CSTARS Center for Spatial Technologies and Remote Sensing

The Benefits, Particularly to Furred and Feathered Wildlife, of the Use of Biodegradable, Particulate Sorbent in Spill Response

The University of California, Davis

Executive Summary

The Benefits, Particularly to Furred and Feathered Wildlife, of the Use of Biodegradable, Particulate Sorbent in Spill Response

This study evaluated one particulate sorbent product made of peat moss for its ability to sorb, i.e., adsorb and/or absorb, crude and diesel oils and reduce the immediate and longer term potential of oiling feather and fur bearing animals, and minimize contamination of shore vegetation. This investigation successfully proved two hypotheses. A) Applying a biodegradable particulate sorbent (peat dust) to petroleum-contaminated marsh vegetation, sand, or fresh water did immediately render the petroleum less sticky to fur and feathers. B) Petroleum products composed of chemicals of different molecular weights, e.g., crude or diesel #2 oils, did adhere differently to bird feathers and mammal fur.

Over a two month trial, the effectiveness of the treatment with sorbent and the rate of decreasing stickiness of Prudhoe Bay crude and Diesel Fuel #2 oils on substrates were investigated using natural and artificial wiper materials. The tested substrates of coastal environments were: 1) marsh vegetation *Salicornia virginica* (pickleweed), 2) sand, and 3) open fresh water. After separate oil applications, half of the substrate surfaces were left either untreated or treated with loose particulate Sphag Sorb peat moss (Earth Care Products, Edmonton, Alberta, Canada). As a feasibility study, four wiper materials were used to simulate bird and animal coats: a) goose feathers, b) lamb sheering pads, c) polypropylene cloth, and d) filter paper. The weight accumulation by the wipers was an indication of the oil stickiness; each wiper was weighed before and after wiping. The wiping began immediately after application and treatment, then daily for the first week, weekly for the remaining first month, and two monthly measurements.

At least one wiper type on each substrate demonstrated that Sphag Sorb peat material significantly reduced the stickiness of the crude oil. Although, the evaporation of oil reduced stickiness over time, there was significantly more crude oil only on the feathers from untreated pickleweed for the first four days. The other wipers on pickleweed showed no significant difference between treated and untreated. The fur wipers determined a significant reduction of stickiness in the treated crude oil on the sand. The water substrate showed the clearest distinction between the treated and untreated. All wipers came away from the treated water with virtually no weight accumulation after drying, while the oils in the untreated water instantly saturated the wipers.

Only feathers and fur wiper types were satisfactory by their strong oil absorption and water repelling characteristics. These wipers were also very effective in cleaning the small areas in the stem nodes of the pickleweed. In general, the polypropylene cloth and filter paper ineffectively absorbed oil and cleaned the pickleweed poorly. Filter paper had what appeared to be a constant rate of oil absorption, but was much too slow for practical measurement. The paper was also not durable after wetting.

Samples for petroleum chemical analyses were collected of the substrates on the second day, first weekly, and first monthly measurement dates. The Total Petroleum

Hydrocarbon concentrations from crude oil on pickleweed were less in the peat treatment. This concentration fell dramatically after the rains in the later weeks of the trial rinsed the peat from the weed. In the sand trial, higher concentrations of both oils in the peat indicate the material absorbed oil from the sand, and possibly reduced the rate of evaporation. For water, there was a low concentration of crude oil in peat material suspended below the surface; 200 times less oil than peat collected from the surface.

Weight accumulation by the wipers and oil concentration results were greatly impacted by the different molecular weight and volatility of test oils. The crude oil remained sticky for the first month, and held both oil and peat on the surfaces. In diesel contamination, there were greater weight accumulations for treated pickleweed due to peat holding oil and adhering to the wipers. The untreated diesel completely evaporated within the first week, leaving clean substrates.

The wiper and chemical sample data supports the visual observations. The effectiveness of the Sphag Sorb treatment was dramatic. On pickleweed, the treatment sufficiently reduced the uptake of crude oil to prevent killing the plants. The Prudhoe Bay crude smothered the untreated vegetation within the first month. In water, peat particulate absorbed all the oil on the water surface and prevented contamination of the wipers.

Susan L. Ustin, Professor, and Michael L. Whiting, Assistant Professional Research Scientist
Department of Land Air Water Resources, University of California, Davis

Scientific Study & Evaluation Program (SSEP) Contract: P0775005
OSPR Sponsor: Jack Ames, DFG, OSPR, MWVCRC, Santa Cruz CA

TABLE OF CONTENTS

1.0 INTRODUCTION

1.1 Application of Loose Particulate Sorbent Materials to Reduce Oil Spill Impacts on Wildlife.

This project evaluates a strategy for petroleum spill containment based on application of biodegradable absorbing material to reduce exposure to plants, animals, and soils. This project was a proof-of-concept for methods of measurement and effectiveness of the organic particulate sorbent. It did not address ecological impacts of oil weathering or toxicity. If the sorbents do reduce petroleum contamination impacts on wildlife, future efforts should evaluate chemical and toxicity changes during oil and peat degradation.

The spill environment was partitioned into three substrates for oil contamination and evaluation: vegetation, sand 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. A previous study by the principal investigator showed that *Salicornia* sp. is sensitive to different molecular weights of crude petroleum (Rosso et al., 2004). The sand is a common shore medium. Open water is probably the most critical substrate with greatest exposure of oil contamination to water birds, water mammals, fish, and other wildlife.

Rapid absorption/adsorption and containment are principal methods of reducing spill expansion and facilitating oil recovery. Application of loose particulate sorbents immediately after a spill may reduce the potential oiling of the feather and fur bearing wildlife, and inhibit damage to shore vegetation. An undated information letter from the sales staff described one case of applying Sphag Sorb, peat moss particulate material, on a Canadian pond surface as efficiently absorbing an oil spill (type of oil not described) and remaining for "natural microbes" to digest the hydrocarbons (Earth Care Products, Edmonton, Alberta, Canada). The contaminated portion of vegetation was removed after the winter freeze when the workers could get on the ice to harvest. Earth Care Products was unaware of any testing of the material on vegetation or its effectiveness in preventing oiling of wildlife (Personal communication, Jack Yanitski, Earth Care Products, Sphag Sorb Sales, September 14, 2007). Additional products and company information may be found at www.sphagsorb.com.

The Canada Environment Protection Service tested the toxicity of a peat moss product from Sphag Sorb International Sales with Rainbow trout acute lethality tests in aerated freshwater according to EPS 1/RM/9 (Environment Canada 1990). No fish died within the 96 hour test period. However, they did report that the pH of the freshwater was reduced below 5 after soaking for one hour (letter: Environment Protection Service, number 4808-13, Edmonton, Alberta, July 14, 1998). Sphag Sorb was also found to be within the acceptable percentile of non-toxic to the environment determined with the Red Abalone--Short-term Toxicity Test (letter: Laboratory & Analytical Business Services, Church Point, Louisiana, October 28, 1993). Sphag Sorb is 91.7 % efficient in absorbing crude oil. Some loss of peat in this evaluation may have been due to dissolution of the material in the oil and solvents (report: Northwest Labs, Edmonton Alberta, Canada, December 12, 2004). In May 2005, State of California, Department of Fish and Game, Office of Spill Prevention and Response issued a license for Sphag Sorb as an oil spill cleanup agent, determined to be a Collecting Agent.

1.2 Study Hypotheses and Objectives

This study addresses Department of Fish and Game, Oil Spill Prevention and Recovery (OSPR) Scientific Study and Evaluation Program (SSEP) intent for research 1.b: effects of oil on fish, wildlife, habitat, and water quality.

A) Applying a biodegradable particulate sorbent (peat dust) to petroleum-contaminated marsh vegetation, sand, or fresh water will immediately render it less sticky to fur and feathers.

B) Petroleum products composed of chemicals of different molecular weights (e.g., crude or diesel #2) have different adherence to bird and mammal feathers and fur.

2.0 METHODS

To determine the effectiveness of Sphag Sorb in reducing oil stickiness, the environmental substrates were sprayed with two grades of oil and half of the contaminated substrates were treated with the peat particulate. Both the treated and untreated substrates were then wiped with feathers, fur and polypropylene patches, and filter paper. The differences in weight accumulated (WA) by the wipers between the treatments determined the change in oil stickiness. Two distinctly different petroleum molecular weight oils were used: Prudhoe Bay crude (PBC) and diesel fuel oil #2 (diesel). Open tanks used to hold the substrates were maintained outside a greenhouse facility at UC Davis to provide open air evaporation of the oil and realistic weather conditions for the two month trial period. The vegetated tanks were aerated and sub-irrigated to maintain plant health and water levels throughout the trial period.

2.1 Substrate Tanks and Plant Growth

The first week of July 2007, existing sheet metal tanks, approximately 3 m by 0.6 m (10 ft by 2 ft), were lined with heavy black plastic for growing pickleweed and holding sand and fresh water substrates. The vegetation tanks were fitted with an aeration system of drip-emitter hose along the tank bottom. Optimum water level for vegetated tanks was controlled by float valves (Fig. 1 through 3). 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.

August 8, 2007, 500 plants from 5 cm (2 in) pots purchased from North Coast Native Plant Nursery (Petaluma, California) were transplanted onto the moist Perlite base. Additional Perlite was packed around the plant root balls, and water level was increased to the top of Perlite base. Within two weeks the plants were between 10 to 15 cm tall (Fig. 4). By the third week of September, the pickleweed was fully grown (Fig. 5). Shading half of the tanks by an adjacent lath house stunted half the plants, and this mistake created a low and high density canopy for the trial. The tanks were moved away from the lath house to full sun in mid-September. The stunted plants continued to grow, but did not reach the size of the full-sun plants. The tanks were sub-divided and received the same oil and Sphag Sorb treatments. The low and high canopy densities were sampled separately for inclusion in the trial statistical analyses.

Fig. 1. Plant tanks with aerator tube held in-place with plastic bags of sand before adding Perlite.

Fig. 2. Close-up of aerators and sand bags before adding Perlite growth medium.

Fig. 3. Submersible pump in well, and float-shutoff for water height control before adding Perlite.

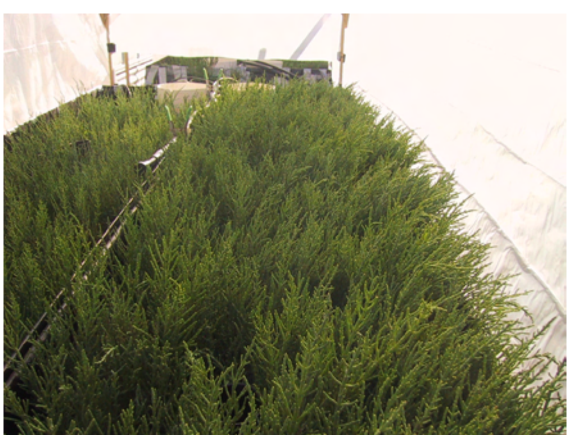

Fig. 4. Pickleweed 2 weeks after transplanting (8/16/07).

Fig. 5. Pickleweed 7 weeks after transplanting (9/21/07). Low and high density canopy on left and right, respectively, of center tank edges.

Our experience in growing *Salicornia* sp. found that commercially available aquarium sea water salt mixture provides the most consistent and easiest to use method (Pearcy and Ustin 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. Evaporated water was replenished by the float valve controlled additions to maintain constant tank volume. Sea water salinity ranges from 34.6 to 34.8 parts per thousand (grams of salt per kilogram of water). The Perlite was saturated with 14.0 to 20.5 ppt, a 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. The plants were fertilized through out the growing period by draining all but approximately 2 cm from the bottom of the tank into a separate tank, adding the salt and dissolvable fertilizer, then returning the water. The dissolvable fertilizer (15-30-15) was added to maintain the nitrate (NO_3) level between 400 to 600 ppm (after dilution for measurement using color cube colorimetry in the Hach Saltwater Master Test Kit #2068600, www.hach.com).

2.2 Substrate Treatments and Sampling

On October 2, the substrates were uniformly coated with either PBC or diesel oil using a garden pump sprayer to the drip point on the vegetation, to surface saturation in the sand, and to a thickness of approximately ½ mm (0.02 in) on the water. Approximately, 3.5 liters of each oil type was sprayed over the 7.25 m^2 of tanks. One half of the tanks with each oil application were treated with Sphag Sorb sorbent using a kitchen sieve to dust the surface, as seen in Fig. 6 through 11. The peat application was within the manufacturer's recommendations of 0.009 m^3 (1/3 ft^3) of Sphag Sorb for 3.8 to 7.6 liters (1 to 2 gallons) of oil. The other half was left untreated. The same amount of Sphag Sorb was used in each tank, sufficient to cover the pickleweed deep within the high density canopy. The substrates were coated with oil and dusted with peat material as uniformly as possible, although wind micro currents created slightly irregular oil spray and dust patterns.

Fig. 6. Immediately after applying crude oil to pickleweed (10/2/07), treated with SphagSorb (left) and untreated (right).

Fig. 7. Immediately after applying diesel oil to pickleweed (10/2/07), treated with SphagSorb (left) and untreated (right).

Fig. 8. Immediately after applying crude oil to the sand (10/2/07), treated with SphagSorb (left) and untreated (right).

Fig. 9. Immediately after applying diesel oil to the sand (10/2/07), treated with SphagSorb (left) and untreated (right).

Fig. 10. Immediately after applying crude oil to the water (10/2/07), treated with SphagSorb (left) and untreated (right).

Fig. 11. Immediately after applying diesel oil to the water (10/2/07), treated with SphagSorb (left) and untreated (right).

To overcome any bias in sorbent application and sampling, plants or areas of sand and 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. The measurement of oil stickiness depended on the weight accumulation (WA) of the wiper before and after cleaning the substrate. Four wiper materials were tested: 1) goose feathers, 7.5 cm (3 in) long bunches similar in appearance to deep-sea fishing jigs; 2) sheepskin sheering pad (0.6 cm pile, 3.8 cm squares (1/4 in, 1-1/2 in); 3) polypropylene cloth (½ mm nap, 3.8 cm squares (0.02 in, 1-1/2 in), as a fur mimic; and 4) Whatman #1 round filter papers (70 mm). The wipers were prepared in individually labeled resealable sandwich bags and weighed. After wiping the substrate surfaces until no additional oil or peat would attach, the wiper was returned to the plastic bag, dried if necessary, and re-weighed. The sampling sequence for a tank started with one wiper of each type before the sequence was repeated; five wipers of each type were used. The wet wiper materials and plants samples were dried for more than two weeks at low heat in a shed used for drying grain and plant samples.

One day before the oil application, all substrates were wiped to estimate the error in measurement (t00). The substrates were again wiped to test oil adherence immediately after application on day 1(t01); then on days 2 (t02), 3 (t03), 4 (t04), 5 (t05), 6 (t06), 7 (t07), 14 (t08), 21 (t09), 28 (t10), 35 (t11), and 62 (t12). The wiping continued until the WA approached the error of measurement level on t00, or in the case of water, the chemical sampling removed nearly all the oil and peat.

The oil and peat treatments were applied to 12 tanks (3 substrates by 2 oils by 2 treatments). Five wipers of each material made the observations within the sample of each tank for the day. The number of samples varied among trials, PBC on pickleweed continued to the maximum sampling duration on t12 and used 250 wipers of each type. In the pickleweed, the odd numbered wipers were used on the full-sun tanks, and even numbered wipers were used on the shaded plants for determining the impact of canopy density.

S-Plus statistical software (ver. 6.2, Insightful Corp., Seattle, WA) was used for analysis of variance (ANOVA) and regression modeling of the wiper observations over time.

2.3 Substrate Chemical Sampling and Analysis

2.3.1 Sample collection: In addition to the oil adherence trial, chemical samples of the substrates, oil, and peat were collected for analyses by OSPR Petroleum Chemistry Laboratory. Their volunteer efforts produced some preliminary estimates of Total Petroleum Hydrocarbon content and compositional change. The substrates were sampled for oil content and/or peat on four dates: pre-trial background (10/1/07), 24-hours after oil and treatment (10/3/07), one week later (10/10/07), and one month later (11/06/07). Whole treated and untreated pickleweed plants were harvested to fill 240 ml (1 cup) jars. Of the sand trial, approximately 120 ml were collected from the first centimeter (0.4 in) of the untreated surface or Sphag Sorb. The open water was sampled both at the surface and within the water column by filling one liter jars. The surface was skimmed with the lower lip of the jar to collect as much of the oil and/or peat and as little of the water as possible. The subsurface was sampled by partially removing the lid under the surface to slowly fill the jar while moving it around the tank.

2.3.2 Sample preparation and chemical analysis: Approximately 30 g sub-samples were split from each pickleweed and sand sample, and entire 1 l water samples were used for analysis. Ortho-terphenyl was added to each sample prior to extraction as a surrogate standard following EPA Method 3550, modified guidelines. These pickleweed and sand sub-samples and water samples were extracted three times with 60 ml aliquots of methylene chloride. The aliquots were individually collected in evaporating flasks after passing through sodium sulfate to remove water. Each extract was concentrated by roto-evaporator to final concentrations of 1 ml per 10 g of pickleweed and sand, and 1 ml per 1 l of the water.

Total Petroleum Hydrocarbon analysis was performed on an Agilent 6890 gas chromatograph flame ionization detector (GC-FID) equipped with HP1 column 30 m x 0.32 mm x 0.25 µm film thickness, using EPA Method 8015A, modified. This method used injector temperature: 300 °C. Oven parameters were 50 °C for 2 min, ramped 10 °C per min to 270 °C, ramped of 20 °C per min to 320 °C, held for 3.5 min. The detector temperature was 325 °C. H_2 flow was 40 ml min^{-1}. Air flow was 450 ml min^{-1}, with constant N_2 makeup flow at 45 ml min^{-1}.

The reported values for Total Petroleum Hydrocarbons (TPH) were derived from a total methylene chloride extraction. Extracts were not filtered through silica to remove organic compounds. Standard concentrations used for both the Diesel #2 and Prudhoe Bay crude standard curves were prepared from the applied diesel and crude oil used in this study. The reported values are for Total Petroleum Hydrocarbons (TPH) expressed as Total Extractable Hydrocarbons (TEH).

3.0 RESULTS

3.1 Observations and Variation Within Substrates

3.1.1 Pickleweed substrate: Due to the variation in canopy density, all pickleweed tanks were physically divided to share the shaded and full-sun plants among the treatments (Fig. 5). At the end of the diesel oil on pickleweed trial (November 2, 2007), equal portions of treated and untreated plants from both plant density tanks were harvested from 0.3 m^2 (4 ft^2) areas and weighted after drying. The diesel oil without treatment had no apparent damage in the vegetation (Fig. 12); however, equal areas of both were included in the canopy samples. The biomass density in the low canopy was 807 g m^{-2} and high canopy was 1084 g m^{-2}. The shaded canopy was approximately 3/4 the biomass per area as the full-sun canopy. There was no effect of canopy density on the measurements, i.e., overall means and variance were nearly identical. ANOVA within each pickleweed trial showed no significant difference in WA between odd and even pickleweed wipers.

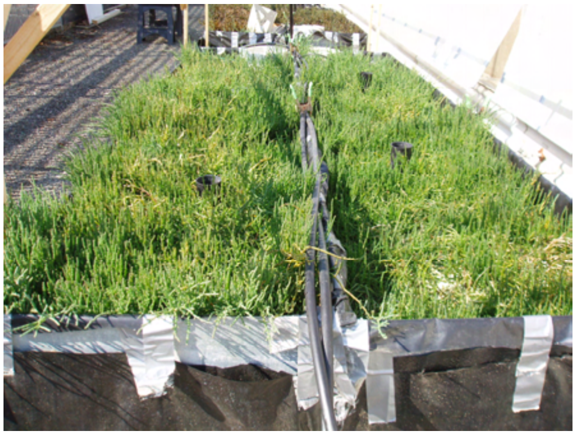

Fig. 12. Diesel oil damage to pickleweed after two weeks (8/16/07), untreated in foreground.

Fig. 13. Close-up of crude oil damage to pickleweed after two weeks (10/14/07), untreated in foreground.

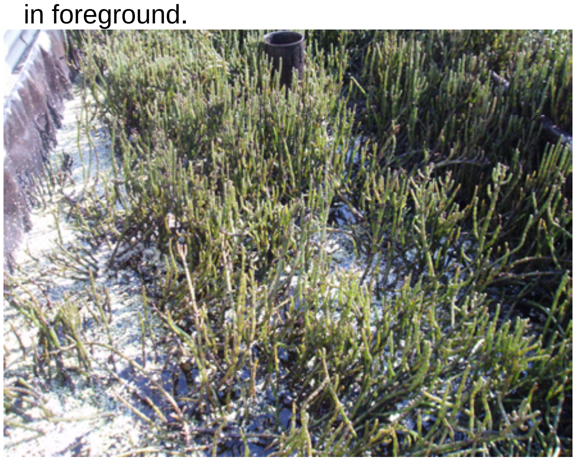

Fig. 14. Close-up of crude oil damage after two weeks (10/14/07) in treated low density pickleweed canopy.

Individual plants removed after wiping were dried and weighed to estimate the amount of biomass (including residual oil and peat) to determine the relationship of WA to the amount of wiped plant material. There was no correlation (r^2 = 0.0006) between biomass and WA of feather wipers, the most effective of the wiper types. Attempts to normalize feather WA by biomass added greater variance within samples, reducing the sensitivity of the measurements. The sampled plants were consistent in dry weight with a mean of 1.5 g in 232 samples (18 outliers removed) and 95 % confidence limits of 1.46 g to 1.68 g.

Sphag Sorb provided substantial protection to the vegetation from the PBC oil (Fig. 13 through 15). The peat material absorbed the oil and significantly reduced the damage, and die back. The plant succulent parts smothered by oil died over three weeks,

Fig. 15. Close-up of crude oil damage to pickleweed after four weeks (10/29/07) in foreground, treated plants in the back ground.

as evident by the branches outside the tank edge that were not sprayed with oil (Fig. 15). Towards the end of November, many of the basal stems re-sprouted slowly before the cooler weather in January and February completely stop growth. The diesel oil trial demonstrated little difference between treated and untreated. The diesel oil volatilized within a few days with no apparent damage to either the treated or untreated plants, and greater WA came from the peat clinging to the branches.

The rainfall impact from the first rain storms before t08 removed nearly all the peat/oil from the upper exposed canopy (October 9, 10, and 12, totals of 7.9, 11.2, and 8.9 mm (0.31, 0.44, and 0.35 in), respectively). An additional storm before t09 cleaned the remaining peat from the treated plants (October 16, total of 3.0 mm (0.12 in)). Rains that occurred before the t11, (October 29 through November 1) totaled 0.4 mm (0.2 in.), and before t12 (November 10 through 11) totaled 19.8 mm (0.8 in). The rainfall totals are from the California Irrigation Management Information System weather station (http://www.cimis.water.ca.gov, CIMIS #6, Davis) which was approximately ½ mile from the tanks.

3.1.2 Sand substrate: The sand trial was a poor test of the effectiveness of the peat and wipers. The sand absorbed the oil readily, and some of the oil was absorbed by the peat. The peat darkened in color by absorbing the oil from the sand, but the sand beneath remained oily, as seen in Fig. 8 and 9. Wipes of the surface PBC oil only slightly adhered to the wipers, with feather and fur being the most effective in collecting oil and peat. The diesel oil wipers were unaffected, except for a slight discoloration by peat and oil.

3.1.3 Water substrate: The water trial demonstrated the effectiveness of the peat immediately with application. The untreated oil surface instantly saturated all wipers with oil. In the peat treatment, Sphag Sorb absorbed the oil and eliminated free oil on the water, preventing oil absorption by the wipers. The wipes came away wet, but not oily. The trial was very short lived due to sampling for chemical analysis.

The first chemical sampling on t02 and volatilization removed nearly all the contaminant, and wiper sampling could not continue. The chemical sampling required filling the jars with as much oil and peat as possible. The second sampling at t07 eliminated the remnant surface oil and peat. The ease of retrieving the oily peat on the water surface with the sample jars indicated the effectiveness of the peat if spread immediately after a spill, then efficiently screening the water surface for the peat and oil contaminant.

The subsurface in the peat treated PBC tank was clear enough to be used to rinse the sampling jars of the peat debris. The peat that did not absorb oil saturated with water and over a short time sank to the bottom. In the diesel oil tanks, the oil absorption by the peat was more mixed. The peat with various contents of diesel oil sank below the surface and was collected with sampling. The remaining peat after sampling stayed suspended through most of October. The amount of oil in the subsurface was seen in the OSPR chemical analysis and is discussed below.

3.2 Evaluation of Sphag Sorb and Wiper Effectiveness

The following visual observations of the trials are in order by the four wiper types, and include references to photos in Fig. 16 through 22. Also, corresponding box plots of sample WA in Fig. 23 through 46 portray the ANOVA statistics for treated and untreated combinations of substrates, oils, and wiper types by sample date. In the plots, box dimensions represent the interquartile distance between the 25th to 75th percentiles of the WA values from each sample. Line hatching over the boxes indicates the range of the 95 % confidence limits, and where cross hatching occurs indicates an insignificant difference between treated and untreated. Within each sample of 5 wipes, only one outlier was removed, if necessary, based on the 1.5 times the interquartile distance (Devore & Peck 2001).

3.2.1 Feathers: The most effective wiper type was feather, although it was the most expensive wiper due to the hand crafting of each jig and the large number needed. The feather absorptive power and WA compared to the base weight made the wiper more effective than fur and far superior to cloth and paper. For vegetation, feathers were superior wipers by the fine, flexible main stem reaching between branches and at nodes where oil accumulated (Fig. 16). Oily peat and minerals from the sand shook off consistently from feathers with two hits on the tank side. Feathers were also far superior by instantaneously saturating with oil preferentially from water; the bane of all birds caught in an oil spill. The peat absorbed the oil on the water surface and the feathers came away clean, but wet from the water.

Fig. 16. Wiping technique for testing the oil stickiness, shown with crude oil on pickleweed.

Feather wipers were able to detect the decline in the difference between untreated and treated over time in pickleweed for both diesel and crude oil. In the box plots for feathers on pickleweed in Fig. 23 and 24, there is a significant difference between treated and untreated for the first four days, with one exception. For the fifth day and beyond there are no differences between treatments. In Fig. 47 and 48, WA is regressed with time of sample date to evaluate the rate of decline in stickiness. The standard errors within WA were used to calculate the 95 % confidence limits bounding the fitted linear least squares means. Early in the trial, the variation in amount of oil removed is apparent, and as the oil hardened with time, less oil and

Fig. 17. Feather after wiping crude oil on pickle weed, one week (10/8/07) after application, treated with SphagSorb (left) and untreated (right).

Fig. 18. Feather after wiping diesel oil on pickle weed, one week (10/8/07) after application, treated with SphagSorb (left) and untreated (right).

Fig. 19. Fur pad after wiping crude oil on pickle weed one week (10/8/07) after application, treated with SphagSorb (left) and untreated (right).

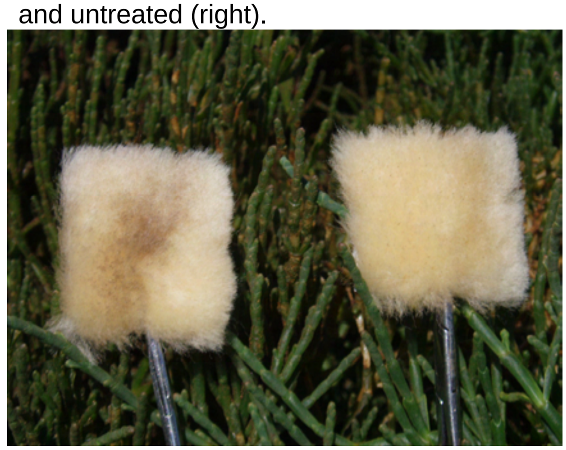

Fig. 20. Fur pad after wiping diesel oil on pickle weed one week (10/8/07) after application, treated with SphagSorb (left) and untreated (right).

Fig. 21. Polypropylene cloth after wiping crude oil on pickle weed one week (10/8/07) after application, treated with SphagSorb (left) and untreated (right).

Fig. 22. Polypropylene cloth after wiping diesel oil on pickle weed one week (10/8/07) after application, treated with SphagSorb (left) and untreated (right).

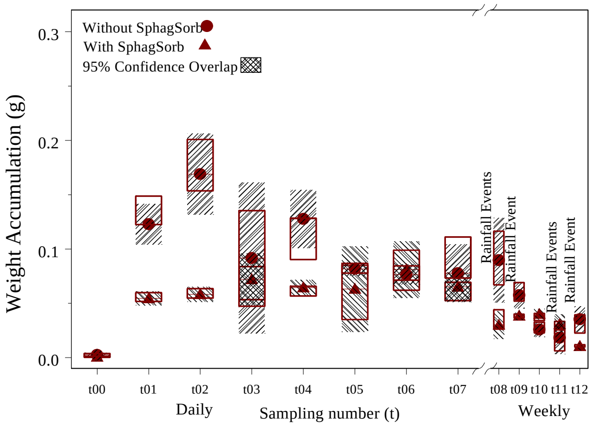

Fig. 23. Pickleweed, PBC, Feathers during two months.

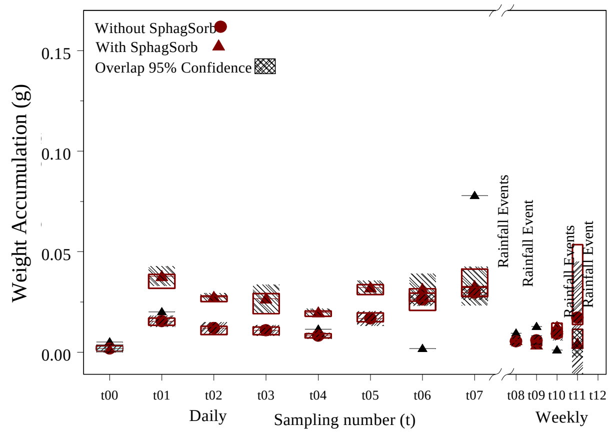

Fig. 24. Pickleweed, Diesel, Feathers during two months.

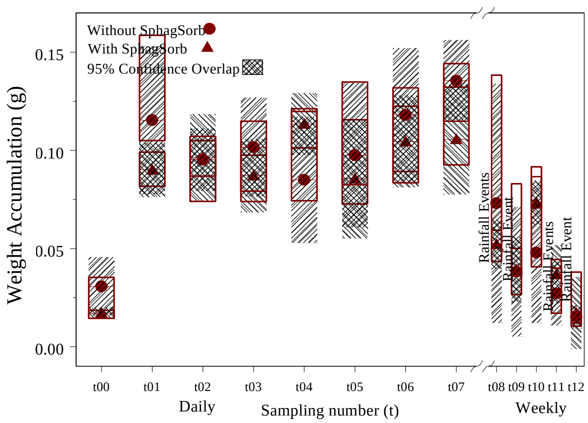

Fig. 25. Pickleweed, PBC, Fur during two months.

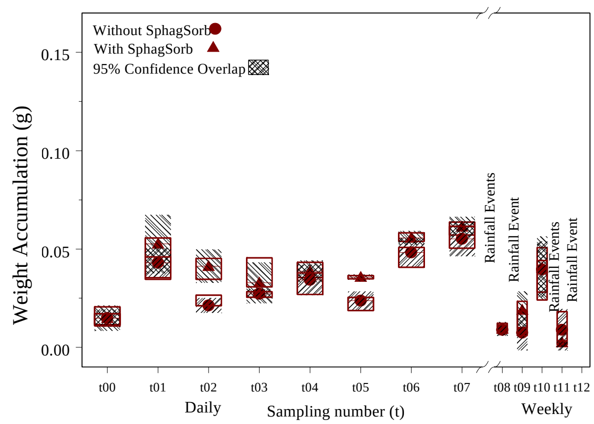

Fig. 26. Pickleweed, Diesel, Fur during two months.

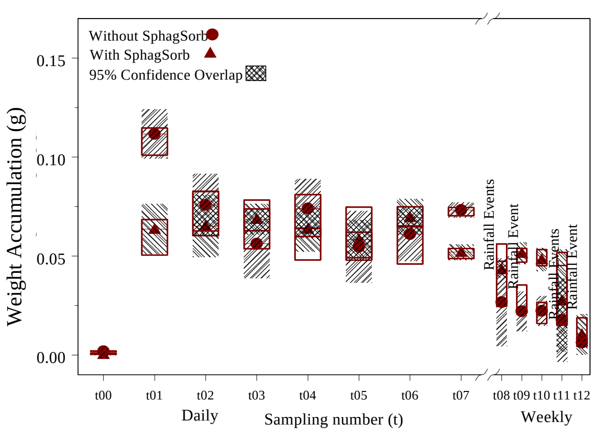

Fig. 27. Pickleweed, PBC, Polypropylene during two months.

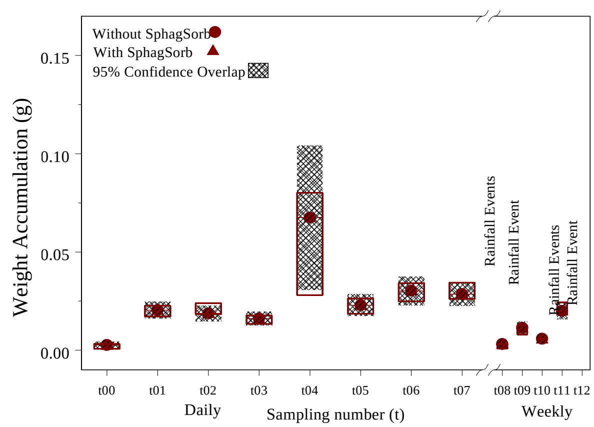

Fig. 28. Pickleweed, Diesel, Polypropylene during two months.

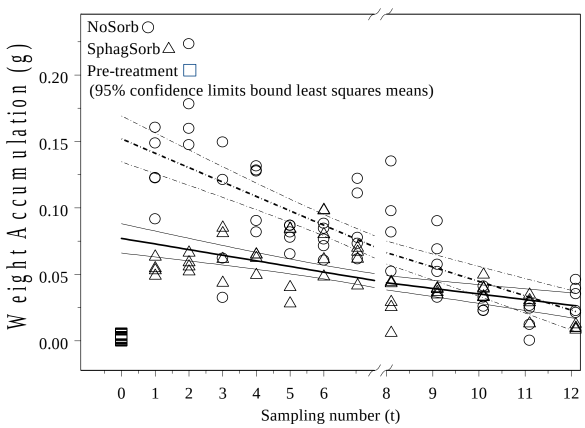

Fig. 47. PBC on pickleweed, WA of feather wipes with significant difference between treatment with Shag Sorb (lower values) and without (upper values) with 95% confidence limits.

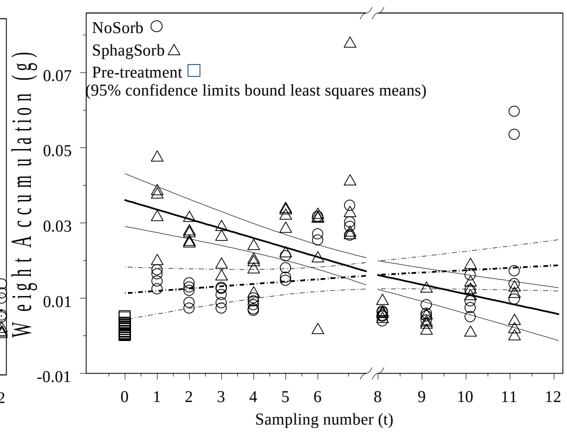

Fig. 48. Diesel on pickleweed, WA of feather wipes with significant difference between treatment with Shag Sorb (upper values) and without (lower values) with 95% confidence limits.

peat adhered to the wipers. With each successive rainfall event beginning before the second weekly measurement (t08), the peat in both oil and vegetation combinations was rinsed off the plants causing a rapid return of WA to pre-treatment values. In Fig. 47, the feather wipes of the untreated PBC show greater WA and faster decline than the WA for the treated vegetation. In Fig. 48, the results were as conclusive, though reversed. The peat material absorbed the diesel oil and adhered to the plants, while the diesel evaporated from the untreated, leaving no residues for the wipers. The wipes in the sand trial had varied success as seen in the box plots Fig. 29 through 34. Feathers were able to show some difference in treatments, but rarely outside the confidence limits of the background wiping (t00) of the moist sand. The sand trial was discontinued after the first week of sampling due to visible lack of adhesion of oil and peat and the WA did not differ from the background measurements. The wiping for this measurement error was not shaken or knocked against the tank side, and moist sand grains remained attached to all wipers. This demonstrates the influence of the weight of the mineral grains.

In the box plots (Fig. 35 through 40, 45 and 46) for the water trials the WA of all the wipers after drying showed extreme separation between the treatments. The WA of the treated and untreated samples supports the observations of the strikingly effectiveness of the peat. In the water trial, the oil acted as a surfactant for feather and fur and rapidly increased oil and water absorption. The water trial was discontinued after t02 due to the efficient collection of nearly all the oil and peat by chemical sampling.

3.2.2 Fur: While the fur material was expensive, cutting the pads and preparing a large number of wipers was rapid. The fur pad with its stiff backing was used to work the hair into the branch nodes. The dense pile has greater absorbance than cloth and could be used to literally buff the vegetation clean. In pickleweed, the fur WA plots (Fig. 25 and 26) support the visual observations of equal adhesion of oil and peat. In the PBC trial there were no measurements where there was a

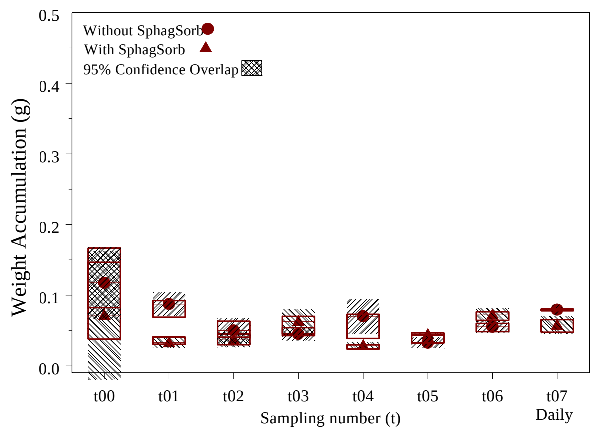

Fig. 29. Sand, PBC, Feathers during the first week

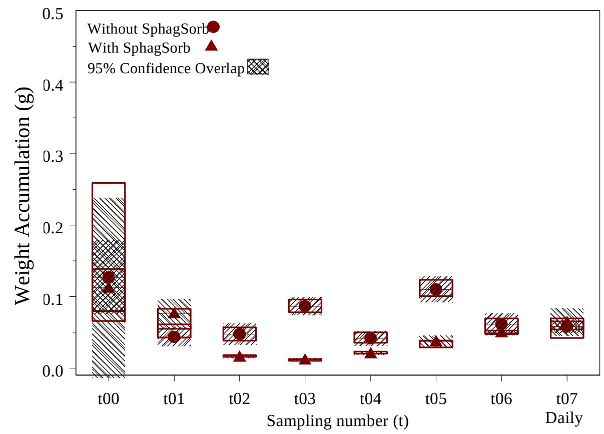

Fig. 30. Sand, Diesel, Feathers during the first week

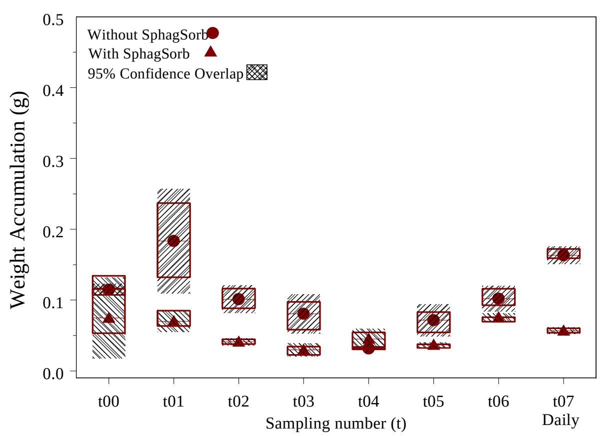

Fig. 31. Sand, PBC, Fur during the first week

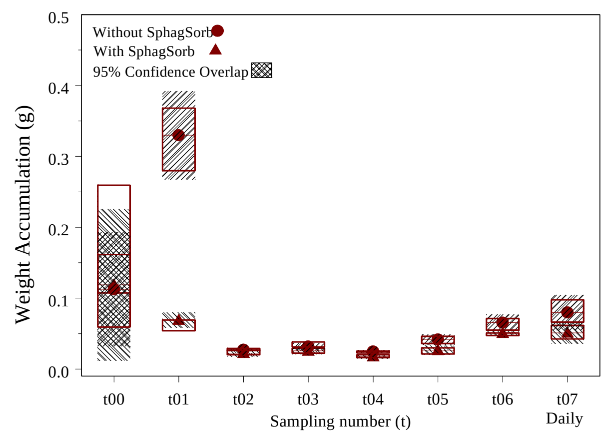

Fig. 32. Sand, Diesel, Fur during the first week

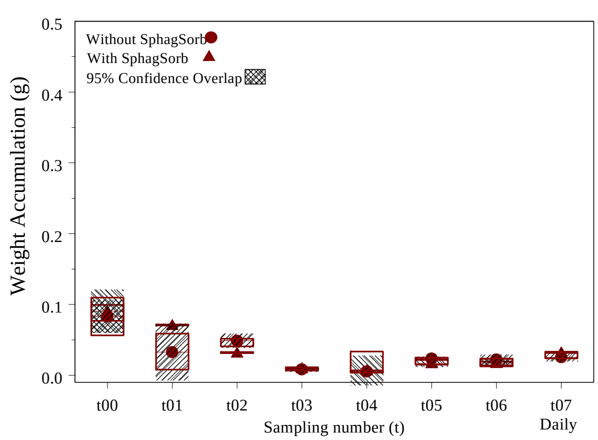

Fig. 33. Sand, PBC, Polypropylene during the first week

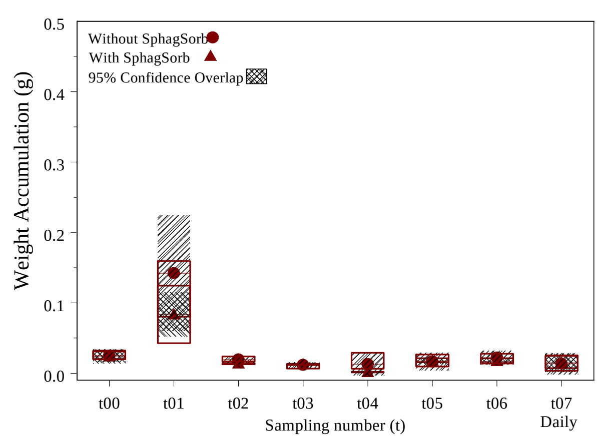

Fig. 34. Sand, Diesel, Polypropylene during the first week

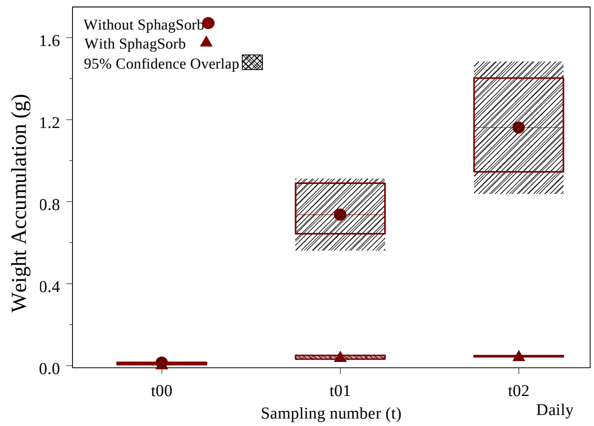

Fig. 35. Water, PBC, Feathers during two days.

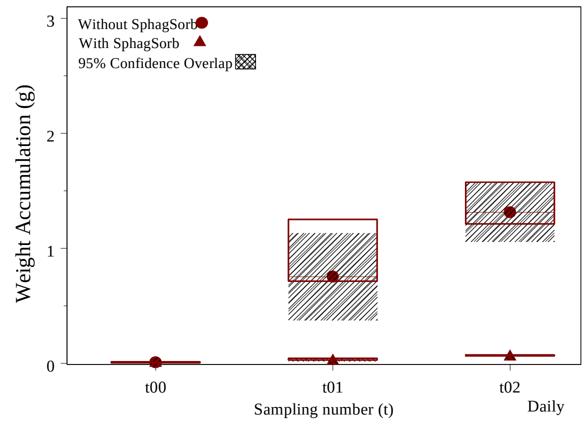

Fig. 36. Water, Diesel, Feathers during two days.

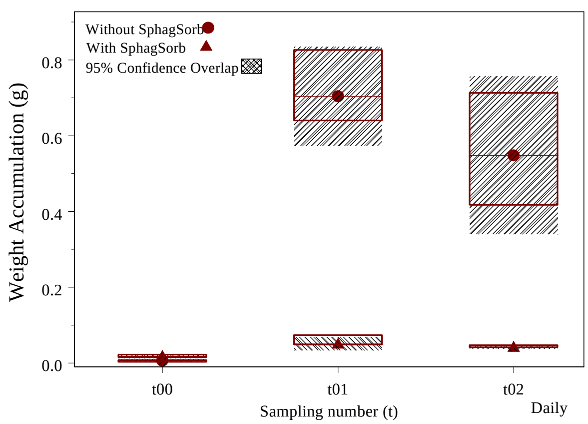

Fig. 37. Water, PBC, Fur during two days.

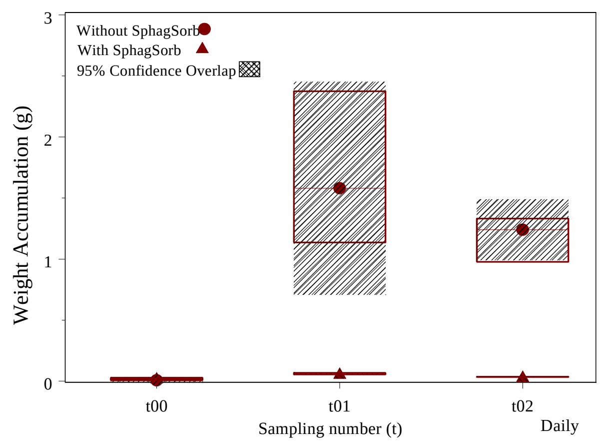

Fig. 38. Water, Diesel, Fur during two days.

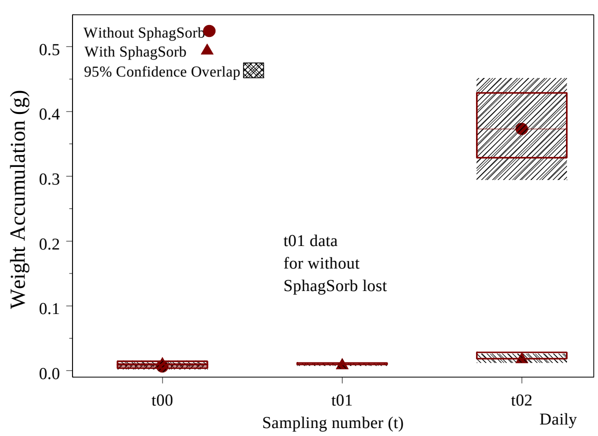

Fig. 39. Water, PBC, Polypropylene during two days.

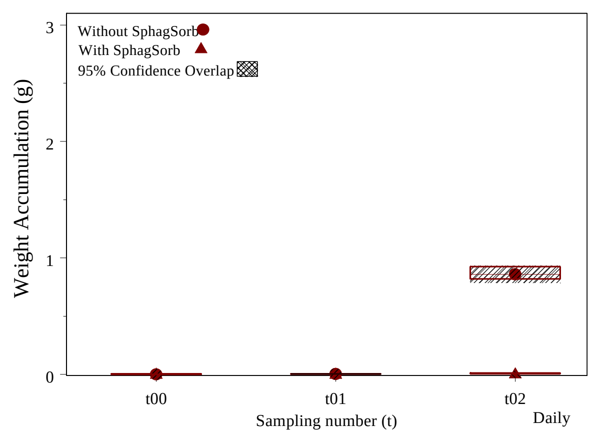

Fig. 40. Water, Diesel, Polypropylene during two days.

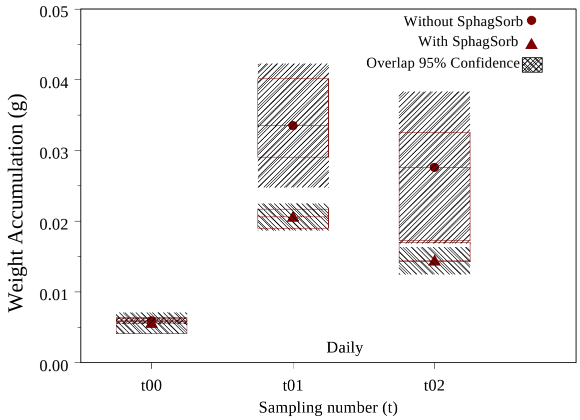

Fig. 41. Paper, Pickleweed, PBC, during two days.

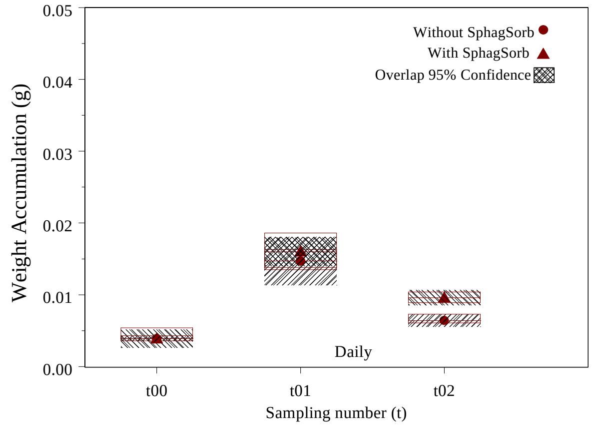

Fig. 42. Paper, Pickleweed, Diesel, during two days.

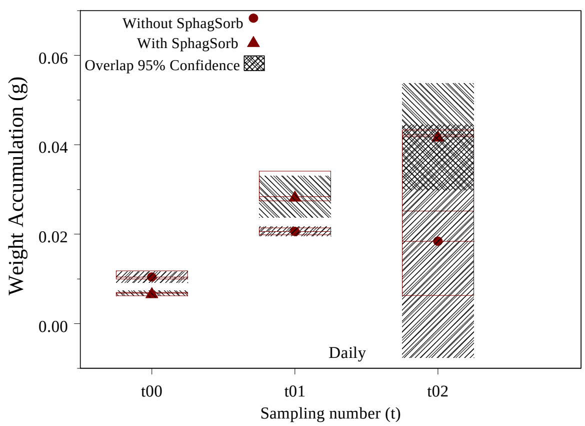

Fig. 43. Paper, Sand, PBC, during two days.

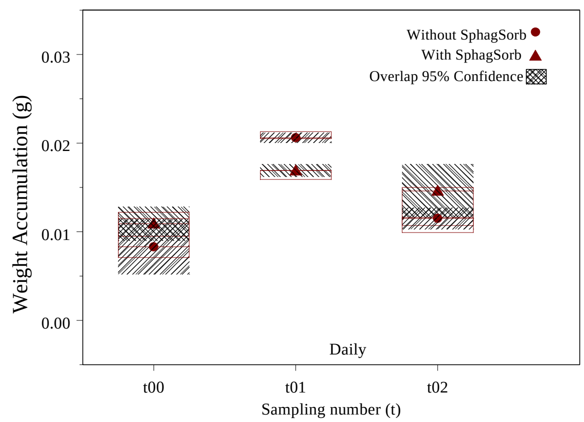

Fig. 44. Paper, Sand, Diesel, during two days.

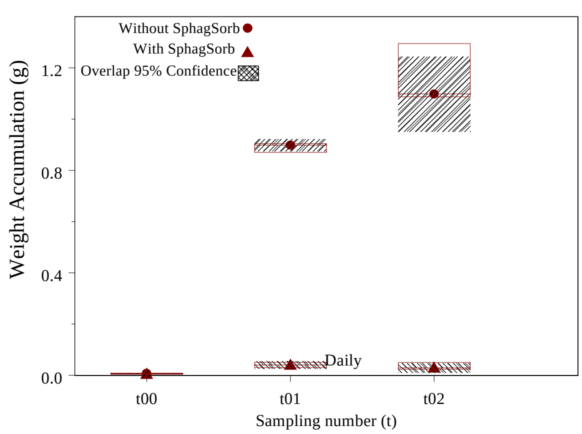

Fig. 45. Paper, Water, PBC, during two days.

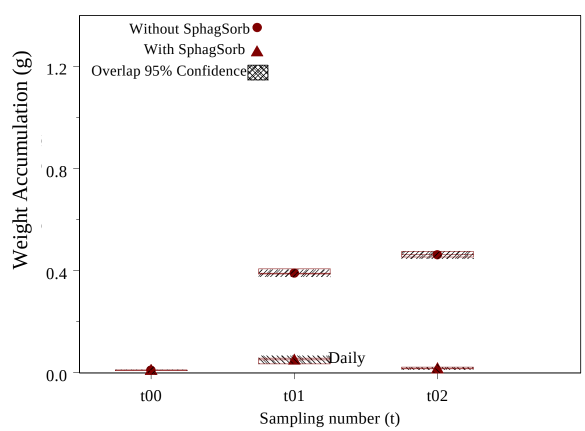

Fig. 46. Paper, Water, Diesel, during two days.

significant difference, and in the diesel trial there are only two within the first week. In the sand trial (Fig. 31 and 32), the peat and sand particles easily attached, though easily knocked or shaken off. However, fur was able to distinguish the treated from untreated in PBC for the first three days (t01 to t03), and in the diesel trial fur was successful the first day (t01). Before the diesel evaporated for the sand, the fur was able to absorb and retain the oil for greater WA than the treated sample.

3.2.3 Polypropylene cloth: The polypropylene wipers were fashioned rapidly and much less expensive than fur. This fleece material with a thin nap was a poor mimic of fur in that it did not absorb oil as well, nor was it hydrophobic in water. In vegetation, the cloth did not appear to absorb oil and peat at the same rate, and it was difficult to get into and around the plant nodes. In the box plots for all substrates and oils (Fig. 27, 28, 33, 34, 39, and 40), the WA is more consistent than fur, though absorbed half as much oil and had no greater ability to separate the treatments.

3.2.4 Filter paper: Paper provided uniform, pre-cut material that would have significantly reduced the time in sample preparation. It was hoped the paper consistency would also provide greater uniformity of oil absorption. The paper was slow to absorb oil, though it saturated instantly in the water and tore easily. The stiffness of the paper severely inhibited wiping within the plant nodes. For these reasons, the filter paper wiping was discontinued after two days. In the box plots for paper wipers (Fig. 41 through 46), the amount of WA is 1/10 to 1/2 of that of the other wiper types in the pickleweed and sand substrates.

3.3 Variation in Hydrocarbon Contents

The variation in oil concentrations in treated and untreated substrates supports many of the visual observations. OSPR, Petroleum Chemistry Laboratory, performed chemical content analysis for Total Petroleum Hydrocarbon (TPH). The concentrations on the substrates are shown in bar charts, Fig. 49 through 54 (Personal communication, Susan Sugarman, OSPR, Petroleum Chemistry Laboratory, March 26, 2008). The initial TPH values for the substrates before oil application were too low to show on the graphics and are reported in Table 1. These values include the background organic contribution from the unfiltered methyl chloride, and considered insignificant compared to the high values after oil application.

3.3.1 TPH in pickleweed samples: The concentration of TPH in the vegetation is similar for both treated and untreated pickleweed for the PBC oil, Fig. 49, until the one month later sampling. The substantial increase in oil concentration in the untreated samples is probably due to

Table 1. Background TPH values (determined by TEH analysis) in substrates before oil application.

	Pickleweed	Sand	Water-Surface	Water-subsurface
TPH (ug/g,ppm)	97 - 970	<20 - 63	0.26 - 0.66	0.23 - 0.57

dominator loss in pickleweed moisture and pigment contents. The treated pickleweed has slightly less oil concentration with this sampling as the peat absorbed the oil and reduced the severity of plant degradation. The October and November rainfall events also continued to rinse oil laden peat from the plants.

The first sampling of the diesel oil trial showed similar concentrations in both the treated and untreated vegetation (Fig. 50). By one week later (t08), there was greater concentration in the Sphag Sorb material. The low concentration in both after a month was probably due to the volatility of the diesel and continued rinsing of the peat from the plants by the rains.

3.3.2 TPH in sand samples: Sand absorbed both oils readily and the heavier PBC oil was observed closer to the surface. The concentration of PBC oil in the sand substrate remains very consistent for the first two measurements a week apart, but after a month the volatiles were gone and the concentration is seen to diminish in both untreated sand and peat (Fig. 51), while the concentration of diesel in the peat materials remains quite high (Fig. 52). On a weight basis, Sphag Sorb appears to be very effective in absorbing and holding the diesel oil. The peat material is very light weight, so it may be somewhat misleading to compare weight ratios of oil to peat vs. to sand. The amount of oil per volume may be an alternative calculation of oil absorption.

The light weight of the peat compared to sand make the peat a preferred material for removing the oil. If further studies should show that peat could draw the oil out of the sand over time or provide a carbon substrate for inoculating with hydrocarbon digesting microbes, the peat material may have a role in sand and soil reclamation.

3.3.3 TPH in water samples: In the first sample, 24 hours after the oil application, the surface PBC oil concentration in untreated is half the concentration of oil in the Sphag Sorb, however, it is very similar to the duplicate for treated sample (Fig. 53). This relationship is repeated one week later, though there is less than a tenth of the oil concentration. For diesel oil the relationships between treated and untreated are reversed (Fig. 53). The oil concentration in water samples collected from within the water column is small compared to those of the surface. The scale in the y-axis in Fig. 54 for the subsurface samples is 100 times smaller than Fig. 53 for the surface. For the subsurface samples, there is consistently greater oil concentration in the suspended peat compared to the untreated water column. The suspension of peat may be due to lower specific gravity by variation in oil absorbed by the peat particles.

The results are not conclusive. No doubt sampling had an impact on the proportion of water, oil, and peat material that was collected. Also, the first sampling nearly cleaned the surfaces of the water, and after the second sampling, a very slight amount of oil disperse readily and irregularly over the surface.

4.0 DISCUSSION

4.1 Statistical Design

One objective of pilot studies is to estimate the variance within samples to refine the number of samples needed in future studies for determining statistical

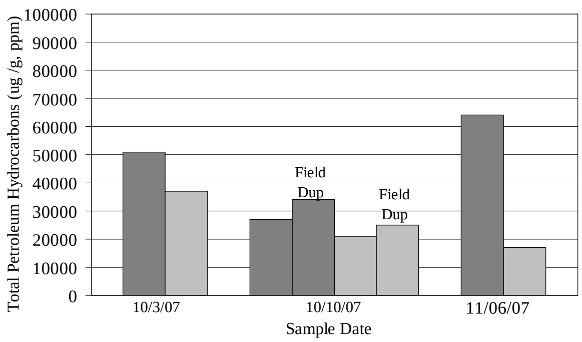

Fig. 49. Total petroleum hydrocarbons from Prudhoe Bay crude oil in untreated pickleweed (dark bars) and treated with SphagSorb (light bars).

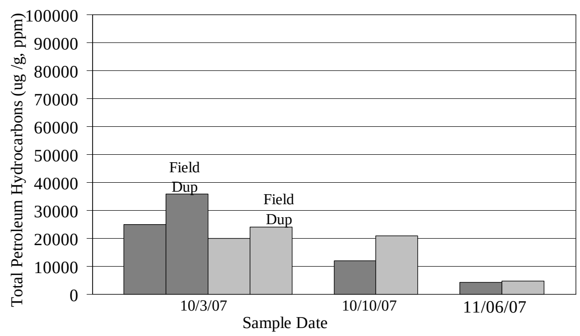

Fig. 50. Total petroleum hydrocarbons from diesel oil #2 in untreated pickleweed (dark bars) and treated with SphagSorb (light bars).

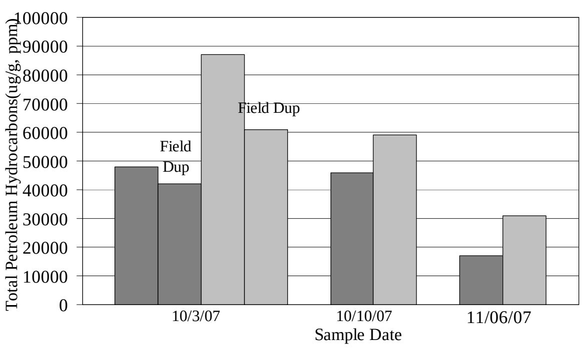

Fig. 51. Total petroleum hydrocarbons from Prudhoe Bay crude oil in untreated sand (dark bars) and treated with SphagSorb (light bars).

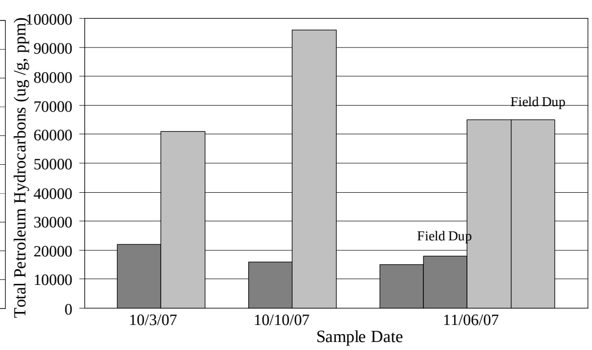

Fig. 52. Total petroleum hydrocarbons from diesel oil #2 in untreated sand (dark bars) and treated with SphagSorb (light bars).

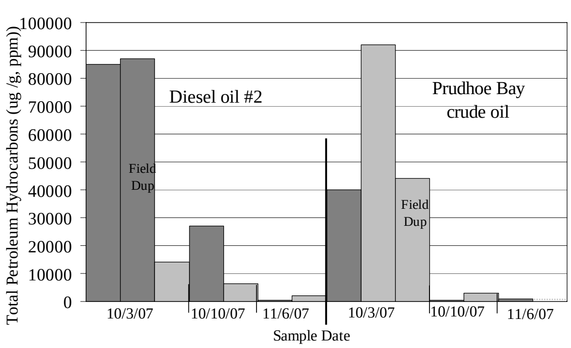

Fig. 53. Total petroleum hydrocarbons from Prudhoe Bay crude and diesel oil #2 on the surface of untreated open water (dark bars) and treated with SphagSorb (light bars).

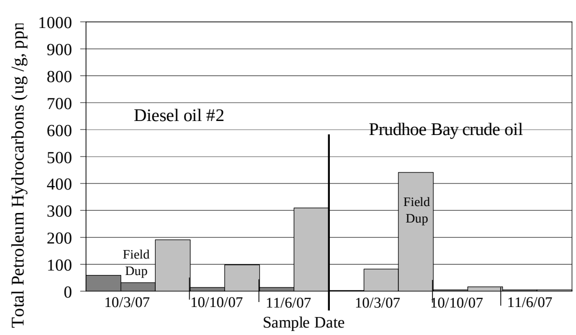

Fig. 54. Total petroleum hydrocarbons from Prudhoe Bay crude and diesel oil #2 below the surface of untreated open water (dark bars) and treated with SphagSorb (light bars).

significance. The number of observations also greatly impacts the time for preparation, sampling, and weighing. The five observations (wipes) chosen for the pilot was a reasonable number within the available time and funding. For chemical analysis, only one sample was collected in the substrates for each time period, so the variability of TPH is unknown, though the few field duplicate samples were similar in most cases to the main samples.

This statistical evaluation was necessary for the proposed 2008 to 2010 study of PBC oil on pickleweed and saline water using feathers and fur wipers. Since the treatment means in the water substrate were so distinct in this study, only the variance in WA for pickleweed with feather and fur wipers was evaluated. The variance used included outliers. Five parameters are necessary for this determination: an estimate of the a) variance and b) measurable mean differences; c) level of significance for correctly accepting the null hypothesis (i.e., chance of rejecting a Type I error); d) confidence level desired for determining there is a difference (power of the test, or rejecting a Type II error); and e) deciding on a one or two tail test (Steel and Torrie 1960). These parameters were used in S-Plus to calculate the number of observations and significant mean differences.

In a two-tail test, there was a 0.068 g difference between treatment means for feather WA in the measurement immediately after application (t01). The calculation suggests that two wipers will provide a 95% level of significance, with a power of 0.9 (or accepting "no difference" 10 % of the time when there is actually a difference). This also confirms that the two wipes of the even numbered samples in shaded plants gave reliable levels of significance. At this significance level, the five wipes used can give reliable separation of treatments at 0.037 g, or reliability to half the mean differences measured in this study.

Greater variability of the WA in fur patches requires a substantially greater difference in treatment means than found in this study. The difference in means for the same measurement (t01) was 0.024 g. The calculation suggests to statistically separate treatments using the determined variance within fur samples will require 29 to 39 wipes. The five wipes used in this study will achieve the same significance level and power when the treatment means differs by at least 0.07 g. In this study with both oils in pickleweed, aggregating the first week of measurements will be needed to attain this difference in treatment means. The fur wiping method requires further thought and discussion.

4.2 Addressing the Study Hypotheses.

4.2.1 Hypothesis: A) Applying a biodegradable particulate sorbent (peat dust) to petroleum-contaminated marsh vegetation, sand, or fresh water will immediately render it less sticky to fur and feathers.

For vegetation, the significantly lower WA from Sphag Sorb treatment is an indication that the peat material immediately reduced the amount of PBC oil adhering to the feathers (Fig. 23). After aggregating for the first week of WA for fur, there is also a significant difference and indication of reduced stickiness. Since the small rain events rinsed peat treated oil from the vegetation, it's likely the peat stuck to animals will also readily rinse off. Further, the TPH analysis indicates that in PBC oil over the month of sampling, and immediately after contamination with diesel oil, there is a greater amount of oil retained on untreated plants (Fig. 49 and 50).

For sand, there is also an immediate reduction of stickiness, as seen in the WA with feathers and fur in Fig. 29 and 31. As for water, the distinction is quite clear. The peat material greatly reduced or eliminated adhesion of the oil to all the wipers (Fig. 35 through 40). The wipers were nearly clean after sampling the peat treated oil. The minimal attached peat rinsed off in the water adjacent to the oil patch. The peat material that absorbed oil remained as floating mats on the surface.

4.2.2 Hypothesis: B) Petroleum products composed of chemicals of different molecular weights have different adherence to bird and mammal feathers and fur.

The two oils gave opposing results due to the differences in volatility, and will impact application decisions for the particulate sorbent. The evaporation of all diesel oil occurred within a few days, leaving actually cleaner substrates. After a few days, little or no oil was collected by feathers and fur. The peat material may inhibiting diesel oil evaporation and will influence the application protocol for peat in spill response. The lighter fraction of PBC oil facilitated Sphag Sorb oil absorption, and held some of it back from the feathers and fur, and from destroying the plants. Over time, the lighter fraction of PBC oil evaporated, leaving tar, and loosing its stickiness and, probably, absorbability by Sphag Sorb.

4.2.3 Evaluating pH variation in the substrates due to peat and oil treatments:

In the DFG and UCD contract, the pH evaluation was mistakenly included for this proof-of-concept study. The contract stipulated one hypothesis more than the two stated in the introduction of this report:

> "There is no change in pH of bulk water, interstitial pore of the sand and sorbent due to degradation of the peat absorbent."

The initial proposal submitted to the Technical Review Committee (TRC) included this hypothesis and one more: "C) Applying biodegradable particulate sorbent to petroleum-contaminated marsh vegetation, sand, or fresh water will not negatively affect the pH of the substrate," and "D) Applying a biodegradable particulate sorbent to petroleum-contaminated marsh vegetation, sand, or fresh water will accelerated oil degradation." The TRC raised the question regarding inclusion of these hypotheses:

> "Please clarify whether the proposal will be limited only to A & B in the hypothesis and objective section, since objectives C and D don't appear to be addressed in the experimental plan. For example, how will project examine oil degradation rates without conducting any type of chemical analyses?"

Our response should have eliminated these hypotheses as deliverables in the contract:

> "Objective C and D should be removed from this proposal and considered as "next steps" if the pilot study is successful. Because of limited funding, it is not possible to include this work in this proposal. It makes more sense to perform the

work sequentially in case the project fails to show any substantial benefit for peat treatments compared to untreated oil contamination."

To effectively evaluate the impact of sorbent and oil on the pH values in the interstitial plant and sand water, and open water, a separate trial is needed under highly controlled conditions specifically for this evaluation. Under the open-air conditions, it will be difficult to separate the cause and effect of these treatments on pH in unbuffered fresh water, and difficult to identify the amount of change in strongly buffered salt waters.

Regardless of the oversight in allowing this question of pH into the final contract, some pH measurements were made to monitor the plant health and water status. While the water was maintained at nearly 1/3 the salinity of sea water, the pH values were approximately 8.0 throughout the trial due to the strong buffering of the salt and fertilizer added to the plant solution. The sea salt and fertilizer probably overwhelmed change that might have been possible due to additions of peat material and oil. In addition, the peat material remained on the plant or was rinsed to the Perlite surface, so there was little or no incubation of the peat within the Perlite that would generate acidic microbial decomposition products. No peat material was visible below the first centimeter of the surface.

The sand substrate was moistened (not flooded) before the initial wipe (t00) and application of oil, but not again, until the second week with the rain event, only then could interstitial water be extracted for measurement. In this case, the pH measurements would not likely accurately portray the effects of the treatments and were not seen as meaningful in these conditions, so samples were not drawn for extracting the soil water.

The water substrate was slightly basic (pH = 7.3) well water, and no sea salt added. The change in pH due to additions of peat materials could not be substantiated in the open tanks. The pH test described in the introduction by Canada Environment Protection Service used a prescribed amount of peat material to water (10 g l^{-1}) for multiple measurements over 96 hours.

The petroleum sampling and analysis did not address the fourth hypothesis in the original proposal. Chemical sample analysis was only performed to estimate the amount of petroleum on the substrates.

5.0 CONCLUSIONS

For crude oil spills, the peat absorption of the oil did significantly reduced the stickiness, and subsequent amount of oil wiped from the substrates within the first few days. The peat material definitely reduced the damage to plants, and has greater absorption than sand, and absorbed crude oil preferentially to water. The volatile diesel oil escaped to the atmosphere quickly, and in the untreated pickleweed did no damage, and evaporated from the water and sand in a few days. The peat material may have prevented the diesel oil from completely evaporating longer than untreated sand, and held the oil longer within the water column. With both oil types, the small rain events completely rinsed the oily peat from the treated pickleweed. The peat material gives the oil a fiber base and makes it possible to screen or rinse the oil from the substrates.

This method of determining oil stickiness using the weight accumulated by wipers can not determine if the bound oily peat may be more easily removed by bird or mammal. Since the sorbent seems to hold the oil better than the tested substrates, it may decrease the amount of oil ingested with animal preening, and subsequently reduce toxic poisoning. Future toxicity studies are needed to demonstrate any reduced danger to the animals.

6.0 REFERENCES

Devore, J., and R. Peck. 2001. *Statistics, The Exploration and Analysis of Data.* Pacific Grove, CA: Duxbury.

Pearcy, R. W. and S. L. Ustin. 1984. Effects of salinity on growth and photosynthesis of three California tidal marsh species. Oecologia 62:68-73.

Rosso, P.H., J.C. Pushnik, M. Lay, and S.L. Ustin. 2004. Reflectance properties and physiological responses of *Salicornia virginica* to heavy metal and petroleum contamination. Environmental Pollution 137 (2): 241-252.

Steel, R.G.D. and J.H. Torrie. 1960. *Principles and procedures of statistics with special reference to the biological sciences.* New York: McGraw-Hill.

Ustin, S. L. 1984. Contrasting salinity responses of two halophytes. California Agriculture 38:27-28.