The impact of using low-saline oilfield produced water for irrigation on water and soil quality in California

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HIGHLIGHTS
• Salts, metals, radionuclides, and DOC were measured in low-saline OPW, groundwater and soil from Kern County.
• Concentrations of inorganic constituents in low-saline OPW were below drinking water and irrigation standards.
• Soil irrigated by low-saline OPW had higher boron and sodium than soil irrigated by groundwater.
• Soil irrigated by low-saline OPW had low radium nuclides, similar to soil irrigated by groundwater.
• Long-term utilization of low-saline OPW could induce boron and sodium toxicity.

GRAPHICAL ABSTRACT

ABSTRACT

The consecutive occurrence of drought and reduction in natural water availability over the past several decades requires searching for alternative water sources for the agriculture sector in California. One alternative source to supplement natural waters is oilfield produced water (OPW) generated from oilfields adjacent to agricultural areas. For over 25 years, OPW has been blended with surface water and used for irrigation in the Cawelo Water District of Kern County, as permitted by California Water Board policy. This study aims to evaluate the potential environmental impact, soil quality, and crop health risks of this policy. We examined a large spectrum of salts, metals, radionuclides (226Ra and 228Ra), and dissolved organic carbon (DOC) in OPW, blended OPW used for irrigation, groundwater, and soils irrigated by the three different water sources. We found that all studied water quality parameters in the blended OPW were below current California irrigation quality guidelines. Yet, soils irrigated by blended OPW showed higher salts and boron relative to soils irrigated by groundwater, implying long-term salts and boron accumulation. We did not, however, find systematic differences in 226Ra and 228Ra activities and DOC in soils irrigated by blended or unblended OPW relative to groundwater-irrigated soils. Based on a comparison of measured parameters, we conclude that the blended low-saline OPW used in the Cawelo Water District of California is of comparable quality to the local groundwater in the region. Nonetheless, the salt and boron soil accumulation can pose long-term risks to soil sodification, groundwater salinization, and plant health; as such, the use of low-saline OPW for irrigation use in California will require continual blending with fresh water and planting of boron-tolerant crops to avoid boron toxicity.

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1. Introduction

The increased volume of wastewater generated from oil and gas operations, especially the flowback and produced waters generated from conventional and unconventional oil and gas production across the U.S., requires adequate management solutions; in particular, this includes the option of reusing it for beneficial purposes (Echchelh et al., 2018, 2019; Haluszczak et al., 2013; McMahon et al., 2018; Rowan et al., 2015; Vengosh et al., 2014; Warner et al., 2014; Stringfellow and Camarillo, 2019). The high concentrations of organic contaminants, salts, metals, and radioactive elements commonly reported in OPW (Vengosh et al., 2014; Stringfellow and Camarillo, 2019; McMahon et al., 2018; Echchelh et al., 2018; Kondash et al., 2014a) pose risks for crops yields, soil quality, possible accumulation of contaminants in agricultural products, and low-quality agriculture return flows. Previous studies have examined possible effects on crop yields (Miller et al., 2019, 2020; Pica et al., 2017; Sedlacko et al., 2019) and human health risks associated with high concentrations of metals in irrigation water (Shariq, 2019) upon reuse of conventional and unconventional oilfield produced water (OPW). These studies have suggested that the chemistry of OPW can have negative effects on the disease resistance of crops such as wheat (Miller et al., 2019, 2020) or direct accumulations of metals in wheat (Shariq, 2019). While these studies carried out greenhouse experimental testing, data on the long-term effects from areas irrigated by OPW are limited, which is the focus of this study. In California, consecutive drought periods and the massive reduction in natural water availability over the last several decades have incentivized and facilitated the utilization of OPW to supplement the local water supply for irrigation in the Central Valley (CARWQCB, 1998, 2015, 2012, 2007; Christian-Smith et al., 2015; USDA, 2017). In Kern County, water authorities have utilized a combination of groundwater, surface water, and OPW in several water districts (Cawelo, Jasmin Mutual, Kern-Tulare, and North Kern; Fig. 1) (CARWQCB, 1998, 2015, 2012, 2006, 2007; Robles, 2016a, 2016b). Through blending treated (i.e., oil-separated and filtered) OPW and freshwater sources, these water districts have extended the amount of water available for crop irrigation (CARWQCB, 2012, 2007; Dalke, 2017; Robles, 2016a). The ability to reuse OPW for irrigation depends on the source and quality of OPW, and consequently the Central Valley Regional Water Quality Control Board has allowed utilization of only blended local OPW with self-reported monthly water-quality monitoring; yet, it has not regularly tested the soil or plant uptake for contamination (CARWQCB, 2012, 2007, 2018; CAWB, 2020; Marshack, 2016; Navarro et al., 2016; Robles, 2016b).

In order to assess the implications of the current policy and regulations that allow for permitting the reuse of OPW for irrigation (outlined...
in the SI), this study aims to evaluate the inorganic chemistry and dissolved organic carbon (DOC) of OPW used for irrigation and the long-term impact on irrigated soil in the Cawelo Water District in Kern County, southern San Joaquin Valley, California. While previous studies have addressed the inorganic and organic contaminants associated with OPW in California (McMahon et al., 2018, 2019; Stringfellow and Camarillo, 2019; Navarro and Mulhearn, 2016; Navarro et al., 2016; Robles, 2016a, 2016b), this study focuses on inorganic chemistry and naturally occurring radioactive materials (NORM) in OPW used for irrigation (raw OPW, blended OPW, groundwater) and soil irrigated by the different water sources. Unlike previous experimental studies that have monitored changes over time in plant yields, plant physiology, and plant metabolomics (Miller et al., 2019, 2020; Pica et al., 2017; Sedlacko et al., 2019), this study is based on water and soil quality data collected from representative sites in the Cawelo Water District in Kern County, aiming to evaluate the long-term impact from irrigation with blended OPW as compared to local groundwater. The objectives of this paper are to evaluate (1) the water quality of low-saline OPW, comparing it to the quality of the local groundwater from the Cawelo Water District and applicable irrigation and drinking water standards; (2) the soil quality degradation and discuss potential plant toxicity that could result from long-term irrigation with raw and blended OPW; and (3) possible accumulation of trace metals in fruits (e.g., pistachios) irrigated by blended OPW.

2. Methodology

2.1. Site characterization and sample collection

Through three sampling campaigns (December 2017, April 2018, September 2018), we collected seven OPW samples from oilfield formations, including one sample from the Edison formation, five from the Dyer Creek oilfield, and one from the Midway Sunset field. The Dyer Creek OPW was used to spray irrigate a field of hay after treatment to remove excess oil. In all other sites blended-OPW from the Cawelo Canal or local groundwater was irrigated via drip irrigation. This process had been occurring for several years before we sampled the soil and water from this location. We collected 17 irrigation water samples in multiple seasons to represent a range of irrigation water quality differences in areas used to grow pistachios and almonds, eight from groundwater sources, and seven from Cawelo Canal water used for irrigation in Cawelo district. The Cawelo canal has been providing blended OPW to farms for irrigation since 1994 (see SI for more information). Water samples were collected directly from nozzles at the beginning of drip irrigation systems at both Cawelo and groundwater sampling sites. All samples were collected directly from nozzles at the beginning of drip irrigation systems at both Cawelo and groundwater sampling sites. All samples were run for major cations on a Thermo Scientific Aquion IC operating at constant room temperature. Calibration standards include eight levels for six cations (Li, Na, NH4, K, Mg, Ca) ranging from 5:1 to 2000:1 dilutions of Thermo Scientific six-cation standard solution (Li of 50 mg/L, Na, K, Mg of 200 mg/L, NH4 of 400 mg/L, Ca of 1000 mg/L). Major anions were run on a Dionex Ion Chromatograph DX-2100. Bicarbonate was calculated via titration with 0.02 M HCl to pH 4.5 in duplicate. Nitrate was analyzed via QuickChem Method 10-107-04-2-D (Nitrate/Nitrite in Waters by Hydrazine Reduction). Dissolved organic carbon (DOC) was measured on a TOC analyzer (TOK-V CPH; Shidmadzu, Kyoto, Japan). Trace metals were analyzed using a VG PlasmaQuad-3 inductively coupled plasma mass-spectrometry (ICP-MS). Trace-metals accuracy was assessed by measuring the National Institute of Standards and Technology (NIST) standard reference material (SRM) for trace elements in groundwater (1643e). All samples were pre-diluted based on total conductivity to stay at or below a conductivity of 200 μS/cm. Strontium isotopes were measured on a thermal ionization mass spectrometer (TIMS) using a Thermo Fisher Triton. The average 87Sr/86Sr of NIST SRM-987 was 0.710249 with a standard deviation of 0.000007 through the analysis process.

Soil samples were oven-dried and packed in plastic dishes (6.5 cm in diameter, 2 cm in height), wax sealed and incubated 21 days or more then analyzed on a Canberra broad energy germanium gamma detector for 226Ra and 228Ra (Lauer and Vengosh, 2016). Additionally, 10 g of dried soil was leached with 20 mL of deionized water for 24 h in 50 mL centrifuge tubes on a shaker table. The soil leachates were then centrifuged and filtered using Whatman filter paper followed by filtration through a 0.45 μm disposable filters. The leachates were analyzed following the same analytical techniques as the water samples. Soil samples were then fully digested for Sr isotope ratios in bulk soil using 34 ± 1 mg of soil weighed in 7 mL Teflon vials and digested overnight at 90–100 °C on a hotplate in a HF-HNO3 mixture (v/v = 2 mL: 1 mL; Optima grade). The digested samples were then dried down completely and re-digested overnight at 90–100 °C in a mixture of 15 M HNO3 (1 mL), H2O2 (1 mL; Optima grade), and quartz-distilled (QD) water (3 mL). Following digestion, 1.2 mL aliquot was dried down completely and re-dissolved in ~500 μL HNO3 before going through the Sr column separation.

Pistachio samples were desheelled, soaked for 10 min in deionized water, crushed using a porcelain mortar and pestle, and oven-dried for 24 h at 60 °C before being powdered. One gram of powdered sample was added to 5 mL of HNO3 over an hour at room temperature. Using a CEM MARS Xpress microwave, samples were heated without caps to

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Soil texture</th>
<th>Saturated hydraulic conductivity (cm/h)</th>
<th>Saturated volumetric water content, porosity for soil (ml/cm²)</th>
<th>Bulk soil density (g/cm³)</th>
<th>Soil moisture coefficient (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater Irrigated Soil</td>
<td>Sandy loam</td>
<td>4.42</td>
<td>0.41</td>
<td>1.5635</td>
<td>4.9</td>
</tr>
<tr>
<td>Blended OPW Irrigated Soil</td>
<td>Clay loam</td>
<td>0.26</td>
<td>0.41</td>
<td>1.5635</td>
<td>8.52</td>
</tr>
<tr>
<td>OPW Irrigated Soil</td>
<td>Loam</td>
<td>1.04</td>
<td>0.43</td>
<td>1.5105</td>
<td>5.39</td>
</tr>
</tbody>
</table>
65 °C for 20 min. Samples were then cooled and capped before being heated to 95 °C, with a 20-minute ramp and held for 10 min, then heated to 150 °C on a 10-minute ramp and held for 10 min. Digested samples were then brought to 50 mL total volume with deionized water and processed for trace metals analysis.

3. Results and discussion

3.1. Characterization of OPW, ground water, and irrigation water

Data from McMahon et al. (2018) and (2019) combined with new measurements reported in this study (Tables S1–6) show that the salinity of OPW in the southern San Joaquin Valley varies considerably from west (Belridge oilfield, Cl of 23,000 mg/L) to east (Fruitvale and Kern oilfields, Cl of 110 mg/L) (Figs. 1, S1). Most dissolved inorganic constituents show positive correlations with Cl (Figs. S1, S2), and thus the low-saline OPW from the eastern side of San Joaquin Valley typically has low concentrations of other inorganic constituents (Tables S1–2). While B is highly correlated to Cl (Fig. 2), all OPWs from southern San Joaquin Valley are characterized by high B and B/Cl (median ratio of 2.2 \times 10^{-2}) (Figs. S1, S2), which is consistent with data reported from flowback and produced water from stimulated wells in Central Valley in California (Stringfellow and Camarillo, 2019) as well as from common oilfield brines from other fields (Vengosh, 2013; Warner et al., 2014). Consequently, even low-saline OPW has relatively high B/Cl and B (e.g., Fruitvale field with B of 0.6 mg/L). Brackish OPW (e.g., Dyer Creek with Cl of 480 mg/L) has B content of 2.2 mg/L, which is above the upper limit (1 mg/L) of the Basin Plan guideline (CARWQCB, 2018). Boron is known to be an important nutrient in plants with a specific range of adequate concentrations in irrigation water and soil; low levels would induce boron deficiency while high levels (commonly above 1 mg/L) may cause boron toxicity, particularly for B-sensitive crops (Ayers and Westcot, 1976; Camacho-Cristobal et al., 2008; Gupta et al., 1985; Nable et al., 1997; Reid, 2007; Shah et al., 2017). Our data indicate that most of the OPW with Cl below the upper limit of the Basin Plan guideline (200 mg/L) have B concentrations above 1 mg/L (Fig. 2), indicating that B can be a limiting factor for utilization of low-saline OPW for irrigation in the southern San Joaquin Valley. Similar to the eastern OPW, groundwater from the east side of the southern San Joaquin Valley is characterized by relatively low salinity. In the Fruitvale oilfield, the Cl in shallow groundwater ranged from 7 to 170 mg/L (median 28 mg/L; Wright et al., 2019). Data from Kern County reported in this study (Fig. 1) show Cl range of 22 to 94 mg/L (median of 82 mg/L; n = 8; Table S1). In contrast to OPW, the B/Cl ratio of local groundwater is of order of magnitude lower (median of 3.3 \times 10^{-2}; Table S1) with relatively low B concentrations (0.02 to 0.12 mg/L; Table S1). While the majority of dissolved constituents in the low-saline groundwater was low or non-detectable, arsenic (As) concentrations were detected in all samples (range of 1.5 to 13.5 μg/L) and in one site exceeded the U.S. EPA Maximum Contaminant Level (MCL) for drinking water (Fig. 3, Table S2; USEPA, 2019a).

The water samples collected from the Cawelo Canal represent OPW-blended water used for irrigation in Kern County. The data show systematic low Cl concentrations (64 to 92 mg/L) within the range of the salinity of local groundwater (Figs. 1 and 2). Similar to the OPW from the southern San Joaquin Valley, the B/Cl ratios of the Cawelo Canal are high (1.92 \times 10^{-2}) with B concentrations of 0.11 to 0.69 mg/L (Table S1). While the B concentrations in the Cawelo Canal were found to be below the Basin Plan guideline of 1 mg/L, the blending of high B OPW with low-B water is the critical mechanism to keeping B at acceptable levels. In addition to Cl and B, all other inorganic constituents in the Cawelo Canal were low and within U.S. EPA MCL standards for drinking water including nitrate, which was high in groundwater samples, but low in blended OPW (Fig. 3). The only exception is As (a range of 8.7 to 26.5 μg/L) that exceeded the MCL threshold (10 μg/L). Other exceedances were NO3 in groundwater samples exceeding the EPA MCL of 10 mg/L in 4 out of 7 groundwater samples, Fe in 1 of 15 samples, and Mn in 1 of 15 samples exceeding EPA Secondary MCLs of 300 and 50 μg/L, respectively (United States Environmental Protection Agency, 2019a).

Similar to the salinity variations, the DOC concentrations of the low-saline OPW-blended water used for irrigation in Kern County (range 2.4 to 17.3 mg/L; mean of 8.9 mg/L; Table S3) were systematically lower than DOC concentrations in saline OPW from other fields in the southern San Joaquin Valley (Fruitvale: 41 mg/L, Lost Hills: 672 mg/L, North Belridge: 191 mg/L; McMahon et al., 2018), as well as saline OPW previously tested for irrigation (369 mg/L; Sedlacko et al., 2019). The low DOC in the low-saline OPW-blended water is consistent with low concentrations of other organic contaminants presented in literature such as benzene, PAHs, toluene, and total petroleum hydrocarbons (Robles, 2016a, 2016b). Likewise, the DOC in the brackish OPW from Dyer Creek (mean of 4.3 mg/L) was low and similar to that in local groundwater (4.2 mg/L; Table S3). Overall, our data show that the quality of blended OPW in the Cawelo Canal is within the Basin Plan regulations and drinking water regulations (except for As) and is not systematically different from the quality of local low-saline

![Fig. 2](image-url) Boron and chloride concentrations in OPW and other water sources sampled across Kern County analyzed in this study. Points with boarders are OPW samples reported in McMahon et al. (2018). The grey box represents Basin Plan limits on boron (1 mg/L) and chloride (250 mg/L) (CA RWQCB, 2018; McMahon et al., 2018). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3.2. Impact of irrigation with OPW on soil quality

In order to explore the effects of crop irrigation with OPW on long-term soil quality, we investigated the salts, DOC, and NORMs occurrences in soil samples from fields irrigated by raw (brackish) OPW (the Dyer Creek site), blended OPW represented by the Cawelo Water District, and local groundwater, along with one unirrigated field near the Dyer Creek irrigated site. The water-leachate chemistry revealed that salts accumulation on irrigated soil depends on the type of irrigation waters; when comparing blended-OPW irrigated- to groundwater-irrigated soil, we observed significantly higher concentrations of Cl, Na, and B in soil (Fig. 4; see t-test results in Table S7). Likewise, we observed systematically higher concentrations of these salts in soil irrigated by brackish raw OPW from Dyer Creek field relative to unirrigated soil from the same site (Fig. 4). While the Cl in blended-OPW irrigated soil was enriched enriched by 1.4-fold relative to that of groundwater-irrigated soil, Na and B enrichments were 2.3- and 4.8-fold, respectively. The enrichment of these salts in raw OPW-irrigated soil was much higher as compared to unirrigated soil from Dyer Creek with Cl, Na, and B enrichments of 6.5-, 17.5-, and 9.2-fold, respectively (Fig. 4).

In contrast, the combined $^{228}$Ra and $^{226}$Ra activities in soils irrigated by blended or raw OPW were not systematically different from groundwater irrigation and/or unirrigated soil (see Table S7 for p-values; Fig. 4), indicating that long-term irrigation of OPW in southern San Joaquin Valley is not causing NORM accumulation in the soil. Likewise, DOC in water leachates extracted from blended OPW-irrigated soil was indistinguishable from DOC concentrations in leachates extracted from groundwater-irrigated soil (Fig. 4). Soil irrigated by brackish raw OPW in the Dyer Creek site had systematically higher DOC concentrations (Fig. 4). The data in the soil leachates do not indicate NORM and DOC accumulation in soil irrigated by blended low-saline OPW in the Cawelo Water District. In contrast, irrigation with raw brackish OPW in Dyer Creek site resulted in much higher accumulation of organic matter in the soil.

3.3. Tracing OPW salts and metals in soil

In addition to the evaluation of the concentrations of salts and metals accumulation in soil irrigated by different water sources, we investigated geochemical tracers that could help the identification of OPW contaminants in soil and possibly in plants (see Supplement Information). The lack of systematic Ra enrichment in soils irrigated by blended and raw OPW relative to groundwater-irrigated and unirrigated soils (Fig. 4) is consistent with the indistinguishable $^{228}$Ra/$^{226}$Ra activity ratios we measured in the different soil samples (Fig. 5). Previous studies have shown that OPW from unconventional shale formations have low $^{228}$Ra/$^{226}$Ra activity ratios (<1) relative to OPW from conventional oil and gas (>1). This is caused by low Th/U ratios that characterize
Fig. 4. Comparison of Cl, Na, B, Mg, As, and DOC in water-leached soils and combined $^{226}\text{Ra} + ^{228}\text{Ra}$ concentrations in bulk soils irrigated with blended and raw OPW relative to groundwater-irrigated soil and unirrigated soil. The data show higher concentrations of Cl, Na, B in soil irrigated by OPW relative to soil irrigated by local groundwater and unirrigated soil, while Ra activities are indistinguishable between the different soil types. Arsenic in soil irrigated by POW is also indistinguishable from soil irrigated by groundwater.
organic-rich shales relative to high Th/U in sandstone rocks that make up conventional oil and gas reservoirs (Lauer et al., 2018). The indistinguishable $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios detected in the different soil samples measured in this study are therefore consistent with the lack of Ra enrichment among the different soils, and reinforce that NORM accumulation is not a factor for irrigation with low-saline OPW in the southern San Joaquin Valley.

Another possible tracer for detecting OPW metal accumulation in soil is Sr and its stable isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$). Previous studies have shown that Sr isotopes of flowback and produced water can be different from background groundwater and other contamination sources, and therefore a useful tracer to delineate the presence of OPW (Chapman et al., 2012; Warner et al., 2014). Yet, in our study we found that (1) the Sr isotope ratio of the local groundwater (mean of 0.7075; $n = 8$) is very similar to that of the blended OPW in the Cawelo Canal (0.70735; $n = 4$); (2) the Sr concentrations in water leachates from Cawelo Canal-irrigated soil are similar to that of groundwater-irrigated soil, and no systematic Sr enrichment is observed in water leachates from soil irrigated by raw OPW to unirrigated soil in Dyer Creek (Fig. S3); and (3) the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the water leachates of soil are not consistent with the ratios in the irrigation water (Fig. 6). The lack of accumulated Sr in the OPW-irrigated soil and the difference between the Sr isotope ratios of irrigation water and water-extractable soil suggest that the relative contribution of Sr from the blended OPW is negligible relative to the bulk exchangeable Sr in the soil. This is consistent with the low concentration of Sr in blended-OPW (mean value of 0.23 mg/L) relative to the local groundwater (0.55 mg/L). Therefore, unlike salts (Ca and Na) and B, Sr from the blended OPW irrigation water tested in this study cannot be used as a reliable tracer to detect OPW contaminant accumulation in soil and most-likely also plants.

3.4. Long-term impact of OPW on soil quality and crop health

Previous studies have suggested that the utilization of OPW for irrigation with water high in salts, DOC, and B concentrations can result in reduced yields, struggles with germination, and may induce abiotic stress making plants more susceptible to pathogens (Miller et al., 2019; Pica et al., 2017; Sedlacko et al., 2019). In this study, we evaluated the potential impact of OPW on soil quality and crop health by measuring critical inorganic constituents such as salinity, sodium, boron, NORMs, and DOC in the soil to detect possible risks for the crops. Unlike OPW from different basins throughout the U.S. with typical high salinities, NORM, DOC and other inorganic and organic contaminants, the results of this study indicate that OPW from Kern County in southern San Joaquin Valley has much lower salinity with also lower concentrations of other contaminants. The levels of contaminants found in the low-saline OPW from Kern County are similar to those in the local groundwater. Yet saline OPW from oil fields in the western side of the San Joaquin Valley has much higher salinity (Fig. 1) (McMahon et al., 2018, 2019). Therefore, blending OPW with fresh water results in low-saline irrigation water similar in salinity and water quality to the local groundwater. We do show, however, that the higher concentrations of Na and B in the blended-OPW, compared to the local groundwater, result in a higher degree of accumulation of salts and B in the soil irrigated with blended-OPW relative to soil irrigated with groundwater (Fig. 4). While the salts and B in the irrigation water were below district recommended levels, their accumulation in the soil can still affect the sustainability of this irrigation practice. Plants absorb water from soil through osmotic potential, exerting a force on the water that is greater than the force holding water to the soil (Ayers and Westcot, 1976). In soil irrigated with high salinity water, its osmotic potential is reduced, which infers less water is available for plants (Ayers and Westcot, 1976). In arid regions such as southern California, the buildup of salts in the soil is of even greater concern because a large portion of the water applied to the soil quickly evaporates, concentrating salts in the remaining soil water. Using sub-optimal quality irrigation water can dramatically speed up this process in the soil by introducing more salts to the system. Three of the main crops grown in Kern County California, almonds, grapes, and oranges are all classified as sensitive to the salinity of both irrigation water and soil, suggesting soil salinity in areas irrigated with OPW should be of increased concern (Ayers and Westcot, 1976; CAWB, 2018). By planting more salt resistant crops such as pistachios and carefully managing the sodium adsorption ratio with the application of gypsum and sulfuric acid to fields, farmers are actively managing soil salinity in this area.

The Na accumulation in the soil irrigated by raw and blended-OPW is of concern. Elevated Na in soil relative to Ca and Mg concentrations (known as sodium adsorption ratio -SAR, see Fig. S4) would reduce the soil permeability and thus lower soil infiltration capacity, making it harder for water to reach the subsoil (Ayers and Westcot, 1976). The local groundwater (SAR between 1.8 and 6.5) and Cawelo blended-OPW (SAR between 4.7 and 8.1) had SAR values that would not affect soil permeability. In contrast, raw OPW from Dyer Creek site samples had high SAR value (16.4 to 25.6), which is equivalent to slight to severe reductions in infiltration (Fig. S4; Ayers and Westcot, 1976). While the addition of sulfuric acid to irrigation water and gypsum to irrigated soils could mitigate the Na accumulation issue, it would require special attention and additional cost in areas irrigated by OPW.

Boron is an essential nutrient for plant health, as it is responsible for providing structure to the cell wall (Camacho-Cristobal et al., 2008; Kobayashi et al., 1996). In soil, B is typically found in concentrations ranging from 0.4 to 5 mg/kg and exists primarily as boric acid (B(OH)$_3$), which is readily taken up by plants (Nable et al., 1997; Shah et al., 2017). While B is necessary for plant growth, elevated levels can also be detrimental. In arid and semi-arid regions, where the salinity is high, B desorption from clay minerals is restricted and thus can accumulate, resulting in increased concentrations in soil through time. When present in high concentrations in irrigation water, accumulation in soil can be exacerbated. Guidelines for water quality in agricultural use have suggested concentrations of B in irrigation water at 1 mg/L, 5 mg/L, and 10 mg/L depending on the crop tolerance to B, while others have recommended a limit of 0.3 mg/L for sensitive plants and up to 4 mg/L for tolerant plants (Ayers and Westcot, 1976; Nable et al., 1997). When elevated B is presented in the soil-plant interface, the production of reactive oxygen species (ROS) increases, causing oxidative damage to the cellular membrane, leading to decreased growth and or leaf necrosis, lower chlorophyll concentrations and decreased photosynthesis, defined as “boron toxicity” (Gupta et al., 1983; Camacho-Cristobal et al., 2008; Reid, 2007; Shah et al., 2017).

Fig. 5. $^{228}\text{Ra}$ versus $^{226}\text{Ra}$ activities in soil samples across Kern County, CA, sorted by the type of irrigation water. The lack of systematic differences between the Ra activities and ratios confirm the lack of Ra accumulation in soil irrigated with OPW.
While B levels in irrigation water investigated in this study rarely reached the boron toxicity levels, many of the districts within the Central Valley have adopted a 1 mg/L B limit on irrigation water derived from OPW (Gupta et al., 1985; Marshack, 2016). Boron levels measured in groundwater (ranging from 0.01 to 0.1 mg/L; mean = 0.07 mg/L) were lower than those from the Cawelo canal (ranging from 0.1 to 0.6 mg/L; mean = 0.42), while Dyer Creek OPW irrigation water had B above 1 mg/L (Fig. 2 and Table S1). Despite Cawelo canal irrigation water having B lower than the recommended 1 mg/L limit, we still observed accumulation of B in the irrigated soil compared to groundwater-irrigated soil (Fig. 4), indicating that blending with low-B fresh water might not be enough to prevent boron accumulation in soil. While allocating additional fresh water for OPW blending could further reduce B levels, blending also reduces the overall fresh water availability for irrigation in the Central Valley and negates the added water volumes from using OPW for irrigation. Nonetheless, blending of the OPW with fresh water seems to be important for the long-term viability of the agricultural sector given the B toxicity risks, and reduction of future fresh water blending would further exacerbate the B accumulation in the soil.

Despite high Na in irrigation water, Sedlacko et al. (2019) have shown that irrigation with low salinity blended OPW could have substantial detrimental effects on wheat health than NaCl enriched water at much higher TDS concentrations, additional constituents in OPW such as B, organic chemicals, or other metals may play a larger role in reducing wheat viability (Pica et al., 2017; Sedlacko et al., 2019). Therefore, the observed plant stress might be different for the low-saline OPW in California. Interestingly, we see increased concentrations of DOC in blended OPW samples (mean of 8.9 mg/L) relative to groundwater samples (4.2 mg/L; Table S3) from the region. At the same time, soil leached DOC is similar in both groundwater and OPW blended irrigated soil (Fig. 4; Table S6).

The accumulation of salts, sodium, and boron in soil irrigated by OPW can induce also risks for underlying groundwater salinization. Numerous studies have shown that irrigation with saline water often results in cycles of salt accumulation and transport through the soil and the unsaturated zone, and consequently results in long-term salinization and contamination of the groundwater (Suarez, 1989; Tanji and Valoppi, 1989; Vengosh, 2013). We posit that the extensive evapotranspiration under the semi-arid conditions in Central Valley could induce high salinity of the recharge water, that over time would also increase the salinity of the local groundwater. The distinction between higher salt levels in soil irrigated by blended OPW relative to soil irrigated by groundwater suggests that such a salinization process can be more effective in areas irrigated by the blended OPW.

3.5. Potential effects of OPW contaminants on crop quality

Previous studies have examined the concentration of organic contaminants in blended OPW (Navarro et al., 2016) and fruits irrigated by blended OPW from the Cawelo water district (Robles, 2016a, 2016b). While these studies measured parameters including volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) of acetone and the petroleum-derived benzene, toluene, ethylbenzene, xylenes,acenaphthene, fluorene, naphthalene and phenanthrene, they did not perform risk assessments (Robles, 2016a). Only acetone and phenanthrene were detected in seven and two fruit samples, respectively, including reference fruit samples irrigated by natural waters (Robles, 2016a). The low DOC measured in this study (Table S3) is consistent with other tracers of organic contaminants measured in the blended OPW and fruits from the Cawelo water district (Robles, 2016a, 2016b). In order to compliment the previous work on organic contaminants, this study examined the presence of inorganic contaminants in water, soil, and pistachios sampled from the district.

Arsenic is a known carcinogen and has been linked with multiple health effects (Ali et al., 2009; Duker et al., 2005; USEPA, 2019a). As such it is regulated in drinking water with a maximum contaminant level of 10 μg/L (USEPA, 2019a). Arsenic uptake by plants tends only to be significant in alkaline soils or As-rich soils (Bowell et al., 2014Ali et al., 2009). Greenhouse experiments have shown that irrigation with water containing As concentrations of 77 μg/L resulted in 7-fold accumulation of As in wheat relative to control conditions (Shariq, 2019), and therefore occurrence of As in irrigation water may pose potential human health risks. In order to test possible As accumulation in crops grown in this region, we conducted preliminary measurements of trace elements in pistachios irrigated by blended OPW in a comparison to pistachios grown outside the Cawelo water district (Table S8). The data show that all metals (Cr, Ni, Pb, Zn, Fe, Sr, Cu, Se, Cu) concentrations including As in the pistachios irrigated by blended OPW were similar or below the concentrations in pistachios grown outside the Cawelo water district, as well as pistachios grown in Turkey (Fig. S6). The trace elements concentrations in the pistachios samples from California and Turkey were consist with literature data for all metals (Taghizadeh et al., 2017), whereas the As results showed systematically lower concentrations. Consequently, we show no metals and As enrichment in pistachios grown in the Cawelo Water District, although a small sample...
4. Conclusions

This study indicates that blended low-saline OPW provided by the Cawelo Water District of Kern County in the southern San Joaquin Valley of California is of comparable quality to the local low-saline groundwater, particularly for the inorganic constituents measured in this study. Salts and metal concentrations in the low-saline OPW in the Cawelo Water District do not exceed the irrigation and drinking water standards, except for arsenic, which was detected also in local groundwater.

The relatively high boron and sodium concentrations in OPW, however, may pose long-term risks to crop health as soil irrigated by OPW show systematically higher B and Na concentrations relative to soils irrigated by local groundwater. The salinity and B concentrations in OPW seem to be the key for assessing the suitability and the long-term impacts of using OPW for irrigation in California, as well as other regions in the U.S. The rise of salinity and B in soil due to global warming and reduced precipitation in southern California could further exacerbate sodicity (soil-bound Na) and boron toxicity in soil irrigated by OPW, especially if more saline OPW is used. In addition, using OPW could result in salt accumulation in the soil and unsaturated zone, and consequently, would increase the salinization of underlying groundwater. Soil sodification and groundwater salinization in San Joaquin Valley have been documented for decades (e.g., Deverel and Gallanthine, 1989; Schoup et al., 2005; Deverel and Fuji, 1988; Bañuelos, 2015; Hansen et al., 2018), and the results presented in this study suggest that even small changes in the Na content of the irrigation water (blended OPW of 113 mg/L relative to 96 mg/L in groundwater) would result in Na accumulation in the soil (122 mg/kg relative to 53 mg/kg, respectively). Therefore, future evaluation of large-scale utilization of OPW for irrigation should also consider the potential effects on soil and groundwater salinity, in addition to crop and human health risks. While preliminary results do not show evidence for metals accumulation in picastios from fields irrigated by OPW, future studies should investigate the likelihood of human health risks associated with the consumption of crops grown with OPW-based irrigation water. Future studies should also investigate the long-term implications of using blended OPW for irrigation on other soil quality parameters such as soil physics, crop yields, and microbiology.

Credit authorship contribution statement

Andrew Kondash: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. Jennifer Hoponick Redmon: Conceptualization, Writing - review & editing, Project administration, Funding acquisition, Elisabetta Lambertini: Writing - review & editing. Laura Feinstein: Writing - review & editing. Erika Weithal: Writing - review & editing. Luis Cabreras: Investigation, Writing - review & editing. Avner Vengosh: Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - review & editing. Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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