

# Preliminary Chemical Characterization of PM<sub>10</sub> Samples from the New River Playa at the Salton Sea

Briefing Prepared by Vic Etyemezian, Ilias Kavouras, and James King

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## Introduction

Three PM<sub>10</sub> filter samples were collected in February, 2008 on the New River Delta playa surface at the Salton Sea (Figure 1). Sampling was conducted by Mr. Al Kalin on windy days (See Table 1) when windblown dust concentrations were expected to be elevated. Each measurement consisted of two filters, one Teflon and one quartz fiber filter. Samples were collected using Airmetrics MiniVol samplers which operate at a low flow rate of 5 liters per minute. The MiniVols were equipped with a nominal PM<sub>10</sub> size selective inlet (Not a Federal Reference Method) to strip out particles larger than 10 microns in aerodynamic diameter. The samplers were mounted onto a platform so that the inlets were approximately 2 meters above ground level.



Figure 1. Salton Sea and location of New River Playa

Table 1. Summary of filter collection times, mass on filters, and PM<sub>10</sub> concentrations

Sample Name	Start Time	End Time	Exposure Duration (hours)	Teflon Filter ID	Quartz Filter ID	Flow rate (liters/minute)	Mass on filter (µg)	PM <sub>10</sub> Conc (µg/m <sup>3</sup> )	Niland average wind speed (mph)/ max wind gust (mph)/-dir
NRP1	2/13/08 16:35	2/14/08 8:43	16.1	NTST011	NTSQ011	5.0	797	163	16/37 – nw, sw
NRP2	2/20/08 15:35	2/21/08 14:34	23.0	NTST012	NTSQ012	5.0	2063	299	16/39 – w
NRP3	2/24/08 16:50	2/25/08 9:51	17.0	NTST013	NTSQ013	5.0	131	26	10/50 – sw, nw

## Mass and Chemical Analyses Methods

PM<sub>10</sub> mass was obtained from the Teflon filters by gravimetry. X-ray Fluorescence Spectrometry (XRF) was conducted on Teflon filters to obtain concentrations of elements with atomic mass equal to and larger than that of sodium (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, U). A portion of each quartz fiber filter was extracted with water for ion analysis. Chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>) anions were analyzed using ion chromatography. Sodium (Na<sup>+</sup>), Magnesium (Mg<sup>2+</sup>), potassium (K<sup>+</sup>), and Calcium (Ca<sup>2+</sup>) cations were analyzed using atomic absorption spectrometry (AA). Ammonium (NH<sub>4</sub><sup>+</sup>) was analyzed using automated colorimetry (AC). Another portion of the quartz filter was used for carbon analysis using the Thermal Optical Reflectance (TOR) method. TOR provides estimates of organic carbon in 4 different fractions (OC1, OC2, OC3, and OC4), elemental carbon in three fractions (EC1, EC2, and EC3), carbonate (CO<sub>3</sub><sup>2-</sup>) carbon, and organic carbon that is pyrolyzed during the thermal cycle (OP).

## Preliminary Results

### PM<sub>10</sub> concentrations

The 24-hour (measured from midnight to midnight) EPA National Ambient Air Quality Standard for PM<sub>10</sub> is 150 µg/m<sup>3</sup>. None of the samples collected as part of this preliminary effort was run for a full 24-hours and samples were not started at midnight. Furthermore, the MiniVol is not a federally approved method for PM<sub>10</sub> measurement. Thus, these data cannot be used to determine compliance with the NAAQS standard as such. Nevertheless, it is worth noting that the measured concentrations for NRP1 and NRP2 exceeded 150 µg/m<sup>3</sup>. In the case of NRP2, the measured concentration was quite high at 299 µg/m<sup>3</sup>. The NRP3 PM<sub>10</sub> concentration was relatively low in comparison, indicating that windblown dust emissions were not as prolific. While the maximum wind gust at Niland was recorded at 50 mph during the NRP3 sampling period, average wind speeds were lower compared to the NRP1 and NRP2 periods, suggesting perhaps that the windblown dust events of NRP1 and NRP2 were comparatively longer-lived.

### Ion Chemistry

All three samples exhibited high concentrations of ions (Figure 2). Prevalent anions included chloride and sulfate, while prevalent cations were sodium, magnesium, and calcium. Carbonate species are included in the figure, but it is not known if they were present in the samples as ions or as calcite. The NRP 1-3 ionic content can be compared to other soil samples collected from various locations in the desert southwest (Soil Dust 1 – 4 in the Figure). It is clear that the samples collected at the Salton Sea are heavily enriched with respect to sodium, sulfate, and chloride.

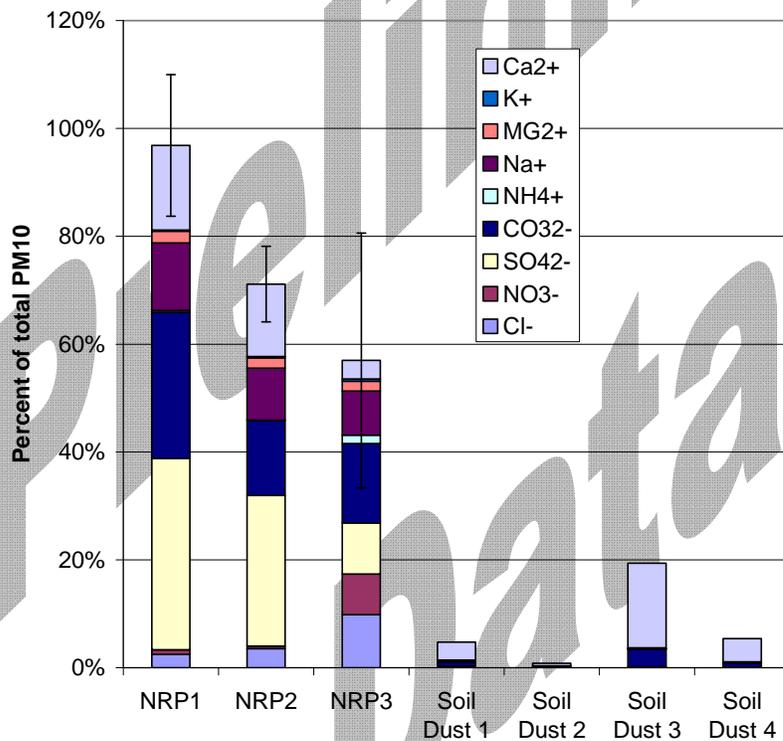
These results are consistent with earlier playa salt crust characterization conducted at the Salton Sea (DRI Task 6). In that work, salt crust samples were collected from various locations around the Salton Sea and subjected to mineralogical analysis. In general, it

was found that crust was composed of mixtures of halite (NaCl), bloedite ( $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ), glauberite ( $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ ), calcite ( $\text{CaCO}_3$ ), thenardite ( $\text{Na}_2\text{SO}_4$ ), hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), and mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ); soluble salts comprised 40 – 65% of the dry crust and calcium carbonate comprised 4 - 12%.

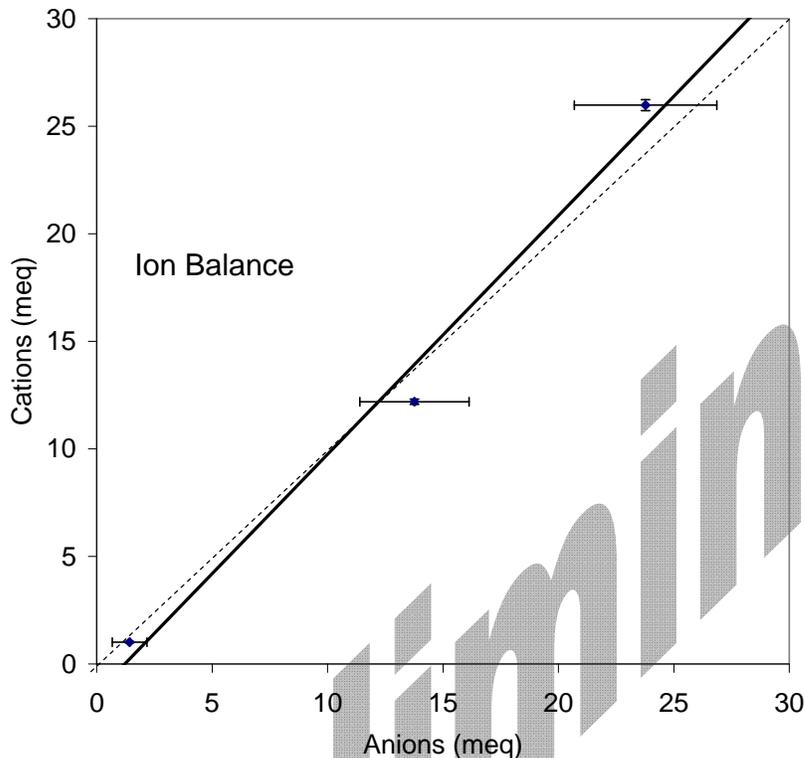
There are other ions (e.g. phosphate, selenate, organics), that could be included in future analyses for a more complete accounting of the ionic species. However, as Figure 3 shows, the positively and negatively charged ions are nearly in balance indicating that the major ionic species have been identified.

### Chemical Signatures – Source Uniqueness

From the perspective of long-term air quality monitoring at the Salton Sea, an important question is “Can particulate material suspended from playa-like regions around the Salton Sea be confidently differentiated from other sources?” That is, if  $\text{PM}_{10}$  (or  $\text{PM}_{2.5}$ ) is sampled near the Salton Sea, is it possible to determine what fraction of the particulate matter was emitted from exposed playa-like areas and what fraction is from other sources? The answer to this question depends on how much the chemistry of  $\text{PM}_{10}$  dust from playa-like surfaces is distinguishable from the chemistry of other sources of dust.

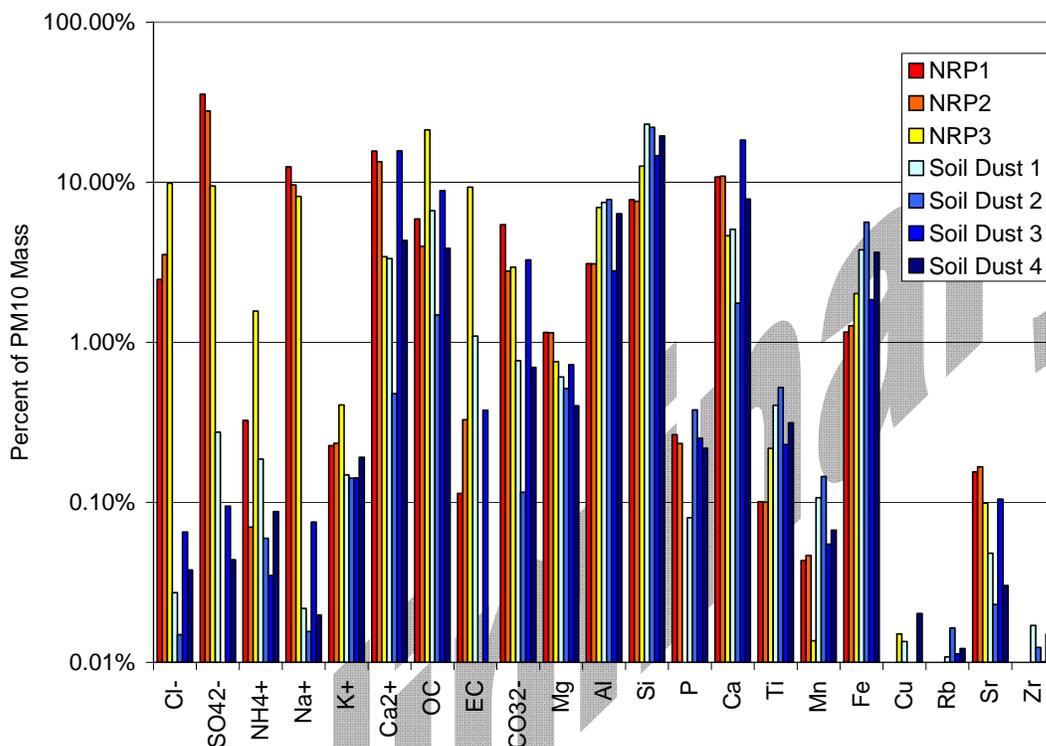


**Figure 2. Ionic species (including carbonate) as percent of measured  $\text{PM}_{10}$  mass. NRP 1, 2, and 3 are samples collected on the New River Playa at the Salton Sea. Soil Dust 1, 2, 3, and 4 are resuspended soil samples collected from locations in the Mojave, Chihuahuan, and Great Basin Deserts.**



**Figure 3. Charge balance of NRP 1-3 samples. Anions include carbonate.**

Figure 4 shows a comparison of the relative abundances of different chemical constituents between the New River Playa samples (NRP 1-3) and other soil dust samples (Soil Dust 1-4) from the southwestern United States. Compared with Soil Dust 1-4, NRP 1-3 are extremely enriched with respect to  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Na}^+$ . The NRP samples are also significantly enriched with respect to  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ , Mg (elemental magnesium), and Sr (strontium). The NRP samples are depleted (compared to Soil Dust) with respect to aluminum (Al), silicon (Si), phosphorous (P), titanium (Ti), manganese (Mn), iron (Fe), rubidium (Rb), and zirconium (Zr). All in all, the chemical signature from the NRP samples is distinctly different than the usual soil dust signature. This suggests that chemical fingerprinting techniques such as Chemical Mass Balance (CMB), factor analysis (FA), and Positive Matrix Factorization (PMF) could successfully be used to determine what fraction of airborne  $\text{PM}_{10}$  collected on a filter originates from windblown dust from playa-like areas around the Salton Sea.



**Figure 4. Comparison of chemical profiles of NRP 1- 3 with resuspended soil dust from southwestern US.**

### Air Toxics

Trace metals that are also toxic such as chromium (Cr), arsenic (As), selenium (Se), cadmium (Cd), antimony (Sb), and lead (Pb) were found in levels that were near or below the detection limit of the analysis techniques. This means that none of those metals was found in huge amounts. However, since some elements and compounds can be toxic at even small concentrations, more sensitive techniques are required to rule out potential hazards from inhalation exposure. Methods such as ICP-MS have much lower detection limits than XRF and are less subject to interferences. Likewise, quantitation of organic toxics would require more sensitive techniques. Furthermore, due to the trace concentrations of toxic compounds, it is likely that much larger samples would be needed for reliable analysis. This in turn may require use of higher flow rate filter collection techniques such as Hi-Volume samplers.

### Summary

Three filter samples were collected using low volume samplers equipped with PM<sub>10</sub> size-selective inlets. They represent periods with high winds when local windblown dust is expected to be present. All filters were collected at the New River Delta playa along the southern shoreline of the Salton Sea.

Chemical analysis of this limited sample revealed:

1. 24-hour  $PM_{10}$  concentrations may exceed EPA NAAQS standards. A true “24-hour sample” from midnight to midnight was not collected as part of this study.
2. Air samples collected at the New River Playa exhibited very high salt concentrations. This is likely the reason that local residents sometimes complain of “burning eyes” during windy conditions. Sodium, magnesium, calcium, chloride, and sulfate were found in much higher quantities in air samples from the New River Playa than in other soil dust samples from the southwestern US.
3. The chemical signatures of air samples from the New River Playa are substantially different from the chemical signature of other sources of soil dust. In addition to the enrichment with respect to salt content, NRP samples were enriched with respect to Mg and Sr and depleted with respect to Al, Si, P, Ti, Mn, Fe, Rb, and Zr. This chemical differentiation indicates that source apportionment techniques can likely be used to discriminate between background soil dust  $PM_{10}$  and  $PM_{10}$  generated locally due to windblown dust.
4. More sensitive analytical techniques and higher sample loadings are required for accurate quantitation of toxic trace metals and organics. Data from this preliminary effort cannot be used to ascertain whether or not toxic compounds are present at levels that may pose a health risk.

Preliminary  
Data