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Understanding the Connection Between Gypsum Blooms and Human Health at the Salton Sea

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Understanding the Connection Between Gypsum Blooms and Human Health at the Salton Sea

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Introduction

The Salton Sea is a closed, hypersaline lake in the Imperial Valley of Southern California (fig. 1). Over geologic time scales, the basin has intermittently flooded and evaporated by the natural movement of the Colorado river. It was last filled from an accidental diversion of the Colorado river in 1905, creating what we know today as the Salton Sea (Frie et al., 2017; Voyles, 2021).

The Imperial Valley is one of the most productive agricultural regions in California, and due to a myriad of disparities including economic and environmental issues, the region has the highest rate of childhood asthma in California (Doede et al., 2020). The area surrounding the Salton Sea may be specifically vulnerable to health disparities due to the airborne toxins emitted from the sea and its playa, or dry lakebed (Doede et al., 2020). Playa exposure can create a large area of highly emissive surfaces and have a high potential to act as dust sources because of their lack of vegetation and emissive salt crusts (Frie et al., 2017). The Salton Sea has received little water input over the past few decades, and because of this, the sea has been receding, exposing more and more of its playa and significantly increasing the major ion concentrations in its water (Holdren & Montaño, 2002). These increasing ion concentrations have led to precipitation of minerals like halite and gypsum. Gypsum is the most common sulfate mineral on earth and can precipitate with increased calcium and sulfate ion concentrations and fluctuations in temperature (Reiss et al., 2021). Because of this, gypsum has been known to precipitate in closed saline lake environments with playas with salt crust and botryoidal morphology. The degradation of these salt crusts can produce sand-sized aggregates that contribute to dust emissions (Sweeney et al. 2016). In other dry saline lake beds, wind has been known to carry dust and toxins for up to 500 km^2 (Indoitu et al., 2015). In an arid climate like the one found at the Salton Sea, low precipitation and ground heating from the lowering water levels and exposed lakebed can increase airborne particulate matter, which can have adverse effects on lung health (Christian-Smith et al., 2015).

In a 2002 study, Holdren & Montaño reviewed past major ion surveys of the Salton Sea. They found that the gypsum saturation level was reached at the Salton Sea in 1989 and from their own major ion survey, deduced that the sea had become supersaturated with gypsum. They estimated 2-3 times the average salt inflow would be required for the sea to reach equilibrium with respect to calcite and gypsum, yet salt levels were expected to rise at a slower rate than from when the gypsum saturation level was reached in 1989 (Holdren & Montaño, 2002). Over time, the Salton Sea has become a site for a phenomenon known as gypsum blooms, where large amounts of gypsum precipitate over the surface of the sea. Upwelling, caused by strong winds in the sea, causes sulfur in the water to oxidize and form gypsum crystals during heat mixing which creates deoxygenation of the water column, creating an anoxic zone that can be deadly to wildlife (Ma et al., 2020; Watts et al., 2001). Gypsum blooms in the sea have been increasing in frequency since 2008 and can affect a body of water for weeks. As of the past five years, more than 40 days out of the year have significant gypsum blooms, where more than 25% of the total sea surface area is covered, with the largest bloom covering 684 km^2 or almost 70% of the sea's surface (Ma et al., 2020). Gypsum blooms appear to have some seasonal and spatial variability as well. With the largest gypsum blooms happening in the summer months and blooms in the eastern and southern regions occurring earlier in the year than in western and northern areas of the sea (Ma et al., 2020). This could be because higher water temperatures may increase gypsum saturation. Gypsum has the ability to incorporate arsenic into its lattice structure, especially at high pH, which has led to many concerns about contamination and lung health (Wang et al., 2018; Zhang et al., 2015). Gypsum also has the ability to incorporate selenium, with the secondary release of selenium from gypsum being of great concern to human health, leading to body deformity, neural disorders, and even mortality (Tian et al., 2022). Gypsum and selenium at the Salton Sea both follow a similar seasonal pattern, with gypsum blooms and selenium enrichment being the strongest in the summer months (Ma et al., 2020; Frie et al., 2017). However, there are still a lot of gaps concerning how the composition of the sea affects these blooms and whether or not they incorporate these metals.

The current study attempts to use a new major ion survey of the sea to understand the current state of the sea, specifically its ability to precipitate gypsum. It does not confirm the presence (or absence) of trace elements within gypsum but does provide a first step towards understanding the potential risks concerning possible incorporation of arsenic and selenium into gypsum.

Major ion data from the sea will be closely compared with the most recent major ion survey from two decades prior to help give context into the changes of Salton Sea chemistry over time and what we may expect in the future. It is hypothesized that major ion concentrations will have increased substantially from Holdren & Montaño's survey in 2002, and that the sea will still be supersaturated with gypsum.

Methods

Field Work/Sample Collection

Samples from the sea and surrounding inlets were collected in November and December 2022 as well as February and April 2023. November samples were collected by student researchers from USD. All other samples were collected by the Salton Sea Environmental Timeseries Community Science Group and transported to the University of San Diego (USD) for analysis. This collaboration resulted in four consistent sites within the sea (SS1, SS6, SS7, and SS8) being collected through all sample dates.

Figure 1. Site map of all sites taken at Salton Sea. Sites in orange and green were only sampled once. Sites in blue were sampled throughout the sample period.

Major Ions

After transport to USD all major ions were analyzed within the EOSC environmental laboratories using four different methods.

Alkalinity

Alkalinity was measured using a Hach Alkalinity Digital Titrator Test Kit Model Al-DT. Sea water samples underwent a 1:2 dilution with 50mL of deionized water mixed with 50mL of sample. Inlet waters were not diluted.

Chloride

Chloride was measured by titration with silver nitrate until color change was observed. At least two replicates were analyzed for each sample. Sea samples were diluted prior to titration. Inlet waters were not diluted.

Calcium, Magnesium, Potassium and Sodium

Major cations (Na^+, Ca^{2+}, K^+, Mg^{2+}) were measured by Agilent 5800 ICP-OES. Sea samples underwent a 100 times dilution in 2% nitric acid. Inlet samples were acidified but not diluted.

Sodium in Salton Sea Waters

Sodium was additionally measured using a Hanna Instruments FC300 Combination Sodium Electrode because it was often reported outside the calibration range of the ICP. Sea samples underwent a 5:1 dilution with deionized water. Inlet samples were not measured by probe as their sodium concentrations were low enough to be accurately measured by ICP.

Sulfate

Sulfate was measured by SEAL Analytical AQ-400 colorimeter. Sea samples underwent a 100 times dilution in deionized water while inlet waters were not diluted.

Quality Assurance/Quality Control

QA/QC checks were performed with charge balance error, RSD (accuracy check), and RPD (precision check) being accounted for throughout analysis. Acceptable ranges were within +/-5 to 7%.

Data Analysis

Gypsum saturation indices were calculated by hand using Debye-Hückel and Truesdell-Jones equations, dielectric constants, parameters, and models. Temperature values were obtained from the Salton Sea Environmental Timeseries (see: https://saltonseascience.org/). Piper diagrams were also created to assess water chemistry and changes over time.

Results

The current major ion survey showed that Salton Sea water samples were relatively close to being ionically proportional with sea water, while inlet samples plotted as mixed waters (fig. 2). However, over time, while the proportions of ions with the Salton Sea seem to mirror sea water, they are exponentially increasing in concentration (fig. 5). Even examining the past two decades, it appears that the major ion concentration of the sea has increased save for Ca^{2+}, K^{+}, SO_4^{2-} and HCO_3^{-} (Table 1). Over the current sample period, results show that there is some seasonal variation of ion concentrations within the sea. Notably, there is a dip in sodium and chloride concentrations in December and April (fig. 3). Spatially within the sea, some variation also seems to be occurring. Specifically, SS6 has a significant drop in sodium and chloride while SS7 has a smaller drop in magnesium but an increase in calcium. Aside from these two sites the major ion concentrations are relatively consistent across each site (fig. 4). Interestingly, regardless of these seasonal variations, gypsum continues to precipitate within the sea (Table 2, fig. 6).

Table 1. Average major ion composition of the Salton Sea through each sample period compared to data from (Holdren & Montaño, 2002).

Average Concentration (mg/L)	November 2022	December 2022	February 2023	April 2023	Holdren & Montaño 2002
Na^+	22499	19349	22144	17819	12370
K^+	380	308	444	292	258
Ca^{2+}	693	573	865	661	944
Mg^{2+}	1716	1580	2440	1779	1400
Cl^-	30930	26479	28966	26933	17240
HCO_3^-	188	305	350	377	245
SO_4^{2-}	10808	11804	16995	9834	10500

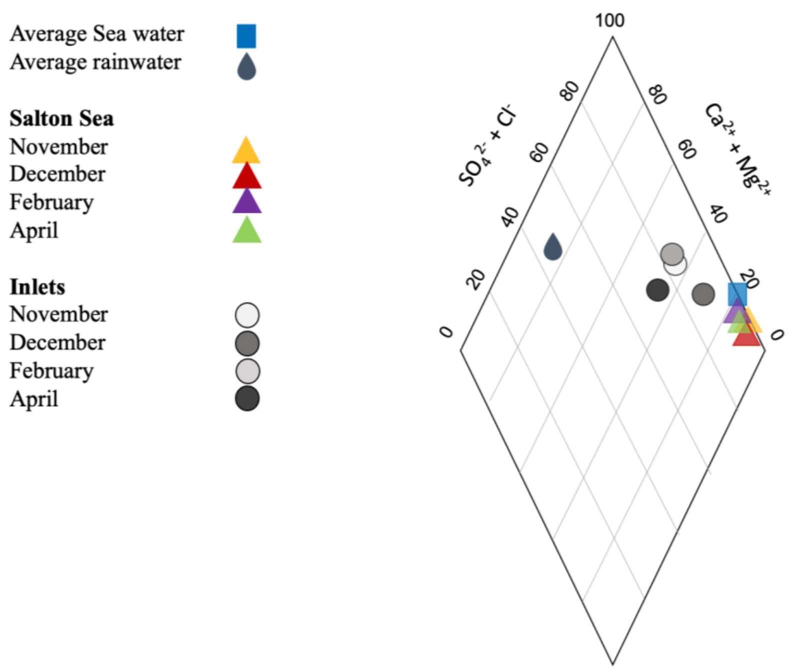

Figure 2. Piper Diagram showing proportionality of major ions within the Sea and 'fresh' inlets compared to average rain and ocean water.

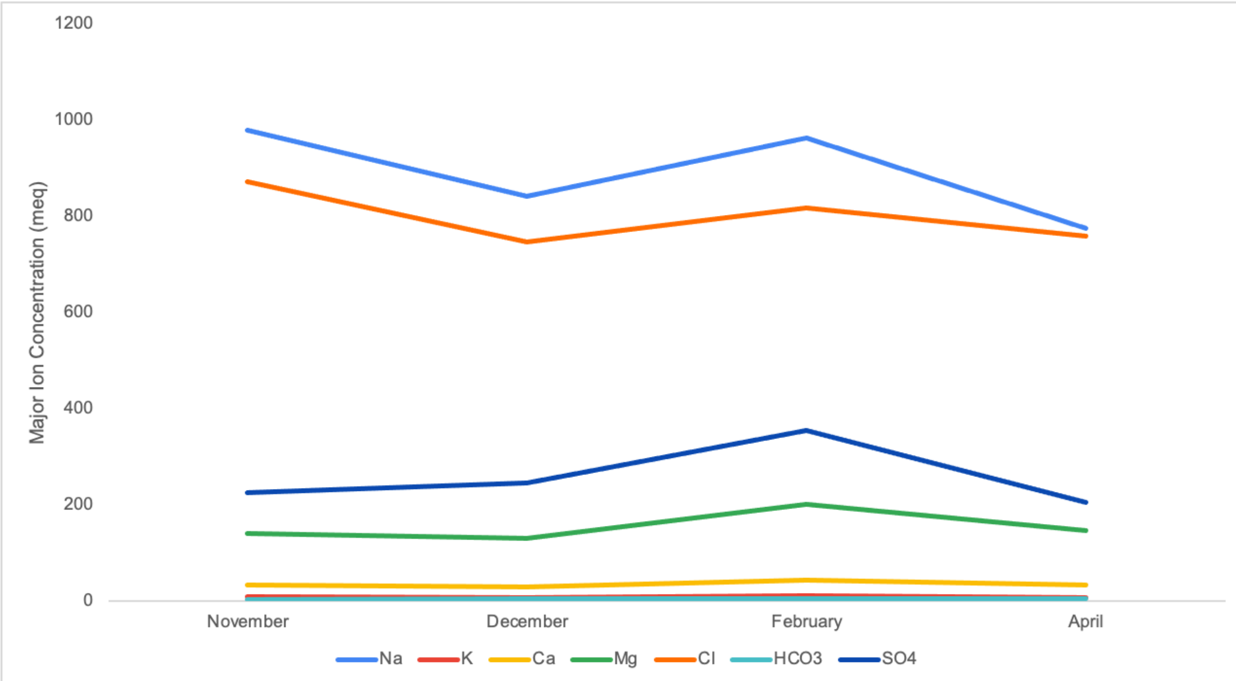

Figure 3. Major Ion concentration (meq/L) across the current sample period.

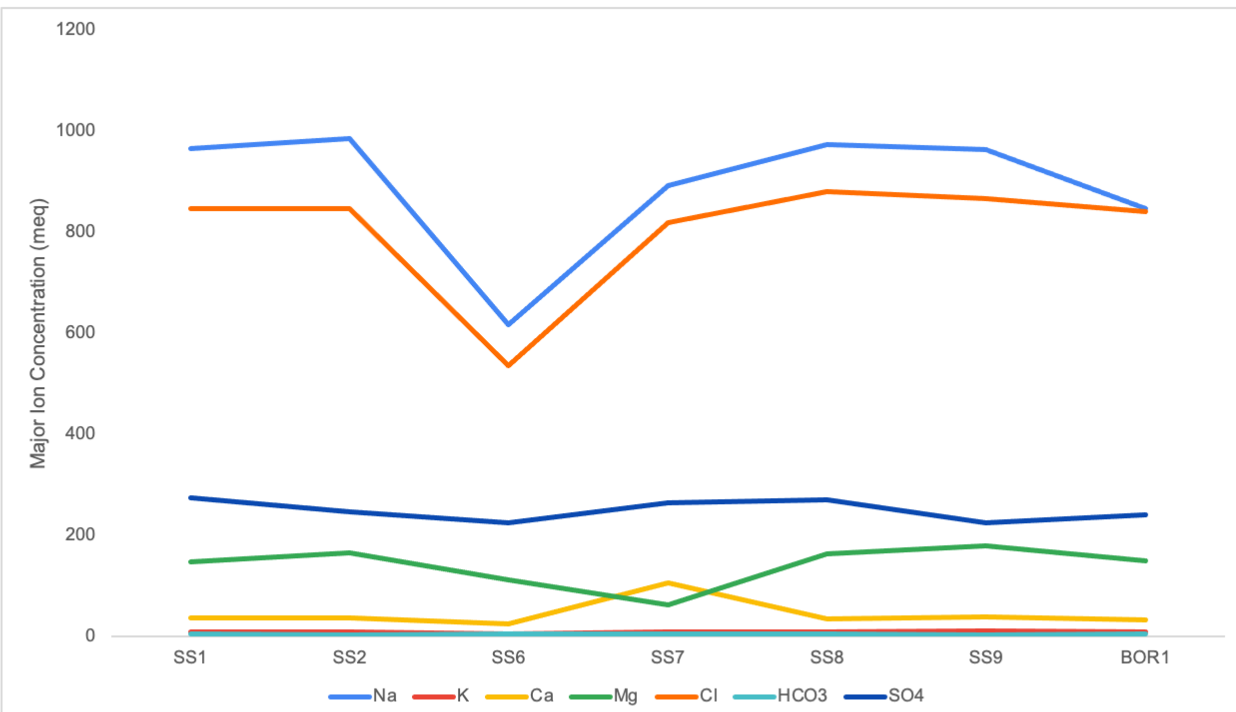

Figure 4. Major ion concentrations (meq/L) across each sample site, averaged across all sample periods.

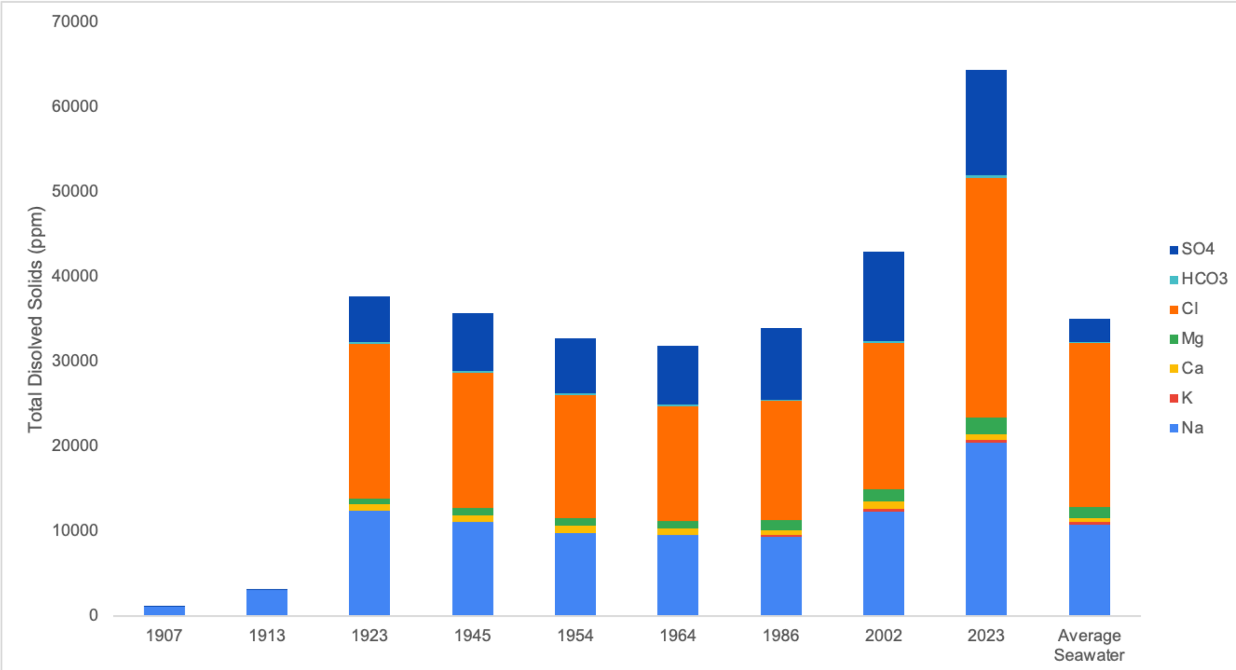

Figure 5. Total dissolved solids (mg/L) compared over time and to average seawater. The 2023 data comes from the current study while all previous years come from Holdren & Montaño (2002), Cory, (1915), Hely, (1966), and Setmire, (1990).

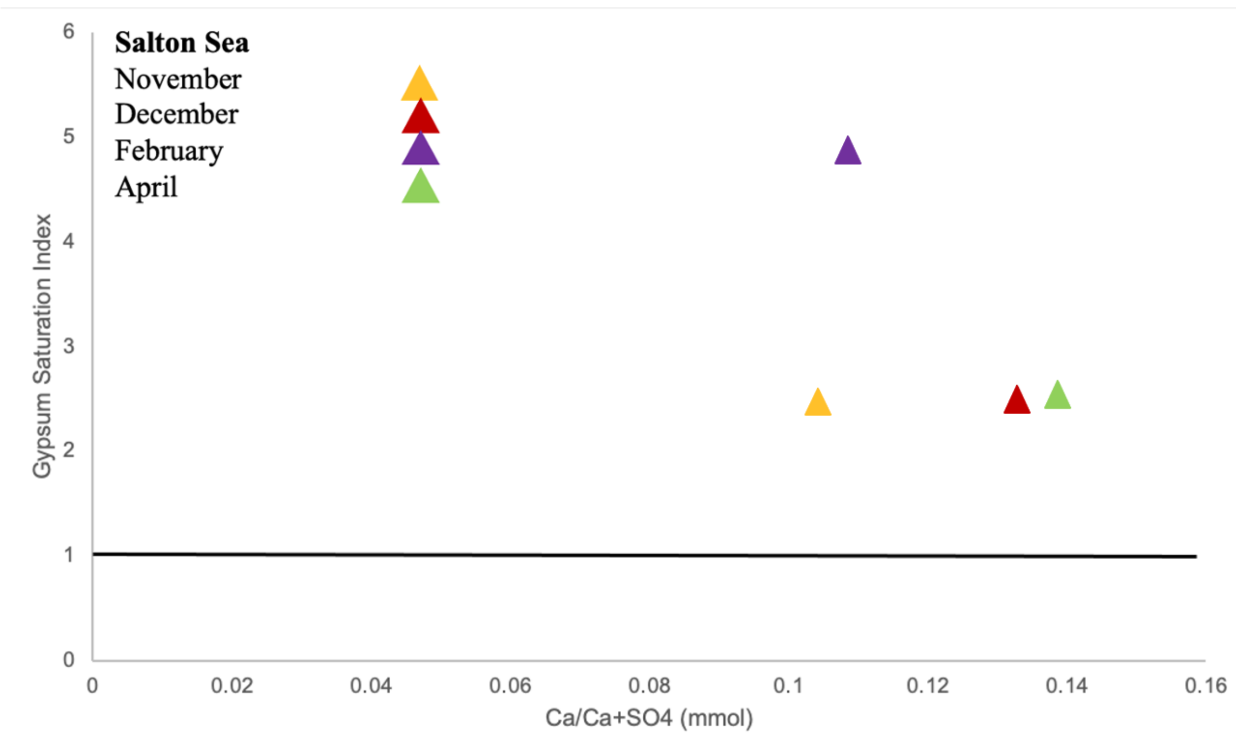

Figure 6. Each of the current sample periods plotted on the gypsum saturation index. Values over one indicate gypsum is precipitating.

Table 2. Gypsum saturation indices

	Activity Coefficient (Ca^{2+})	Ionic Activity (Ca^{2+})	Activity Coefficient (SO_4^{2-})	Ionic Activity (SO_4^{2-})	IAP Gypsum/ Ksp	Gypsum Saturation
November 2022	0.24	4.10×10^{-3}	0.13	1.51×10^{-2}	2.45	Precipitates (oversaturated)
December 2022	0.24	3.42×10^{-3}	0.14	1.77×10^{-2}	2.41	Precipitates (oversaturated)
February 2023	0.25	5.32×10^{-3}	0.13	2.28×10^{-2}	4.83	Precipitates (oversaturated)
April 2023	0.23	3.88×10^{-3}	0.16	1.60×10^{-2}	2.48	Precipitates (oversaturated)

*All samples are averaged from all sea sample sites from each sample period.

Discussion

From our current fieldwork and analyses of previous major ion surveys of the Salton Sea conducted over the past century, we have observed that the sea is getting substantially more saturated over time (fig. 5). This is because of the large-scale evaporation happening at the sea, making it shrink and become more concentrated with some variability associated with more inputs (Holdren & Montaño, 2002). Indeed, there have been varying inputs into the Salton Sea since the diversion of the Colorado river. Some of the main freshwater inputs is the Whitewater, New, and Alamo Rivers that continue to flow into the sea today. Other major inputs have been runoff from agriculture and irrigation which may have contributed to pollution in the area. However, in 2016 the Imperial Irrigation District put in measures to control irrigation run-off and windblown dust emissions (Adams et al., 2017). Regardless, the sea is becoming more saline as time goes on. Generally, ocean water contains about 35 g/kg of dissolved salts, while recent analyses of the Salton Sea show that dissolved salts can reach as high as 75 g/L, almost double that of normal ocean water. Further, the sea is becoming more basic. A year ago, the pH of the

Salton Sea was 8.5, now in 2023, it is 9.3. The water of the sea is becoming more alkaline, another effect of the evaporation present at the sea (SSET, 2023). By adding our current dataset to Holdren & Motaño's from two decades ago we can see that not only is the major ion concentration of the sea increasing, but that, as they predicted, gypsum has continued to precipitate as the sea has become more concentrated (Holdren & Montaño, 2002). While the current major ion survey did see some seasonal variability as well as slight variability depending on site location, these variations did not account for much change in overall ionic concentration of the sea. At SS6, the site closest to the Whitewater River, we saw lower ion concentrations compared to other sites. This is indicative of slight variability in chemistry depending on location. Spatially within the Sea, some variation also occurs. It seems that while there were increases in stream height from the Whitewater River due to rainfall, these were most substantial in February and April (fig. 7). Further, while we can see some rain influencing the ion concentrations at the site closest to the mouth of the stream (SS6) it appears that this had minimal to no effect on the other sites within the sea (Table 3). However, even with a heavy rain year, the water coming in from these fresh inlets reduces the Salton Sea's ability to precipitate gypsum negligibly. Gypsum does continue to precipitate throughout the fall and winter seasons as our saturation index calculations show (Table 2). With February appearing to have the highest saturation index while having the lowest average temperature. This is opposing previous research that found more frequent gypsum blooms in summer months, and the northwest area of the sea experiencing bloom later in the year (Ma et al., 2018). Though, knowing that gypsum is continuing to precipitate even outside of the summer season it is important to ask what this means for the Salton Sea and those who live around it (Ma et al., 2018). Arsenic and selenium have been found in trace amounts in the playa and dust within and around the sea (Frie et al., 2017). Since it is also known that these metals incorporate very well into gypsum's structure, we are hypothesizing that these metals may incorporate into the gypsum that is constantly precipitating at the Salton Sea. Further, if this phenomenon is occurring, it is crucial to understand the potential health impacts of gypsum dust as these trace metals have been found to have adverse health effects in humans (Tian et al., 2022, Zhang et al., 2015).

Table 3. Average Major Ion concentrations (mg/L) by site, averaged across all sample periods. SS6 is highlighted for interest.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}
SS1	22180	369	733	1805	30009	329	13203
SS2	22666	393	737	2018	30026	142	11850
SS6	**14178**	**181**	**507**	**1375**	**19001**	**280**	**10818**
SS7	20499	378	763	2108	29032	373	12742
SS8	22385	377	701	1986	31243	312	12954
SS9	22154	409	795	2180	30735	190	10844
BOR1	19473	364	660	1825	29837	332	11562

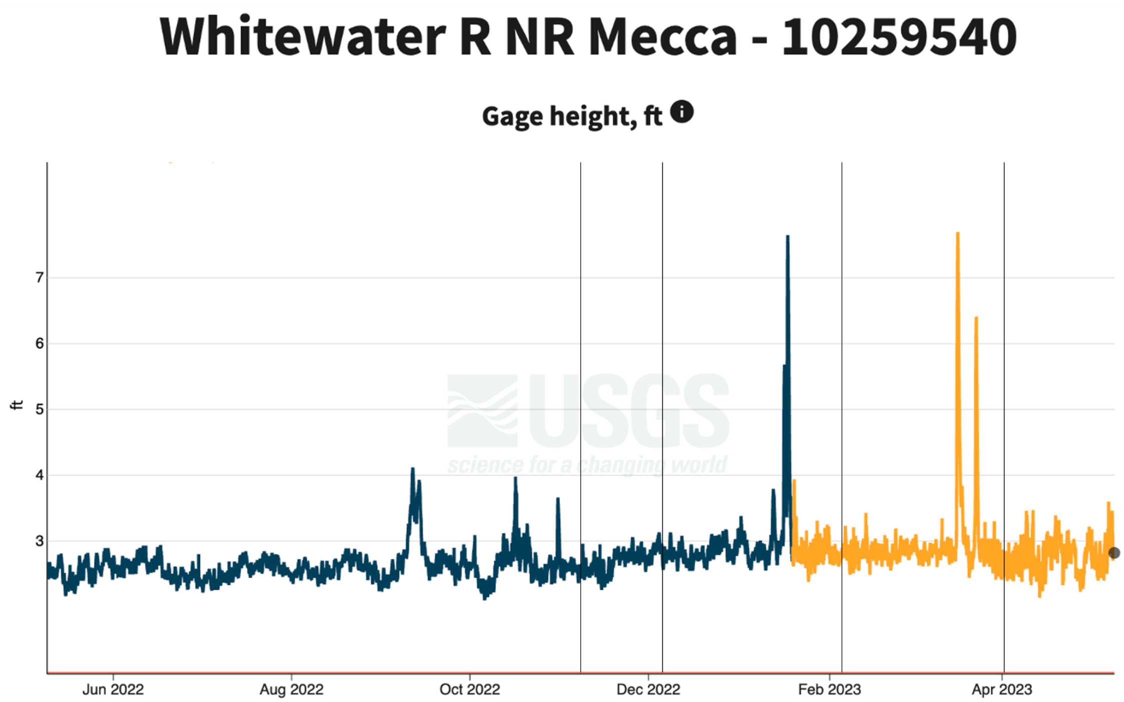

Figure 7. Stream gauge data of Whitewater River taken from USGS. Orange indicates 2023, blue indicates 2022. Current sample dates are marked with a black line.

Conclusion

The current study has found that the Salton Sea is more concentrated than it was two decades ago and appears to be becoming even more concentrated over time (fig. 5) (Holdren & Montaño, 2002). There also appears to be some existence of spatial and annual variation within the concentration of the sea (fig. 3, fig. 4). Overall, the major ion concentration of the Salton Sea is an important key to understanding the ever-changing water chemistry at the Salton Sea and its unique environment. Water chemistry can show both seasonal and spatial changes that may affect the precipitation of gypsum. This means that the water chemistry at the Salton Sea could be an important precursor or tool for estimating when and where gypsum will precipitate. This may help us further understand the wide-scale suspension of gypsum dust that will negatively impact air quality and potentially carry hazardous metals to the population of the Imperial

Valley. Therefore, it is important to continue monitoring the water quality of the Salton Sea consistently so we have an accurate picture of the changes to potential hazards it poses as this dynamic environment continues to change.

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