiping with feathers and wool pads on oil treated vegetation and water surfaces.

As a further demonstration of the previous 2007 pilot study results, the feather and fur wiper method was sufficiently sensitive to separate effectiveness of sorbents in reducing adhesion of oil in water, and less so in the pickleweed. In the box-whisker plots above, the variation in the effectiveness among sorbents was evident by either significant separation of the means among sorbents or to the control WC. Elimination of oil sticking to animal feather and fur was determined for some sorbents while others only reduced the contamination in both pickleweed and water.

In pickleweed, the wide range and variance in control WC for t01 did reduce the ability to separate all but the most effective sorbents (agricultural cellulose products) from the control WC, and only one sorbent Kenaf was successful in eliminating the oil adherence to both wiper types. For the water substrate, we observed uncontaminated wiper samples returned after rinsing in the water cleansed by sorbents. This cleaning was seen later in the low WC for the wipers. The sensitivity of the method is also demonstrated where agricultural cellulose WC separates from recycled cellulose products, and where the Pozzolan mineral is distinctly superior to Stardust mineral product (Fig. 9 c and d).

c) Different particulate sorbents likely vary in their effectiveness to absorb spilled oil on marsh vegetation and water, and in the ability to reduce the adherence of oil to feathers and fur.

The project is summarized in Table 2 a and b by grouping means for WC within the 95 % confidence limits for the measurements over the first four days. For pickleweed in Table 2 a, some organic sorbents were significantly better compared to mineral products. For oil directly on pickleweed, the consistently best sorbents are Kenaf and Dri-Zorb.

In the 2007 study, there was no sorbent for comparison to Sphag Sorb and it appeared highly effective and still is, although for all the organics the amount of WC was 1/5 to 1/2 of that for the control with feathers, and 1/10 to 1/2 the control with fur. Distinguishing mineral sorbents from the control was more difficult, in part due to the density of the products, though observed effectiveness supported the higher stickiness measured.

In Table 2 b summarizes the effectiveness of sorbents in reducing adherence of the oil and sorbent in the water. While all sorbents are significantly different from the control, the variation among the sorbent mean WC over the four days spans an order of magnitude. With exception of NaturSorb and Stardust, all sorbents are similar in low WC. Of these, Kenaf and HiSorb are the lowest WC. Some materials sunk readily to the bottom without absorbing oil, such as Cheetah Sorbent and Stardust, and as such were not efficient.

Table 2. Significant groupings of sorbents by wiper mean weight change (g) for first four days,

a) on pickleweed

Sorbents	Feather		Fur	
Pretreat, no oil	0.0019	a	-0.0362	a
Kenaf	0.0193	b	0.0095	b
Dri-Zorb	0.0240	b	0.0043	b
Sphag Sorb	0.0372	c	0.0339	c
Cansorb	0.0413	c	0.0448	c
Oil Gator	0.0611	d	0.0585	c d
NatureSorb	0.0666	d e	0.0357	c
Stardust	0.0721	d e	0.0957	d e
Pozzolan	0.0969	e	0.1020	e
Control	0.1119	e	0.0841	d e

b) on water.

Sorbents	Feather		Fur	
Pretreat, no oil	-0.0026	a	-0.0048	a
Kenaf	0.0160	b	0.0026	b
HiSorb	0.0114	b	0.0102	c
Dri-Zorb	0.0281	c	0.0069	b c
Sphag Sorb	0.0437	d	0.0211	c
Pozzolan	0.0442	d	0.0178	c
Cansorb	0.0328	c d	0.1763	d
Oil Gator	0.0527	d	0.0064	b c
Cheetah-Sorb	0.0537	d	0.0183	c
Nature-Sorb	0.6365	e	0.3204	d
Stardust	1.0763	f	1.5455	e
Control	1.4699	g	1.4019	e

5.0 CONCLUSIONS

This method of determining oil stickiness using weight change of wipers found that binding oil with sorbents may reduce the amount or eliminate the oil clinging to the animal, and suggests the amount ingested by bird or mammal with preening will be reduced, as well as subsequent toxic poisoning. For the effective sorbents, the oil strongly bound to the sorbents and would facilitate cleaning both the substrates and animals.

Early in trial, the water substrate demonstrated that oil and water readily saturated the wipers due when fresh oil eliminated the hydrophobicity of feather and fur. These observations validate the use of feather and fur wipers to simulate water fowl and mammals caught in an oil spill and their rapid encasement in oil.

Although the effective sorbents bound most of the oil off the substrates, some oily sorbent stuck to the wipers. We found some or all oily sorbent was removed after shaking the wipers from pickleweed and rinsing wipers in water cleared by the sorbents. Our technique of wiping the pickleweed and water substrates with feather and fur forced the transfer of as much oily sorbent onto the wipers as possible. In the water substrate, full contact was made with the wipers on the oily sorbent surface and would have easily saturated with oil (as seen in the control samples) had sorbents not bound the oil. Significantly lower WC for sorbent treatments compared to those of the control was due to less oily sorbent adhering to the wipers and suggests that the sorbents would be effective in reducing the amount of oil clinging to the animal, and possibly being ingested by the animal during preening. However, other factors regarding the interaction of the oil residues, sorbent types, interaction with animal digestive tracks and other bodily process were not part of our investigation.

Vegetation contaminated with fresh oil could be saved by sorbent application. During the 2007 trial, the oil absorbed by Sphag Sorb on pickleweed remained on the plant until a rainfall event in the second week rinsed the plants clean of sorbent and oil. These plants were not damaged by PBC. Without a rinsing event in the 2009 trial, plants did not fair as well, and many died back.

Also in the water substrate, the organic and mineral materials varied in the amount required, and amount that remained on the surface. Dusty and low density peat moss and most agricultural cellulose products stayed on the surface where it would be possible to net the residues. Peat moss and Kenaf were hydrophobic, and rapidly absorbed oil into "islands" of oil. These organic materials did slowly lose some but not all hydrophobicity to hang at different levels in the water column after the first week. After two months, the organics did eventually sink to the bottom in still water. The recycled cellulose materials generally sunk due to the high density of the particulates. The minerals generally sunk rapidly as well, if not in contact with oil immediately. The mineral Pozzolan absorbed the oil rapidly as it hit the surface, but it also rapidly absorbed water. The polymer HiSorb remained floating on the surfaced the entire trial, absorbing all the surface oil. These pellets may be less likely to be ingested by fish and other organisms. While mineral and plastic medium may be less appetizing to fish than organic matter, all of these oily sorbents may contaminate the bay or sea floor. This raises the need for further research into the toxicity of oil once combined with the sorbent media and the availability or appeal to recently hatched fry, mollusks, and other organisms within the water column and sea floor. In addition, further research is needed into the rate of chemical and toxicity degradation of the oily sorbent in emergent vegetation substrates. Our 2007 and 2009 studies did not address ecological impacts of oil weathering or toxicity.

Fig. 11. Peat moss sorbent applied to wood plank after contaminated with oil spill tar. Rubbed with finger to exposed unabsorbed tar.

Issues regarding the timing and method of application for each sorbent require investigation. Our trials demonstrated the application of sorbents were effective for only fresh oil on vegetation and water, and applying the sorbent later following the spill will likely result in different measures of effectiveness. Evaluation of methods of dusting the surfaces and then collecting the oily sorbent with booms and other screening traps is needed to efficiently arrest the spread of oil. However, the vast differences between our tank studies and the open bay and ocean waterways amplifies the mechanical difficulties of delivery caused by rough water and wind, and then screening the immense volume of oily sorbent. As observed in the pickleweed marsh near Richmond, California, following the *Cosco Busan* oil spill in 2007, if applied too late the sorbents are ineffective. Floating globs of oil-tar had adhered to rocks and other solid surfaces before the U.S. Coast Guard contractor applied a peat moss product on the marsh. Once the tar contamination was attached, the peat moss particulate did not absorb the petroleum (Fig. 11.). Had the particulate been applied to the water shortly after the spill, the oily peat moss may not have stuck to any surface.

6.0 ACKNOWLEDGEMENTS

We would like to thank Don Cuffel, Valero Refining Company; Jack Yanitski, Earth Care Products (Sphag Sorb); Ron Bertram, Western Pozzolan (Pozzolan); and John Hanson, Dyneon LLC, 3M Company (HiSorb) for their contributions of oil and sorbent. We would also gratefully acknowledge the support of UCD Plant Science Department, Lead Greenhouse Manager Garry Pearson and staff, and our student interns Emily Hom, Anna Lue, Gabriel Chu, and Harry Lum.

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8.0 APPENDIX
Sorbent Descriptions and MSDS

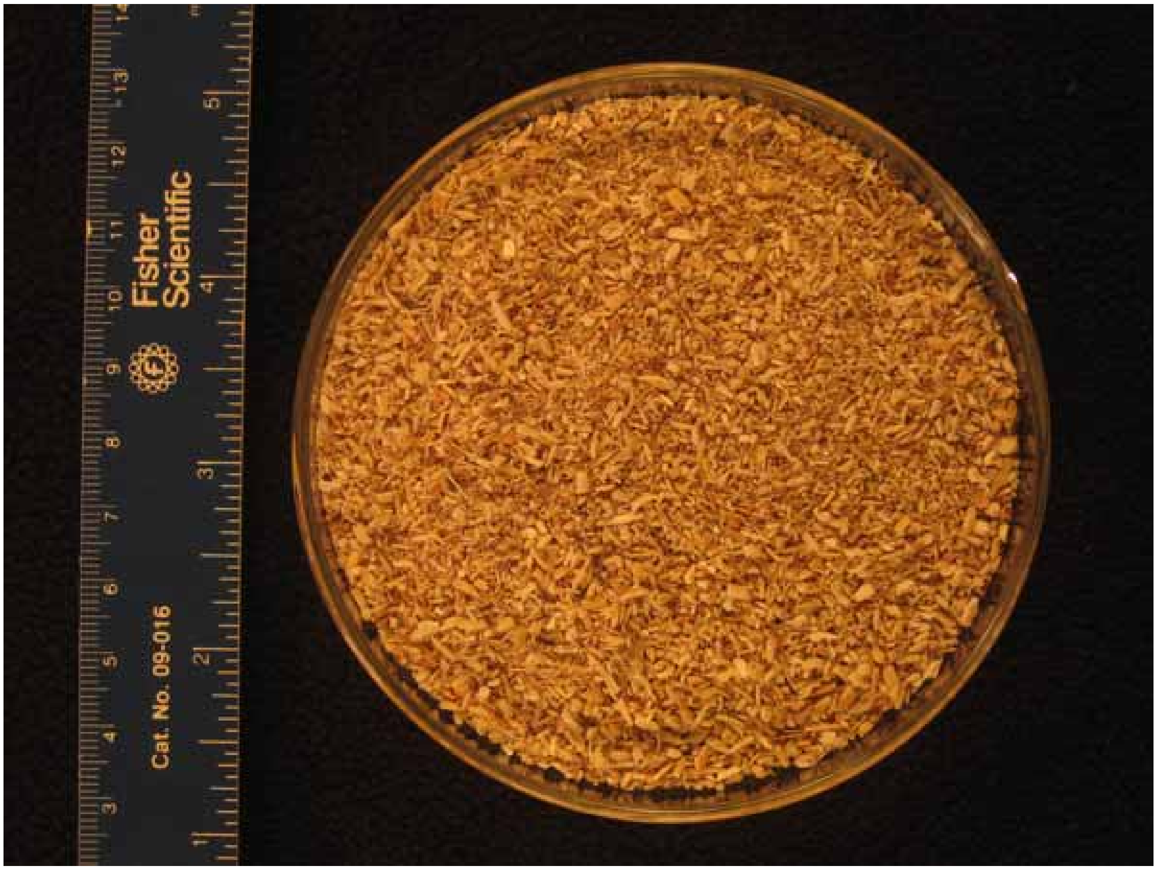
a) SPHAG SORB
Earth Care Products, Edmonton, Alberta, Canada

Photograph of dry Sphag Sorb sample.
Description: Short fibrous and dust of sphagnum peat moss material.

b) Cansorb
Annapolis Valley Peat Moss Co. Ltd. Nova Scotia, Canada

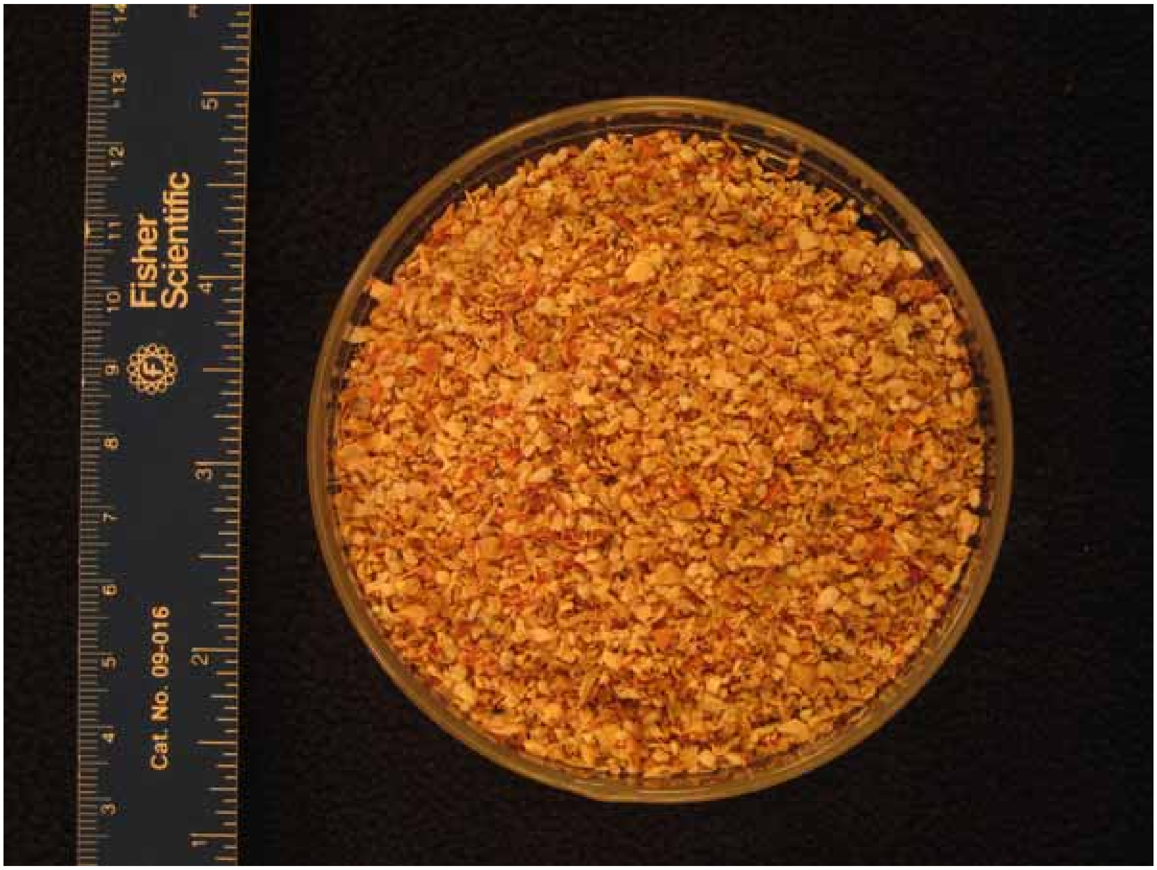
Photograph of dry Cansob sample.
Description: Short fibrous and dust of sphagnum peat moss material.

c) Kenaf Organic Absorbent
Kengro Corp., Charleston, MS



Photograph of dry Kenaf sample.
Description: some ground grain-like material and dust of kenaf plant are still identifiable.

d) Dri-Zorb
The Andersons, Inc., Maumee OH



Photograph of dry Dri-Zorb sample.
Description: ground material and dust of corn cob plant are still identifiable.

e) Oil Gator
Product Services Co., Jackson, MS

Photograph of dry Oil Gator sample.
Description: dust of cotton residues and partially ground material are still identifiable in bag.

f) CheetahSorb
CEP, Houston, TX

Photograph of dry CheetahSorb sample.
Description: chunky, dry, shredded paper product and partially still identifiable material.

g) NatureSorb
Ram Energy Limited, Sunderland, UK

Photograph of dry NatureSorb sample.
Description: dry, ground, fibrous, recycled cellulose material.

h) Pozzolan
Western Pozzolan Corp., Doyle, CA

Photograph of dry Pozzolan sample.
Description: powder dry, ground, diatomaceous mineral.

i) Stardust Super Absorbent
Paradigm International, Inc., Santa Ana, CA

Photograph of dry Stardust sample.
Description: powder dry, ground, pumice mineral.

j) HiSorb 1151
Dyneon LLC (3M), Oakdale, MN

Photograph of dry HiSorb sample.
Description: extruded, pellet, dry, plastic material.