

Preliminary Draft Proposal

Task 8: Collaborative Long-term Monitoring of Dust Emission Potential, Salt Crust Genesis, and Aerosol Chemistry at the Salton Sea

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1. Introduction

The conditions at the Salton Sea may be producing surfaces near the shoreline that are seasonally susceptible to wind erosion. From a combination of water level reduction, temperature fluctuation, rainfall, sediment composition, and water chemistry, some of the surfaces around the Salton Sea may have a relatively low threshold velocity for producing substantial dust emissions. Previous research has shown that potential dust emissions vary considerably between different times of the year at the Salton Sea, but that between the winter and spring the surfaces are the most susceptible to wind erosion (Task 3, Etyemezian et al., 2006). The rate of change of dust emissions from the Salton Sea from one year to the next for the same time of year is unknown. At present, the Preferred Alternative Restoration Plan has not been approved leading to the potential of more shoreline at the Salton Sea to be exposed. In addition, even if the Preferred Alternative is approved there is at least a five-year period where the water level may still recede. As the shoreline area increases, the potential for larger dust emissions from the Salton Sea air basin also increases. Moreover, research that evaluates the changes in soil properties and the potential for those surfaces to be susceptible to wind erosion can also be transferred to the exposed soil sediments within the Salton Sea basin if the Preferred Alternative Restoration Plan is approved. It is then essential to measure soil properties and associated dust emission potential data.

When the groundwater table is located near the surface, the modification of salt crusts can occur on a variety of time-scales, including days, months or years depending on other climatic conditions and soil properties (Pelletier, 2006). With salt crusts present on a surface, fine particles can be transferred to the soil surface through soil heaving and new fine particles can be created through salt weathering, thermal expansion, and salt mineral dissolution and precipitation (Amit et al., 1993; Cooke, 1981), increasing the amount of fine particles potentially available for aeolian transport (Buck et al., 2006; Reheis, 2006). These processes are complicated by the dynamic nature of surface salt crusts that vary in roughness, hardness, mineralogy and structure to provide a large range of resistances to wind erosion. Furthermore, the salt crust formation is dependent on solar radiation, relative humidity, water chemistry, temperature, rate of change of temperature and humidity, and other meteorological conditions. This complex set of conditions that alters salt crust formation can result in a variety of salt crust resistances to wind erosion and further the difficulty in which those resistances could be predicted.

Determining the effects of salt mineralogy and crystal habit on the physical properties of the salt crust and their potential aeolian dust emissions (rate and chemistry) is the goal of this research. The proposed research will monitor these variables over time (years) at a subset of areas that represent the different soil conditions around the Salton Sea through a series of transects parallel to the shoreline.

The ‘age’ of an exposed surface around the Salton Sea is related to its distance from the shoreline. It is proposed that measuring the potential windblown emissions along a transect from a known starting point towards the shoreline will elucidate trends in terms of dust emission as a function of exposure age. In addition, characterizing the surface salt crusts along the transects will aid in describing the temporal changes in the crust physical, chemical, and mineralogical composition over the exposure period.

2. Scope of Work

The scope of this task is embodied into three procedures that are linked together by their methodology and will rely on one another to strengthen their results. The three procedures include measurement of the flux of potential dust emissions; the physical, chemical, and mineralogical characteristics of the surface crusts; and the chemical composition of the potentially inhalable emissions from the Salton Sea shoreline as the water level recedes. This section describes the methods involved for each procedure, the sampling scheme and site selection justification, and the long-term goals of the proposed research.

2.1 *PI-SWERL*

Synopsis and Objectives

A portable wind tunnel-style instrument will be used to obtain estimate of the dust emission potential along transects that cover the distance from the edge of the waterline to the edge of the recently exposed (last 10 years) sediment. Locations and sampling scheme used for transects are described in a later section.

The objective of this effort is to understand what happens to exposed Salton Sea sediment over time – especially with regard to the potential for dust emissions. Earlier DRI work (Task 3 and Task 6) provided snapshots of dust emissions and salt crust characteristics at a point in time. The Salton Sea exhibits very dynamic responses to changes in environmental conditions. Whereas at conventional playa regions changes in sediment characteristics occur over timescales of decades or centuries, recent DRI experience at Salton Sea indicates that significant landscape changes can occur over timescales of a year or less. This suggests that sediment exposed today could behave quite differently – with respect to dust emissions – a year or three years from now. It is important to understand how exposed sediment ages and what effects this has on dust emissions. Is there a tendency for fluffy surfaces to become more stable with exposure (and distance from groundwater) or is there a tendency for seemingly stable surfaces to become fluffy? What implications would this have for planning for air quality mitigation? Are estimates of dust emissions obtained from current shorelines at all representative of the potential for dust emissions over time?

Methods

The PI-SWERL to be used for this study is a smaller version (Fig. 2) of an earlier design described by Etyemezian et al. (2007). It is a cylindrical chamber ($D = 30$ cm, $H = 20$ cm) that has an open end which is placed over the soil surface to be tested. Soft foam along the circumference of the open end forms a seal with the test surface. Ventilation of the PI-SWERL chamber is accomplished by a DC blower (AMETEK, Mini-Jammer) and monitored by a mass flow meter (TSI, Model 42350101). Filtered air that is introduced by the blower, mixes with the air in the chamber and the flow is exhausted through a port (diameter = 5.0 cm) at the top of the chamber. A clean air flow rate of 100 lpm corresponding to 7 air changes per minute has been found to provide a satisfactory degree of ventilation while avoiding the undesirable suspension of dust by inlet blower air.

Once the measurement cycle is initiated, one-second concentrations of PM_{10} (particles with aerodynamic diameter ≤ 10 micrometers) are measured by a nephelometer-style dust monitor (TSI, DustTrak Model 8520). Although the DustTrak does not provide a true mass based measurement, it is used in conjunction with the PI-SWERL because it is very portable, has a fast response (1 second), and can measure concentrations over four orders of magnitude ($\sim 10 \mu\text{g}/\text{m}^3$ to $100 \text{mg}/\text{m}^3$) with reasonable precision and accuracy when properly calibrated (Chung et al., 2001; Moosmüller et al., 2001; Niu et al., 2002).

Dust suspension within the chamber is induced by a rotating, flat annular ring. The annular ring (inner diameter = 16 cm, outer diameter = 25 cm) is coupled through a metal shaft to a 24-volt DC motor that is fastened to the top of the PI-SWERL chamber. When in motion, through the formation of a velocity gradient, the rotation of the ring results in shear stress being generated at the soil surface. In concept, this is similar to Couette flow where one infinite plate moves parallel to another resulting in shear flow without the presence of a pressure gradient in the principal direction of the flow. Within the PI-SWERL, the flow is turbulent and symmetry is axial rather than planar. This design is based on the principal that windblown sediment transport and dust emission are driven by wind that is tangential to the soil surface and is often parameterized as a shear velocity (u^*) or shear stress (e.g. (Bagnold, 1941; Chepil and Milne, 1939; Gillette, 1978). For straight-line wind tunnels, some substantial fetch is required prior to achieving an approximate steady boundary layer (Gillette, 1978) and surface shear stress. Practically, this requires that a straight-line tunnel have a length of at least a few meters. By employing a rotating, flat annular blade, the PI-SWERL design is aimed at ensuring that the average flow over the soil surface is at steady state and symmetrical about the axis of rotation.

The vertical dust flux is calculated based on the measured air flow rate, dust concentration, and the effective area of influence from the annular blade. The shear stress distribution at varying RPM has been measured with Irwin sensors mounted onto a smooth plywood surface onto which the PI-SWERL had been placed and operated (Irwin, 1981) as well as hot-film anemometry. Results indicate that shear stress increases with RPM and is concentrated in an area underneath the annular blade (Sweeney et al., 2008).

The PI-SWERL measures the PM_{10} concentration (C , mg/m^3) at an outlet with a DustTrak that records at 1 Hz while a blower vents clean air through the PI-SWERL at a constant rate (F , m^3/s). By calibrating the PI-SWERL with the University of Guelph field wind-tunnel (Task 3) and from shear stress measurements made under the PI-SWERL in the laboratory this can be converted into an emission flux ($\text{mg}/\text{m}^2/\text{s}$) or amount of PM_{10} per area per second by:

$$E_{i,cum} = \frac{\sum_{begin,1}^{end,i} C \times F}{t_{end,i} - t_{begin,i}} \bigg/ A_{eff} \quad [1]$$

Where the summation occurs over every 1-second measurement during level i , beginning at $t_{begin,i}$ and ending at $t_{end,i}$, with t as integer seconds. The measured dust concentration and flow rate are converted to an emission flux by the effective area of the PI-SWERL, A_{eff} which is 0.07 m². The PI-SWERL is also capable of gauging the amount of saltating sand-sized particles during its measurement cycle with a series of three or more optically-based sensors within the PI-SWERL chamber. Two specific tests can be run with the PI-SWERL to investigate the emissive properties of a surface. The first type of test is called a step-test, which is utilized to estimate the potential dust emissions from a surface. The second type is called a ‘ramp-test’, which estimates the transport threshold of a surface for dust emissions. The PI-SWERL cycle has three major portions to a test: First, The blower is turned on to flush any residual dust in the chamber from setting the instrument down or from a previous test; Second, the annular blade is cycled through a set of pre-determined speeds (usually 4 or 5) that straddle the sediment transport threshold equivalent wind velocity, that are maintained for a duration of 120-200 seconds each before ramping up to the next velocity (in the case of the step-test), or one continuously increasing speed for the ramp-test; And lastly, a second flushing step (blower fan remains on, while annular blade slows till stopped) that lasts between 30 and 60 seconds.

A recent addition within the PI-SWERL chamber is an optical particle sensor for calculating the horizontal sand flux. The sensor, consisting of an LED photodiode (~1 mm beam aperture) and a photoreceiver that are separated by 10 mm, is polled and processed at 10 KHz. An algorithm has been developed that utilizes the high sampling rate to detect individual grains that move through the sensing volume while filtering out light extinction by small dust particles. Numerous tests on constructed soil plots in addition to tests conducted in a sediment-tolerant wind tunnel have been completed with this sensor; they indicate that the sensor provides a consistent measure of sand movement that is proportional to sediment transport measured by Safire instruments (Baas, 2004) and highly correlated with ($R^2 > 0.95$) sediment flux collected from wedge-shaped sediment traps.

Below are data from previous tests showing both types of tests: a) step-test, b) ramp-test (Figure 1). The step-test resolves the potential PM₁₀ emissions by applying Eqn. 1 for every ‘step’ of the test (including the prior steps) and more recently it also calculates the sand-sized transport rate (g/m²/s) by high response (10KHz) optically-based sensors. The ramp-test is a wind tunnel application first utilized by Gillette et al. (1980) to predict the erosion threshold of desert soils by incrementally increasing the wind velocity in a wind tunnel until dust emissions are produced. Figure 1 displays two important details in regard to dust emissions, which is not a characteristic of every soil but the majority of soil types in arid environments. The amount and timing of the first PM₁₀ sized dust is within a discrete unit that comes to a peak and subsides. This is associated with the direct entrainment of dust by the wind shearing forces that occurs whenever the surface either has produced fine particles through soil processes or by when dust is directly deposited on the surface over time. The second emissions flux in the time series at a higher shear velocity is associated with larger particles being initiated into motion by the wind and by other particles bombarding the surface also initiated by the wind shearing forces. It is noted that the amount of emissions from the higher shear velocity is larger, however the emissions from the lower shear velocity has the potential to occur more frequently (depending on the wind regime distribution).

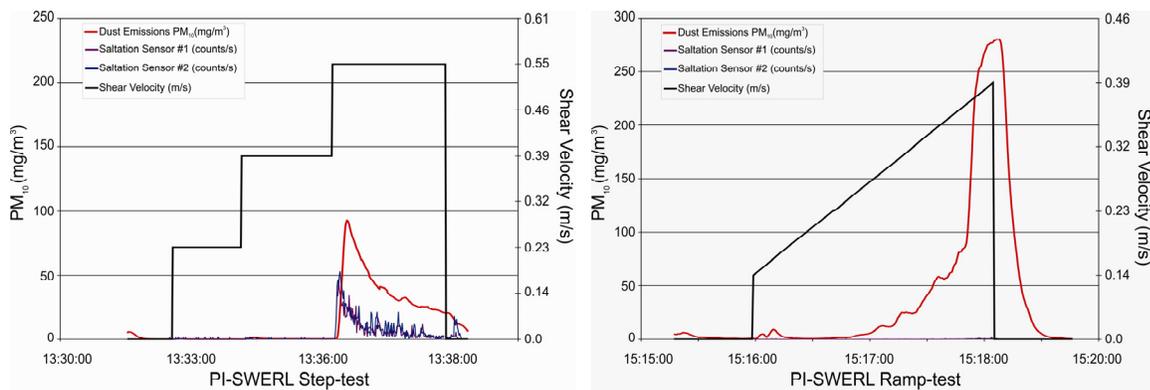


Figure 1: Example PI-SWERL results from a step-test and ramp-test

2.2 Soil Analyses

Synopsis and Objectives

In conjunction with the PI-SWERL measurements along shoreline transects, the characteristics of the salt crust will also be examined using techniques employed in an earlier pilot-scale study (Task 6). The techniques, described in detail below, include characterization of the salt crust mineral content, salt crystal habit, soil texture, and other bulk properties such as organic material content and electrical conductivity.

As with the PI-SWERL work described above, the objective of the salt crust characterization over transect lines and over multiple years is to obtain a mechanistic understanding of what salt properties affect dust emissions. This includes answers to questions like: How are salt crust properties and dust emissions linked? How do salt crusts change/evolve as they age and as the sediment's interaction with the water table decreases (water levels decrease)? To what extent does rain washing of sediment alter the salt crust composition in the long term? What implications does this have for implementation of the Preferred Alternative, where the groundwater table in the center (nominally dry) portion of the lake will be quite high?

Methods

The soil analyses detailed here complement the dust emission potential measurements by providing the specific condition and relative physical measurements of the surface at the time of the dynamic wind tunnel measurements. However, these soil-based analyses are presented here as a stand alone section to allow for their potential use within other research arenas in researching the Salton Sea dynamics. First, the specific field techniques are discussed that allow for the unbiased acquisition of soil samples for laboratory analyses in addition to in situ field tests; this is followed by the description of the laboratory analyses proposed.

2.2.1 Field Methods

At each of the sites, a series of shallow soil pits (~0.3m) will be dug to aid in the discussions of the genesis of the salt crusts (if any) by examining the soil profile. The soil profile layers will be described using field methods to determine the color, strength, moisture, sediment size, and relief

properties. The visual inspection of the soil profile facilitates an accurate description of soil genesis (past conditions) and potential surface characteristics (future conditions). The physical surface strength will be tested using both a field penetrometer when above detectable limits and the ball drop method. The crust strength measurements will be repeated at each site along the transects to investigate the correlation with distance from the shoreline for every field campaign. Samples of the intact surface crust, bulk surface crust, and a bulk sample of the top layer of soil will be collected for the laboratory analyses detailed below. In addition, DGPS locations of the transects lines, surveying of the transect topography and shoreline position, and site descriptions will be collected at each site location.

2.2.2 Laboratory Methods

2.2.2.1 X-ray diffraction (XRD)

XRD data are obtained using the powder method. No water is used during sample preparation for these analyses. The XRD analysis is conducted on only the uppermost portion of the soil or crust. Air dry soil crust samples are gently ground by hand with mortar and pestle, and then transferred into a 32 mm diameter powder mount utilizing ~1.0g of each sample. XRD analyses of the powdered samples are performed by step scanning using a PANalytic X'Pert PRO diffraction system. $\text{CuK}\alpha$ radiation ($\text{K-alpha1} = 1.54060 \text{ \AA}$, $\text{K-alpha2} = 1.54443 \text{ \AA}$) is used at 40 kV, 40 mA with a 0.0080° 2θ step interval and a step-counting time of 0.14 s to achieve a 15 minute run time. A 10 mm X-ray beam mask along with 0.5° antiscatter and 0.25° divergence slits are used to focus the beam during analyses. Diffraction patterns generated from a $6^\circ - 75^\circ$ 2θ range are imported into X'Pert High Score software where sample mineralogy is determined by matching diffraction profile peaks via auto-identify and user-defined database queries. The score generated for each of the minerals in the samples is a semi-quantitative number associated with the amount by volume that that mineral occupies within the sample so that the sum of the scores equals 100.

2.2.2.2 SEM/EDS

Salt crusts are to be collected from the field and transported to the lab in conditions as close to the field as possible. Subsamples of the crusts are broken using dental tools into small fragments and affixed with carbon glue to 10- or 30-mm diameter aluminum studs. Smaller studs are used for the more cohesive salt crusts. The carbon glue is allowed to air dry overnight before sputter coating with gold. Smaller samples are coated initially for 75 s, with some samples requiring an additional gold coating of 20 s to reduce charging during SEM analyses. Larger samples are coated with gold for 90 s. Analyses are to be performed on a JEOL 5600 scanning electron microscope and an Oxford ISIS energy dispersive X-ray system at the Electron Microanalysis and Imaging Laboratory of University of Nevada, Las Vegas. Surface and subsurface salt crust samples will be analyzed. Multiple EDS analyses will be performed on each SEM image to identify all salt minerals present within an image.

2.2.2.3 Gravimetric Water Content

Gravimetric water content will be determined using NRCS Soil Survey Laboratory method 3C3 (Soil Survey Staff, 2004). Samples collected in the field, and transported back to the laboratory in sealed metal sample tins, are to be dried in a 105° F laboratory oven for 12

hours. Pre (Field Moist, FM) and post-drying (Oven Dry, OD) weights were used to calculate percent gravimetric water content.

**Soil samples will be sieved using a 2mm sieve before each of the following pretreatment / analyses are performed. These pre-treatments are performed to determine Organic matter content, % soluble salts, % CaCO₃, and texture of the non-soluble fraction. All mineralogical tests are performed on samples that are not pretreated in any way and stored in conditions as similar to the field as possible.*

2.2.2.4 Organic Matter (OM) Removal

OM will be removed by combustion in a 400° C muffle furnace. Approximately 15 g subsamples will be heated in open aluminum tins for 12 hours until an approximate 100g total bulk sample weight was achieved for each sample. Percent OM is calculated from pre and post-combustion sample weights.

2.2.2.5 Soluble Material Removal

Using soil remaining after OM removal, soluble material is then removed by rinsing with RO water (Soukup et. al, in press). Bulk samples are split into two subsamples and transferred to 250 mL centrifuge containers with approximately 150 mL of RO water (volume of RO water varied to balance centrifuge). Before centrifuging, samples are agitated at ~120 cycles/min for 30 minutes on a mechanical sample shaker. The samples are then centrifuged at 1500 rpm for 10 minutes. Centrifuged samples are decanted and the rinsing process repeated until the electrical conductivity (EC), monitored by a Fisher Scientific Accumet AB30 conductivity meter, between successive rinses reflected no change. At least 6 rinses will be performed for each sample for consistency. Lastly, samples are transferred to pre-weighed 400 mL beakers and dried overnight in a 105° F laboratory oven. Percent soluble material is calculated from pre-rinsing and post-oven sample weights.

2.2.2.6 Carbonate Removal

Carbonate and any remaining soluble salts will be removed using a sodium acetate buffer solution (Kunze and Dixon, 1986). Using the soil remaining after soluble material treatment, the samples are rehydrated with 100 mL of RO water. 10 mL of a sodium acetate buffer (NaC₂H₃O₂ · 3H₂O, 0.5M, 136 g/L, adjusted to pH 5 with acetic acid) is added to the hydrated sample and stirred occasionally until visible and audible carbon dioxide release is no longer observed. At a minimum, a total of five sodium acetate treatments will be administered per sample. Remaining soil samples will be transferred to 250 mL centrifuge bottles and centrifuged at 1500 rpm for 10 minutes, followed by decanting of the supernatant liquid. All samples are then rinsed until the odor of acetic acid is undetected by olfactory observation. At least 5 rinses are conducted on all samples for consistency. Lastly, samples are transferred to pre-weighed 400 mL beakers and dried overnight in a 105° F laboratory oven. Percent carbonate is calculated from pretreatment of the sodium acetate buffer and post-oven sample weights.

2.2.2.7 Texture Analysis

Soil texture will be determined using the hydrometer method (modified from Gee and Bauder, 1986). Approximately 20 g of dried soil remaining after OM, soluble material, and carbonate removal will be transferred to a 1 L graduated cylinder. Samples are rehydrated using

a sodium hexametaphosphate solution (50 g sodium HMP/L) until graduated cylinders are brought to the 1 L mark. All graduated cylinders are agitated, covered, and left overnight. On the following day the temperature of each cylinder is noted and reagitated on a 3 minute offset. At the 30 s and 45 s time intervals a hydrometer measurement is recorded then averaged for a sand fraction percentage. The settling soil particles are left undisturbed for six hours, upon which another temperature measurement is recorded. This temperature measurement dictates whether the samples need to settle for more time or not, in order to collect a representative clay fraction percentage. After the required time the clay fraction is measured using the hydrometer; the silt fraction is then calculated by subtracting the sand and clay fractions from 100 percent. An experimental blank will also be used to eliminate weight fraction errors due to the sodium hexametaphosphate solution.

2.2.2.8 pH and EC

Both pH and EC measurements are acquired with a 1:1 saturated paste using NRCS Soil Survey Laboratory methods 4F2 (Saturated Paste), 4C1a2a1 (pH), 4F2c (EC extraction), and 4F2b1 (EC measurement) (Soil Survey Staff, 2004). A 600 mL pre-weighed beaker is filled approximately $\frac{3}{4}$ full (~200g) with FM soil collected in plastic sample bags (non-pretreated samples). RO water is added to each sample and stirred lightly until the 1:1 ratio is achieved. Samples are then covered and left undisturbed for 24 hours. pH is recorded using a Thermo Orion 720A+ pH meter directly inserted into the saturated paste. EC is recorded using a Fisher Scientific Accumet AB30 conductivity meter, which measures conductivity on an extracted soil solution acquired by filtering the soil samples remaining in the 600 mL beakers after pH measurement. Soil extract is collected with a filter funnel (no.1 Whatman filter) into a 500 mL Erlenmeyer flask with the aid of a mechanical vacuum pump.

2.3 *Assessment of Particle Collection Techniques for Chemical Characterization*

Synopsis and Objectives

Particles will be collected on PM₁₀ and PM_{2.5} filters as well as with particle sizing instruments (MOUDI) to assess the potential for significant differences in chemical characterization resulting from differences in particle collection methods. 10 sets of filters will be collected through size selective inlets directly from the PI-SWERL exhaust. These will correspond to a subset of the locations where transect measurements will occur. Filter analyses will target the elemental composition of the suspendable particles, organic and elemental carbon concentrations, and ion chemistry. Filters will also be analyzed for hexavalent chromium. At each of the 10 locations where filters will be collected directly from the PI-SWERL exhaust, grab samples will also be collected and processed in the lab. Grab samples will be subjected to conventional resuspension techniques and resulting particles will be sampled through size selective inlets onto filters in a manner identical to that used for “in-situ” sampling from PI-SWERL exhaust. In addition to these filter-based measurements, particle size distributions obtained through a MOUDI impactor both in-situ” through the PI-SWERL exhaust and using the resuspension technique will be compared.

The chemistry of the Salton Sea sediment, especially the inhalable fraction, is critically important for at least two reasons. First, the chemical content of inhalable particulate matter will determine to a large extent the potential for toxicity of suspendable dust. Second, the potential for the particles at Salton Sea to exhibit unique chemical characteristics can allow for application of source apportionment techniques. In laymen's terms, Salton Sea dust may have a unique fingerprint in the region and this fingerprint could be used to determine what fraction of the dust that is measured in the air (at some site downwind) originated from the Salton Sea. It is important that the "fingerprinting" of the Salton Sea sediment and the analysis of potential toxicity of inhalable particulate matter be characterized accurately. The objective of this proposed work is to examine two different techniques for obtaining a sample for such analysis. The collection of particles from the PI-SWERL exhaust, in principle, should lead to a more accurate representation of the dust that is actually suspendable from the surface. However, owing to the principle of operation of the PI-SWERL, there is an inherent tendency to sample some particle sizes with bias over others. In contrast, when grab samples are resuspended in a chamber, particles within the size ranges of interest (nominally less than 10 microns) are collected without bias. However, in the case of grab samples, it is not clear if the parent material actually represents what would be suspendable in the field. In the field, only the surface of the sediment is available for suspension. Grab samples tend to include several inches of soil. Thus, each of these techniques has advantages and disadvantages that need to be characterized in the context of what particles are actually available for inhalation during high wind events.

A secondary objective is to bound the range of chemical compositions of suspendable sediment at the Salton Sea and screen for potentially high concentrations of toxic materials. However, it is important to remember that this effort is primarily aimed at identifying the preferred method for carrying out future measurements, and not at quantifying the toxicity of dust emissions from the Salton Sea.

Methods

Filter samples will be collected at 10 different locations (chosen for variety from among the 8 transect sites) using the PI-SWERL chamber to generate dust emissions and a filter collection apparatus, complete with size selective inlets, to collect suspended PM₁₀ and PM_{2.5} particles. At those same 10 sites, grab samples will be collected for subsequent laboratory resuspension and collection of filters using size selective inlets. For both the in-situ (PI-SWERL) particle collection and the laboratory based technique (resuspension of grab samples, followed by particle collection) particles will be collected on two types of filters, Teflon and quartz fiber. Teflon filters are used for gravimetric analysis (simple PM₁₀ and PM_{2.5} quantitation) and also subjected to X-ray fluorescence (XRF) spectroscopy to quantify elemental composition. Quartz fiber filters are used for analysis of carbon, ions, and hexavalent chromium. In addition to the 10 in-situ samples and the 10 resuspension samples, a Micro Orifice Uniform Deposit Impactor (MOUDI) will be used to collect particle size distributions at 2 sites in the field and also for the 2 corresponding resuspension samples in the lab. This combination of techniques will allow for comparison and contrast of measurements made in-situ with the PI-SWERL as the "resuspension" chamber and those made in the lab using grab samples and a conventional resuspension chamber. Parameters in this comparison will include the particle size distributions, bulk size-selective measurements (PM₁₀ and PM_{2.5}), and associated chemistry.

2.3.1 PI-SWERL and Resuspension Sample Collection

To collect the 10 in-situ samples of PM₁₀ and PM_{2.5}, the Harvard Impactor sampler will be used to sample air out of the exhaust port of the PI-SWERL. The Harvard sampler includes: a) an elutriator to achieve laminar flow prior to entering the size selective inlet; (b) a size selective inlet to remove particles above the nominal cut-point using a 2- μm porous metal plate as impaction substrate and; (c) a 37 mm filter holder. The calibration curves for both PM_{2.5} and PM₁₀ inlets are presented in Figure 2. A standard flow rate of 10 liters/min will be used for this study. A programmable, flow controlled pumping unit, connected by a hose is used to draw air through the sampler inlet.

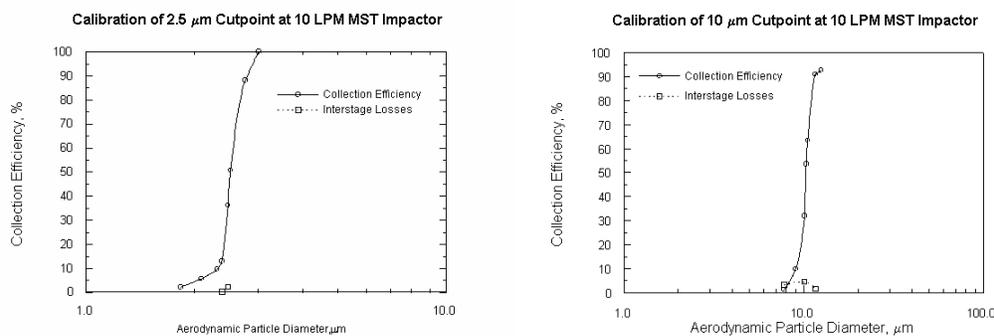


Figure 2. Calibration of PM_{2.5} and PM₁₀ size selective inlets

Particle size distribution samples from the PI-SWERL exhaust will be obtained with a MOUDI impactor. The MOUDI is the same as any inertial cascade impactor with multiple nozzles. At each stage, jets of particle-laden air are impinged upon an impaction plate and particles larger than the cut size of each stage are collected on the impaction plates. Smaller particles with less inertia follow the air streamlines and proceed onto the next stage. The nozzles of each succeeding stage are smaller than the prior stage, giving a higher velocity through the nozzles, and a smaller particle size cut. The air flow continues through a series of eight impactor stages until the smallest particles are removed by the after-filter. The basic sampler is an eight-stage cascade impactor operated at a flow rate of 30 liters/min controlled by a ball valve downstream of the sampler. The 50% cut points are 0.105, 0.148, 0.37, 0.54, 1.0, 1.8, 3.2, 5.6, and 15 μm . The stages of the MOUDI will be used to collect particles for subsequent weighing to obtain size distributions as well as for chemical analyses.

2.3.2 Laboratory Resuspension of Grab Samples

Ten grab samples will be collected alongside the 10 locations where PI-SWERL-based filter collection will be completed. These grab samples will be subjected to a standard resuspension process, allowing for collection of PM₁₀, PM_{2.5}, and MOUDI size segregated samples. The resuspension process is designed to suspend bulk material as a uniform aerosol onto Teflon membrane and quartz fiber filters for gravimetric and chemical analyses. The resuspension process is intended to mimic the natural wind-blown processes of bulk soils, the resuspension of road dust by motor vehicles, or simply provide a uniform deposit of other types of material on a filter for subsequent analyses. The benefits of laboratory resuspension include control over filter loading and size fractionation. Materials are sieved to < 38 μm diameter (400 mesh screen),

resuspended in small quantities using a high velocity air stream, blown into a large chamber for dispersion and mixing, and collected onto filters using Harvard Impactor samplers equipped with PM₁₀ and PM_{2.5} size selective inlets (identical to those used for collection from PI-SWERL). The resuspension chamber is a large cellulose chamber specially constructed to minimize dead space and insure homogeneous distribution of the aerosolized sample introduced at one end. It serves to hold the resuspended material over the sampling inlets until the sample settles to the bottom of the chamber (typically about 3 minutes), while filtering makeup air to eliminate contamination from ambient dust. The chamber is sealed with tape to the resuspension table to insure all makeup air is pulled through the hi-vol quartz fiber filter mounted on the top of the chamber.

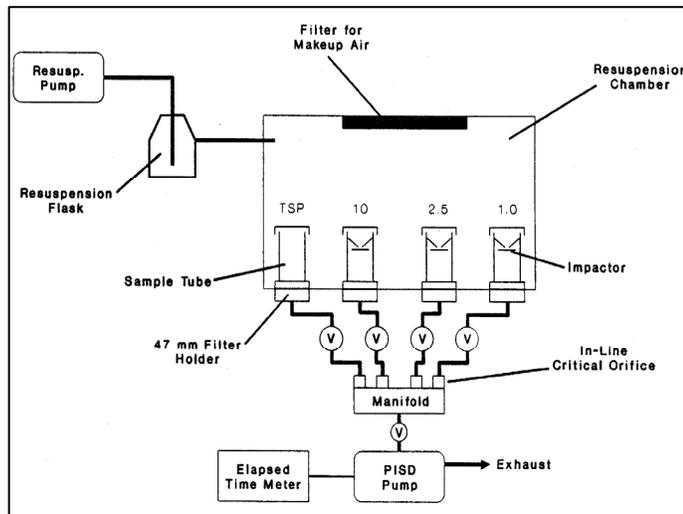


Figure 3. The resuspension chamber

The chamber is sealed with tape to the resuspension table to insure all makeup air is pulled through the hi-vol quartz fiber filter mounted on the top of the chamber.

2.3.3 Laboratory Particle Characterization

Gravimetric Analysis: PM₁₀, PM_{2.5} Teflon filters and MOUDI size fractions

Teflon filters are weighed before and after sampling to calculate the mass of collected particles using a Mettler Toledo MT5 Microbalance. The precision of mass measurements for unexposed and sampled filters is 3 to 8 µg/filter and 5 to 10 µg/filter, respectively. Measurement accuracy is 1 µg. The sensitivity of the Microbalance is 1 µg in the 0 - 250 mg range. In operation, a filter is placed on the weighing pan and the door of the glass draft shield is automatically closed. After approximately 20 to 30 seconds, the filter weight is registered on the digital display of the evaluation unit. Filters are equilibrated and weighed in a temperature and humidity controlled environment (20 to 23 °C and 30% to 40% RH acceptable, 21.5 ± 2 °C and 35% ± 5% RH preferred). Static electrical charge on the filters is dissipated by placing the filters over a radioactive ²¹⁰Po ionizing radiation source for 30 to 60 seconds prior to weighing. Static charge accumulations in the balance itself are reduced by electrically grounding the balance.

Elemental Analysis: PM₁₀, PM_{2.5} Teflon filters

Analysis of aerosol filter samples using the XRF analyzer is based on energy dispersive x-ray fluorescence of elemental components in a thin film sample. The emissions of x-ray photons from the sample are integrated over time and yield quantitative measurements of 38 elements ranging from aluminum (Al) through uranium (U) and semi-quantitative measurements of sodium (Na) and magnesium (Mg). Spectra are collected for a specified length of time and stored for processing. The instrument is calibrated using commercially prepared thin-film standards. Calibration is verified with NIST glass film SRM's 1832 and 1833. Filter loadings between 15 and 1000 µg/cm² may be used, but results for heavily loaded samples may require manual corrections during data processing and results for lightly loaded filters will have concentrations below detection limits for many elements. Typical minimum detection limits for

Teflon membrane filters are presented in Table 1. Precision is $\pm 10\%$ on each element or within ± 3 times the analytical uncertainties, whichever is larger. The analytical uncertainties are propagated from the counting statistics of the sample and background spectra.

Carbon Analysis: PM₁₀, PM_{2.5} quartz fiber filters

The DRI thermal/optical carbon analyzer is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (normally 0.536 cm²) taken from a quartz fiber filter; 2) converting these compounds to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂); 3) reduction of CO₂ to methane (CH₄) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH₄ equivalents by a flame ionization detector (FID). The carbon analyzer can effectively measure between 0.05 and 750 $\mu\text{g carbon/cm}^2$. All quartz filters originating from DRI are pre-fired for a minimum of four hours at 900°C and are acceptance-tested for blank levels before use. Average pre-fired blank levels are $0.41 \pm 0.2 \mu\text{g organic carbon/cm}^2$, $0.03 \pm 0.2 \mu\text{g elemental carbon/cm}^2$, and $0.44 \pm 0.2 \mu\text{g total carbon/cm}^2$. The minimum detection limit (MDL) of the DRI carbon analyzers are:

total organic carbon	0.82 $\mu\text{g/cm}^2$
high-temperature organic carbon	0.81 $\mu\text{g/cm}^2$
total elemental carbon	0.19 $\mu\text{g/cm}^2$
high-temperature elemental carbon	0.12 $\mu\text{g/cm}^2$
total carbon	0.93 $\mu\text{g/cm}^2$

The precision of this analysis has been reported to range from 2 to 4%. The precision of carbonate analysis results is approximately 10%. The accuracy of the thermal/optical reflectance method for total carbon determined by analyzing a known amount of carbon is between 2 to 6%. Accuracy of the organic/elemental carbon split is between 5 and 10%.

Table 1. Lower Quantifiable Limits of Elements Determined by XRF

	MDL (ng/cm ²)		MDL (ng/cm ²)		MDL (ng/cm ²)
Na	236	Cu	2	Sb	21
Mg	89	Zn	2	Cs	3
Al	21	Ga	9	Ba	2
Si	24	As	1	La	3
P	7	Se	6	Ce	4
S	19	Br	4	Sm	6
Cl	5	Rb	3	Eu	20
K	4	Sr	6	Tb	7
Ca	5	Y	4	Hf	42
Sc	17	Zr	10	Ta	35
Ti	3	Nb	8	W	43
V	1	Mo	7	Ir	11
Cr	3	Pd	13	Au	24
Mn	6	Ag	12	Hg	7
Fe	8	Cd	15	Tl	7
Co	1	In	9	Pb	8
Ni	1	Sn	11	U	13

Ion and Ammonium Analysis: PM₁₀, PM_{2.5} quartz fiber filters

Ion Chromatography (IC) using the Dionex 500 is a liquid chromatographic technique based on an ion exchange mechanism and suppressed conductivity detection for the separation and determination of anions and cations. During routine operation, a filtered aliquot of sample is pumped through an ion exchange column where the ions are separated. The eluent ions from this separator column are then neutralized in the anion self-regenerating suppressor (ASRS) Ultra, and the sample ions are converted to their corresponding strong acids for detection with a conductivity detector. The conductivity responses are associated with ionic species by their elution times. Ionic concentrations are quantitatively determined from conductivity peak heights or area. The Dionex 500 is capable of measuring the ions F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, Li⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺ down to the 10 - 30 ppb range. Table 2 lists the LQLs resulting from various ion chromatography analyses. The accuracy is primarily limited by the uncertainties in the standard solution preparation and is typically within ± 5%. Precision as estimated by replicate analyses is in the range of ± 10% to ± 30%, depending on the analyte and the concentration of the analyte.

Table 2. Lower Quantifiable Limits of Anions and Cations Determined by Ion Chromatography

Ionic Species	(µg/m³)	µg/ml
F-	0.0017	0.05
Cl-	0.0017	0.05
NO ₂ -	0.0017	0.05
NO ₃ -	0.0017	0.05
SO ₄ -	0.0017	0.05
Br-	0.0017	0.05
PO ₄ =	0.0017	0.05
Na ⁺	0.05	0.005
Mg ⁺⁺	0.0008	0.010
K ⁺	0.07	0.005
Ca ⁺⁺	0.05	0.025

The measurement of ammonium ion in water and waste water by the Technicon TRAACS 800 is based on the Berthelot reaction. Indophenol blue, a blue dye, is formed when phenol and hypochlorite react with ammonium in an alkaline solution. The sample is drawn into the reaction coils by a peristaltic pump, mixed with alkaline phenol, sodium nitroferricyanide, sodium hypochlorite, and the disodium salt of ethylenediaminetetraacetic acid (EDTA), passed through a heated zone (37 °C for two minutes), and passed through a photocell detector. The absorbance at 660 nm is measured and converted to µg/ml. Brij-35 is added as a surfactant to the EDTA solution to aid in bubble formation. The minimum detection limit of ammonium is 0.022 µg/ml. The precision is less than ±10% and accuracy is typically within ±10%.

Hexavalent Cr Analysis

The method relies on the reaction of 1,5-diphenylcarbazide with hexavalent chromium in sulphuric acid solution to form magenta chromagen that absorbs at λ = 540 nm. The filter is leached with dilute sulphuric acid to dissolve any soluble hexavalent chromium compounds present, the colorimetric reagent (1,5-diphenylcarbazid solution) is mixed with the sample solution, and the color developed is measured after a ten minute delay using a colorimeter. The qualitative and quantitative detection limits for hexavalent chromium are 0.04 µg and 0.14 µg,

respectively. For the minimum air sample volume of 30 litres this corresponds to hexavalent chromium-in-air concentrations of 0.0015 mg/m^3 and 0.005 mg/m^3 , respectively.

2.4 Site Sampling Protocol and Selection Criteria

Synopsis and Objectives

The actual locations for transect lines for conducting PI-SWERL measurements and salt characterization are identified. In total 9 locations for conducting measurements are selected based on the underlying soil properties. These locations will be re-visited three times within a year coinciding with the lowest, highest, and winter average water levels. Although the proposed scope of work is outlined for only one year (for ease of description), it is suggested that the proposed work is repeated annually to maximize the research benefits.

The objective of transect site selection is to identify sediment properties that have an effect on dust emissions. To that end, it is important that the sites represent a diverse range of conditions. This is in contrast to selecting locations for “representativeness”. For currently inundated areas, one tool available for differentiating characteristics of the Salton Sea sediment is texture analysis conducted by Agrarian research (2003) at several depths (5, 10, 15 ft). Using this dataset, our objective was to select sites that are nominally homogeneous in texture as well as sites that are mixtures of several different soil textures.

Methods

A set of eight sites are to be chosen based on the degree of either homogeneity or heterogeneity of soil properties with distance off-shore (Agrarian, 2003) and associated potential emissions. The sampling scheme at each site is chosen to monitor these properties at the same site over time and at new locations at the same site as the water level recedes along parallel transects and is detailed below followed by the site selection process.

For the PI-SWERL step-test measurements, the transect will initially consist of 3 inline consecutive segments, each consisting of 5 measurement locations for a total of 15 measurement locations that span between the starting point and the shoreline (See diagram below). Initially, measurements will be spaced at equal distances from one another. As shoreline recedes (either seasonally or over a period of years), additional measurement locations will be added to the front of the transect (closest to the shore). To accommodate these new measurements (and keep the total locations at 15), measurement locations at the back (near the starting point) will be eliminated on a one out of three basis. This sampling plan results in a thinning of the density of sampling locations over time, while *maintaining* some of the original 15 sampling locations within each segment. This is illustrated in the figure below. The numbers in the figure below represent the segment (initially only 3) and each numeral represents a measurement location.

present time and the more southern site (No. 9) is more accessible but shows a little bit more variation in texture. One of these sites will be chosen for the final subset, but it will be chosen based on a field reconnaissance trip because of the stated uncertainties of accessibility.

The other five sites listed on the map represent heterogeneous sites in soil texture around the Salton Sea and are all proposed transect locations for this research. They vary in other parameters previously measured by DRI in earlier Task Orders, including slope, salt content, variability in the potential emissions, and carbonate content. The two sites located in the south (No. 7, 8) are both based at the delta of a river where the input of new sediment creates a juxtaposition of finer river sediments over coarser wash sediments. These sites also exhibit a very shallow slope and will contribute a rich set of data as the water level recedes for investigating the role of the water level in soil properties and the potential for dust emissions. Additionally, the heterogeneous site in the north (No. 1) is also near the mouth of a river. The site is slightly south of the Whitewater River and the clockwise circulation nature of the currents in that portion of the Salton Sea produces spatially mixed texture sediment characteristics. The other two proposed transect locations are located on older alluvial fan sediments. The site on the eastern side (No. 12) is characterized by a steep slope and a sandy near shore area and a clay-based off-shore region. Although this area will not be exposed very quickly it could exhibit high potential emissions if the sand-sized particles are liberated to sandblast the clay surface. The site on the western side (No. 4) is just north of Salton City and represents an area previously visited during DRI's Task 3 and Task 6 field campaigns. It has a relatively coarse older shoreline but because of its shallow slope has no exposed finer sediments. In addition, earlier work conducted near the site indicates a relatively high carbonate content.

These final 9 sites are to represent the different types of sediments currently found at the Salton Sea. They include 4 sites with relatively "homogeneous" texture (1 sand, 2 loam, 1 clay) as well as 5 sites with that exhibit more of a mix of textures. By choosing a large variety of different sediment types along with other different characteristics the long-term monitoring and measurement at these locations can aid in understanding the staging process of exposed sediments and the related air quality issues that could arise.

3. Research Schedule

The proposed research outlined in the scope of work will aid in answering key questions about how the soil properties, soil mineralogy and potential dust emissions can change over a variety of surface types at the Salton Sea as they become exposed. The schedule is to re-visit the sites three times within a year during the low, high and average (but only in the winter) water levels. These visits would be preceded by a period of preparation for the field deployment of the instrumentation and appropriate purchasing of materials for the soil samples. During the first field campaign in June, 2008 the proposed research given will be conducted including the particle collection for chemical characterization. After this first campaign the resuspension chamber would be fabricated and the procedures associated with it would be conducted, followed by the analyses of the samples from both the resuspension chamber and the field. In addition, the soil analyses would also be conducted immediately following the field campaign including the time-sensitive SEM and XRD procedures. The following field campaigns would be conducted in the later fall months and then in the early spring. These visits would include the PI-SWERL measurements and associated soil analyses (both field and laboratory). The effectiveness of this research would be increased if this schedule was repeated for more than one year.

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