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Characterizing the Impact of Salton Sea Water Management and Restoration Practices on Regional Air Quality

Principal Investigators:

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Technical Completion Report for project: NIWR2015CA335B
Project period: March 1, 2015 – February 28, 2017

Project Summary

Understanding particulate matter (PM) composition around the Salton Sea is particularly important as the water level decreases and playa is exposed, potentially greatly increasing playa-sourced dust emissions in the Salton Sea Basin. During this reporting period, the elemental composition and sources of ambient, size-selected particulate matter (PM), collected in 2015 and 2016 at the Salton Sea, California (**Figure 1**), were investigated. PM and soil samples were analyzed for total Ca, Na, As, Al, Cr, Fe, Mn, Ni, V, Ba, Cd, Co, Se, Ti, and K. Al-referenced enrichment factors (EFs) and factors resolved from positive matrix factorization (PMF) were used to quantify the influence of playa and desert soils as dust sources in the region. Playa soils were found to be significantly enriched in Ca, Na, and Se relative to desert soils. PM samples were significantly enriched in Se, V, Cr, Ni, As, Ba and Fe when compared to both soil types. PMF modeling of PM₁₀ best resolved the data with four factors, identified as Playa-like, Desert-like, Ca-rich, and Se. Seasonal variation within PM₁₀ Se concentrations, PM Se EFs, and the PMF Se factor may be evidence of a seasonal cycle of Se volatilization in the Salton Sea Basin. Extrapolating from major elemental concentrations within PM₁₀, playa-like and desert-like sources are estimated to contribute to a daily average of 8.9% and 45% of PM₁₀ mass, respectively, during this sampling period. These results provide evidence of the importance of playa as a source of PM mass and a controlling factor of PM composition within the Salton Sea Basin.

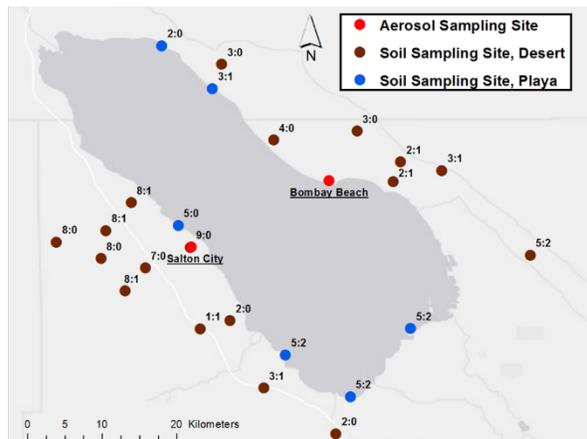


Figure 1. Map of soil and aerosol sampling sites. Labels represent the number of ED-XRF and ICP-MS analyzed soil samples from each site, presented as ED-XRF:ICP-MS.

Research Program

During March 1, 2016-Feb. 28, 2017, wet-lab analysis of aerosol and soil samples and interpretation of data were completed to determine sources of aerosols in the region using Positive Matrix Factorization (PMF). As shown in **Figure 1**, seven playa and ten desert samples were analyzed for elemental composition with inductively coupled plasma, mass spectrometry (ICP-MS). Twenty-five playa and 88 desert samples, collected from a wider area around the Salton Sea, were also analyzed via energy dispersive X-ray fluorescence spectroscopy (ED-XRF) to confirm representativeness of the smaller sample set analyzed by ICP-MS. ED-XRF and ICP-MS elemental analysis revealed consistent and unique characteristics of playa and desert soil.

For both techniques, playa soils were observed to have significantly ($p \leq 0.05$) larger elemental abundances of Na, Ca, and Se and desert soils were observed to have significantly larger abundances of Ti and Mn. The larger ED-XRF dataset also revealed significantly greater abundances of Al, Fe, K, V, and Cr within desert soils. Notably, arsenic was not significantly different between playa and desert soils using either techniques, and Cd was observed at near

or below detection limits of both techniques. Given these trends, increased emissions of PM from playas are expected to increase abundances of Na, Ca, and Se in airborne dust particles relative to typical desert soil emissions.

Mass concentrations of major elements (Al, Fe, Na, and Ca) were found to be within the range of previously observed values in rural areas of the American southwest. PM₁₀ Na concentrations averaged at 482 ng m⁻³. Although trace elements do not significantly increase the mass of PM, their concentrations are of interest due to their potential to increase toxicity. Cd, Se, Cr, As, Mn, and Ni can increase the toxicity of PM at high concentrations. Median mass concentrations of each of these metals were below California EPA reference exposure levels (RELs) for chronic toxicity, by factors of 77, 14e3, 18, 250, 7, and 2, respectively. Nickel was the only element to breach its REL during sampling, during 3 of the 25 sampling periods.

This finding indicates that these metals likely do not increase the likelihood of PM₁₀ toxicity at conditions encountered during this campaign. Mass concentration differences between seasons were not significant for most elements. Only Na and Se displayed significant differences ($p \leq 0.05$) between summer (at Salton City and Bombay Beach) and winter (at Salton City) sampling. Average Na concentrations were 850 ± 670 ng m⁻³ and 370 ± 159 ng m⁻³ during the summer and winter, respectively.

Average Se concentrations were 2.1 ± 2.7 ng m⁻³ in summer and 0.3 ± 0.4 ng m⁻³ in winter. The lack of a seasonal difference in concentrations of the major elements other than Na suggests that separate factors control Na emissions and common desert emissions. Such variation would be expected from a playa source, as playa emissions are thought to be influenced by additional meteorological factors such as relative humidity (RH) (Buck et al., 2011), while typical dust emissions are not thought to be as sensitive to RH. Larger oscillations in RH are thought to affect the hydration state of playas, increasing irregularity in mineral structure and potentially increasing emissivity (Buck et al., 2011).

Enrichment factors (EF) have been used widely in atmospheric and soil literature to track normalized changes in composition that are driven by anthropogenic or geologic forces. For this study, Al is used as the normalization element because it is relatively immobile in soils and has been shown to be conserved upon emission. EF in soils and aerosol samples were calculated using the following equation:

$$EF = \frac{(M_{Measured}/Al_{Measured})}{(M_{UCC}/Al_{UCC})}$$

Where M_{measured} is the ICP-MS measured mass concentration of an element within a sample (ppm), A_{measured} is the ICP-MS measured mass concentration of Al within a sample (ppm), and M_{UCC} and A_{UCC} are the analogous values for the UCC. Upper Continental Crust (UCC) composition as reported by Wedepohl (1995) was used. Samples with enrichment factors of 1 have the same elemental ratios as the UCC, values larger or smaller than 1 indicate differences from the UCC. EF

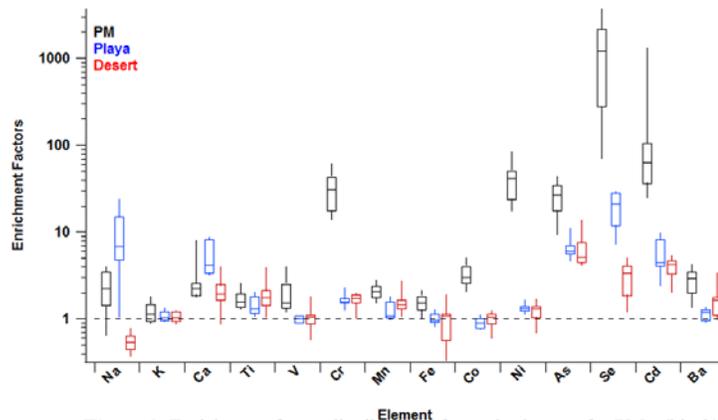


Figure 2. Enrichment factor distributions for each element for PM_{10} (black), playa soils (blue), and desert soils (red). Box and whiskers highlight 10th, 25th, 50th, 75th, and 90th percentiles.

distributions for playa soil, desert soil, and PM_{10} are shown in **Figure 2**. Playa soils were significantly ($p \leq 0.05$) more enriched in Na, Ca, Se than desert soils. PM_{10} was significantly more enriched than both soil types in Se, V, Cr, Ni, As, Ba and Fe. Minor and trace elements were more concentrated on smaller particles, consistent with contributions from anthropogenic emissions, while the fractions of crustal elements, those with high concentrations in the upper continental crust (Fe, Al, Ca, Ti), were concentrated on larger particles. Iron was the only major element significantly enriched in PM_{10} relative to both soil types. A combination of suspension enrichment and anthropogenic contributions are reflected in the observed enrichments in PM_{10} . PM_{10} was significantly enriched in Na relative to desert soils, but not significantly different than playa soils.

This finding shows that Na enrichments in PM_{10} may arise from mixing of two sources, i.e., playa and desert soil. This enrichment suggests that playa emissions are contributing significantly to the Na within PM_{10} . Selenium displayed the largest enrichments among the trace elements and the strongest seasonal dependence: median summer and winter Se EFs were 1890 and 257, respectively. The seasonal variations in EF of Se, As, and Na, but not in elements associated with desert soils, indicates that sources of these elements are likely controlled by factors different than those controlling traditional desert emissions.

The four factors produced by PMF to describe the major sources of PM_{10} were identified as playa-like, desert-like, selenium, and Ca-rich. Notably, elements normally associated with anthropogenic emissions (such V, As, Ni, Cr, and Ba) which were observed to be enriched in PM relative to playa and desert soils were not isolated in an independent factor, likely due to the low concentrations and relatively high uncertainties associated with these elements. The playa-like factor was characterized by a prominence of Na and the presence of dust tracers such as Fe, K, and Ti.

The desert-like factor was identified by the prominence of Al, Fe, K, and Ti, all of which are major elements in the earth's crust and have been observed to be prominent in regional deserts' soils. The desert-like factor is likely sourced from nearby desert and mountain surfaces. The Ca-rich factor has been found in previous source apportionment studies and often attributed to

construction, secondary dust sources such as limestone or gypsum deposits, or resuspension of road dust. The Se factor was identified by the prominence of Se; 77% of all sampled Se is attributed to this factor. Given that coal combustion is the major anthropogenic source of Se and the lack of coal usage in this region, the Se factor was likely not anthropogenic in nature. One other potential Se source is Se volatilization and condensation onto PM. In this study, summer median Se EFs were seven times greater than winter, suggesting that Se volatilization from the sediments/soil and condensation onto PM is an important process at the Salton Sea. If Salton Sea playas have a greater rate of Se volatilization than Salton Sea sediments, volatilization may have become an increasingly important process after the relatively recent exposure of playas.

To quantify the burden of PM₁₀ emission sources at Salton Sea, the mass contribution of major sources needs to be calculated. PM mass associated with the Desert-like factor can be estimated using the elemental concentration of Al, Ca, Fe, and Ti in dusts and the formulation from the Interagency Monitoring of Protected Visual Environments (IMPROVE) program and modified by Clements et al. (2013). Using this method, and averaging over the sampling periods, the average crustal contribution was $45.2 \pm 26.4\%$ of the total PM₁₀ mass, indicating that on most days crustal sources played a major role in the observed PM₁₀ mass loadings at these sites.

An equation was developed using our PMF results and the playa mineral frequencies described by Buck et al. (2011). Assuming this subset of playa samples is representative of emissive playas around the Salton Sea, the ratio of Na to total mineral mass of a typical playa can be calculated. Next, using the PMF estimated Na concentration of the Playa-like factor, the total mass contribution of playa sources can be estimated, assuming that mineralogical frequencies are conserved through the emission process. Using this estimation, playa sources contributed at an average of $8.9 \pm 5.6\%$ to PM₁₀ mass over all sampling periods. The contribution of playa to PM at these sites is measurable and not negligible at current levels of playa exposure.

These contributions will likely increase with increasing playa exposures, aggravating air quality and ecological issues in the region. High dust emission events with prevailing winds crossing over the exposed playas were not sampled during this project. Since PM emissions are controlled in part by wind speed and the presence of airborne particles to aid in saltation, playa emission rates are expected to increase under higher wind conditions. Therefore, the observations here may only represent the lower bounds of current playa contributions to PM₁₀. Future PM source apportionment studies need to resolve the contributions of playas during high mass events, as playa contributions will likely be much higher and playa sources increasingly more important.

Information Transfer/Outreach Program

- Oral presentation by PI's Ph.D. student at the Annual Meeting of the American Association for Aerosol Research
- A manuscript summarizing the results is in review at *Environ. Sci. Technol.*
- PI and her Ph.D. student have introduced the project to Riverside County high school students as part of an outreach program lead by the PI.

Preliminary results were discussed with a freelance writer for *News Deeply, Water Deeply*

Student Support table

A Ph.D. student was partially supported by this grant (equivalent to 12.75% time out of a year). The remaining support for this student was through UCR Graduate Division Fellowship, Dean's Fellowship, and Departmental Teaching Assistant Funds.

	Students Funded Through This Project		Supplemental Awards	Total
	Federal Funding	State Funding		
Professional Researchers	0	0	0	0
Masters Students	0	0	0	0
PhD. Students	0	0.1275	0.8725	1
Acad. Coordinator	0	0	0	0
Other Acad./Researchers	0	0	0	0
Professor/summer	0	0	0	0
Total	0	0	0	0

Publications from prior projects

The Effect of a Receding Saline Lake (The Salton Sea) on Airborne Particulate Matter Composition, Frie, A.L., J.H. Dingle, S.C. Ying, and R. Bahreini, Submitted to Environ Sci. Technol. (April 2017)

Metal Composition and Source Identification of Particulate Matter around a Shrinking, Saline Lake (Salton Sea) via Pb Isotope and Metal Ratio Analysis, Frie, A.L., J.H. Dingle, S.C. Ying, and R. Bahreini, American Association for Aerosol Research Annual Meeting, Portland, OR, Oct. 2016.

California Is Running Out of Time to Save the Salton Sea, by P. Nagappan, Aug. 31, 2016
<https://www.newsdeeply.com/water/articles/2016/08/31/california-is-running-out-of-time-to-save-the-salton-sea>