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# Is Food Irrigated with Oilfield-Produced Water in the California Central Valley Safe to Eat? A Probabilistic Human Health Risk Assessment Evaluating Trace Metals Exposure

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Reuse of oilfield-produced water (OPW) for crop irrigation has the potential to make a critical difference in the water budgets of highly productive but drought-stressed agricultural watersheds. This is the first peer-reviewed study to evaluate how trace metals in OPW used to irrigate California crops may affect human health. We modeled and quantified risks associated with consuming foods irrigated with OPW using available concentration data. The probabilistic risk assessment simulated OPW metal concentrations, crop uptake, human exposures, and potential noncancer and carcinogenic health effects. Overall, our findings indicate that there is a low risk of ingesting toxic amounts of metals from the consumption of tree nuts, citrus, grapes, and root vegetables irrigated with low-saline OPW. Results show increased arsenic cancer risk (at $10^{-6}$) for adult vegetarians, assuming higher consumption of multiple foods irrigated with OPW that contain high arsenic concentrations. All other cancer risks are below levels of concern and all noncancer hazards are far below levels of concern. Arsenic risk concerns could be mitigated by practices such as blending high-arsenic OPW. Future risk assessment research should model the risks of organic compounds in OPW, as our study focused on inorganic compounds. Nevertheless, our findings indicate that low-saline OPW may provide a safe and sustainable alternative irrigation water source if water quality is adequately monitored and blended as needed prior to irrigation.

**KEY WORDS:** Food safety; oilfield produced water; trace metals

## 1. INTRODUCTION

The state of California is a longstanding producer of both agricultural crops and oil (Sheridan, 2006). California is one of the most productive agricultural regions in the United States, accounting for 18% of total U.S. agricultural sales, with the San Joaquin Valley alone contributing 8% of total U.S. agricultural sales (and a large portion of the world's production of specialty crops such as almonds and pistachios) (USDA, 2019). While productive, these agricultural regions suffer from chronic water shortage (USGS, 2016), as some areas in California are also the driest in America, with longer and more intense droughts becoming more prevalent over the last few decades (Christian-Smith, Levy, & Gleick, 2015; NIDIS, 2020).

California accounted for about 4% of U.S. oil production in 2019 (US EIA, 2020); although it has

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not seen a dramatic rise in production that has occurred in other states with the use of hydraulic fracturing, it remains an important oil producer in the United States (Vengosh, Jackson, Warner, Darrah, & Kondash, 2014). As a byproduct of both conventional and tight oil extraction operations, California oil wells also generate high volume of oilfield produced water (OPW). Managing California's OPW is a major challenge for both operators and regulators because of the large volume (134 billion gallons in 2018); the wide range of salinity, organic chemicals, and naturally occurring metals and radionuclides; and, for, hydraulically fractured wells, the use of various chemicals during the production process (Stringfellow & Camarillo, 2019).

The combination of high agricultural productivity, dry climate, chronic water shortages, and abundant OPW has led California farms, water districts, and oil companies to develop a symbiotic relationship. Since the mid 1970s, farms have been utilizing OPW to supplement agricultural irrigation water( CA RWQCB CVR, 1974). By the early 1990s, water districts began to form agreements with oil companies to use OPW to supplement freshwater sources for crop irrigation (CA RWQCB CVR, 2012; Hurst, 1988). The largest share of OPW covered by these agreements has been supplied to the south San Joaquin Valley's Cawelo Water District in Kern County to supplement the reduction in natural water availability, but other nearby water districts within Kern County have more recently begun accepting OPW to supplement groundwater and surface water resources, especially during consecutive drought periods (CA RWQCB CVR, 2006, 2007, 2012, 2015).

While plentiful, OPW used as irrigation water poses a number of potential drawbacks: its chemical properties may negatively affect (1) soil permeability (e.g., reduction due to accumulation of sodium); (2) crop productivity (e.g., salinity and boron toxicity to plants due to elevated chloride and boron levels); and (3) food safety (e.g., preferential bioaccumulation of trace metal constituents in plants) (Harkness et al., 2015; Vengosh et al., 2014; Warner, Christie, Jackson, & Vengosh, 2013). Since beneficial reuse of OPW as irrigation water began in the region, water districts have monitored certain water quality parameters, comparing the results to specific water quality irrigation guidelines (CA RWQCB CVR, 2012, 2018; Christian-Smith et al., 2015) for arsenic, boron, chloride, sodium, electrical conductivity, and total dissolved solids (CA RWQCB CVR, 2006, 2012). However, existing guidelines are limited to those six parameters and do not address all metals or other inorganics that could be present in OPW and taken up by crops irrigated with OPW (CA RWQCB CVR, 2006, 2012). Organic constituents are typically monitored by conducting oil and grease monitoring, which generally detects any nonpolar compound in water but is not specific to petroleum hydrocarbons or specific organic compounds (Robles, 2016b). Additional organic constituents of interest in OPW include volatile organic compounds such as acetone, benzene, ethylbenzene, xylenes, and toluene, along with polycyclic aromatic hydrocarbons such as acenaphthalene, chrysene, fluorene, naphthalene, phenanthrene, and pyrene, plus total petroleum hydrocarbons as an indicator for petroleum-based oil and grease. Recent water district-sponsored studies have evaluated organic compounds in OPW used, for crop irrigation (Echchelh, Hess, & Sakrabani, 2018; Echchelh, Hess, Sakrabani, de Paz, & Visconti, 2019; Navarro, Jones, & Mulhearn, 2016; Robles, 2016a, 2016b), but did not consider trace metals in OPW. ERM (2016) recently completed an oil industry-funded deterministic risk assessment (Navarro et al., 2016) on both organic and inorganic constituents, but methodological limitations and their funding source make it unsuitable for answering safety questions for at-risk populations (Navarro et al., 2016).

To date, no peer-reviewed risk assessment on trace metals in OPW has been completed to substantiate policy decisions and address concerns over the potential risk of using OPW for irrigation water on soil quality, crop health, and human health. A lack of robust scientific research studies on the topic has affected how the public perceives the risk of consuming crops cultivated with OPW. In the absence of information, some consumers have opted to boycott food crops grown with OPW (Food & Water Watch, 2018; Harkinson, 2015; Monaco, 2016).

Overall, continued or expanded beneficial irrigation use of OPW is hindered by a current lack of publicly available, peer-reviewed scientific evaluation of the risks associated with OPW irrigation. Our recently published study (Kondash et al., 2020) begins filling in this data gap by examining the occurrence of inorganic contaminants in OPW used for irrigation and in OPW irrigated soil in the Cawelo Water district in Kern County (Kondash et al., 2020). The objective of this research is to use original data from Kondash et al. (2020) combined with publicly available data on trace metals concentrations in OPW that is currently been used for irrigation in California to estimate the potential human health risk associated with consuming foods irrigated with OPW. Key questions are as follows: (1) Can OPW be beneficially reused to augment regional water availability, in particular for the agricultural sector, without increased food safety and human health concerns from trace metals exposure? (2) If there are concerns, what conditions are associated with elevated human health risks from OPW use for crop irrigation, and what measures can be taken to reduce potential human health risks? While OPW chemistry and salinity vary spatially in the oil and gas fields across the United States, this study is focused on relatively low-saline OPW from Kern County with significantly lower concentrations of salts, metals, and organic contaminants relative to OPW from other oil and gas fields in the United States.

## 2. METHODS

### 2.1. Study Characteristics

#### *2.1.1. Crops Evaluated*

Kern County, in the south San Joaquin Valley, is the site of seven of the top 10 oil producing formations in California (Supporting Information Table A1) and home to three of the five water districts that have formed agreements to use OPW as an alternative irrigation water source (Table A2). The main crops grown in Kern County and irrigated with OPW, by acreage, are tree nuts (pistachios and almonds; 37% of planted acreage in Kern County); grapes (13% of planted acreage); citrus (tangerines and oranges; 7% of planted acreage); and root vegetables (carrots, potatoes, and garlic; 6% of planted acreage); collectively, these crops account for nearly two-thirds of the planted acreage in Kern County (USDA, 2019). Based on crop growth in the region with the greatest OPW use, we modeled the following five crops (or categories of crops) for the risk assessment: citrus, grapes, almonds, pistachios, and root vegetables.

#### *2.1.2. Environmental Setting*

We included the Central Valley (not just Kern County and the south San Joaquin Valley) in our environmental setting to account for potential expansion of OPW (assuming it is treated to similar guideline levels as Kern County OPW) use for irrigation into other regions where the crops evaluated are currently grown or could potentially be grown. We used climate data to partition the region into 24 relatively homogeneous climate areas, each with an associated meteorological station (Fig. S1; Delano on that map is at the north edge of Kern County). We obtained 10 years (January 2008–December 2017) of climate data from the California Irrigation Management Information System (2018) and soils data for those areas from California's published soil survey database (2005) to characterize the environmental setting (CA DWR, 2018; Johnson & Belitz, 2003; USDA, 2005).

**Table I.** Constituents Evaluated

Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Total Chromium
Chromium VI
Cobalt
Copper
Iron
Lead
Lithium
Magnesium
Manganese
Molybdenum
Nickel
Rubidium
Selenium
Silver
Strontium
Thallium
Vanadium
Zinc

#### *2.1.3. Constituents Evaluated*

Previous studies focused mainly on evaluating organic constituents in OPW, with only one considering inorganic constituents (Navarro et al., 2016; Robles, 2016a, 2016b). Inorganics, including metals and salts, occur naturally in both ground and surface water and are also frequently found in OPW (McMahon, Kulongoski et al., 2018; McMahon, Vengosh et al., 2019; Vengosh et al., 2017; Wright, McMahon, Landon, & Kulongoski, 2019). Therefore, we focused on 27 inorganic constituents commonly found in OPW in this study (Table I). Additionally, given that our data set has concentration information on both total chromium and hexavalent chromium (chromium VI), and that chromium VI is more toxic than chromium III, we make the conservative assumption that all present chromium in each sample is chromium VI. As such, we did not model how changes in pH and redox state in the soil and plant would change chromium speciation.

## 2.2. Data Collection

We used two types of data: samples collected specifically for this study and publicly available monitoring data.

### *2.2.1. Field Sample Collection and Laboratory Analysis*

We collected field samples of irrigation water, soil, and edible crops on selected Central California farms that had irrigated fields with OPW for at least two consecutive years. We identified regions and water districts that use and distribute OPW for irrigation (Table A2), as well as independent producers (i.e., growers with oil wells on their property who use their own OPW for irrigation instead of purchasing it from a water district). We identified crops grown on fields that are potentially supplied with OPW by submitting Freedom of Information Act requests to water districts requesting lists and maps of farms receiving OPW. The Cawelo Water District in Kern County mixes OPW with local groundwater and distributes this water to farms within the district through canals. We obtained permission to enter and sample OPW by contacting local growers directly and by working with California State University in Bakersfield (CSUB). Sixteen water samples were collected in the field using U.S. Geological Survey protocol for sampling, filtration, storage, and preservation according to the analysis type (United States Geological Survey, 2011). Additional information on sample collection and laboratory analysis methods are available in Kondash et al., 2020.

### *2.2.2. Publicly Available Data*

The sampling data were supplemented with publicly available data sets, which were compiled, georeferenced, reviewed for quality assurance and control, and organized into a database. This database includes three water sources: OPW (effluent coming into the water districts, OPW classified as "effluent-other" was excluded in this report), groundwater from monitoring sites, and the blended OPW and irrigation water delivered to farmers. California Senate Bill 4, signed in 2013, mandated "strategic, scientifically based groundwater monitoring" of the state oil and gas fields (Esser et al., 2015). The state of California monitors the volume of OPW used for irrigation and makes testing results for irrigation water samples publicly available (CA DOGGR, 2016; CAWB CVR, 2016; Heberger & Donnelly, 2015). Publicly available monitoring reports from as early as 1967 were identified, with most from 2013 to 2017. Sources included the California Oil Fields Food Safety Website (CAWB CVR, 2016) and Central Valley Regional Water Quality Board (CA RWQCB CVR, 2018; CAWB CVR, 2016). Currently, the Central Valley Regional Water Quality Board endeavors to provide irrigation water that meets quality standards for arsenic, boron, chloride, sodium, and electrical conductivity (CAWB, 2016).

### *2.2.3. Overall Data Set*

In all, we compiled 4,809 data points in OPW, groundwater, and irrigation water (blended OPW and groundwater): 432 from sampling data and 4,377 from publicly available reports, all from Kern County. About one-third of these were nondetects. Among the detections, there was considerable variability in the data, with as much as four to five orders of magnitude between the minimum and maximum values in any particular type of water.

## 2.3. Risk Assessment

A probabilistic modeling framework was applied to evaluate potential risks from eating foods grown in OPW-irrigated soil. The probabilistic modeling framework consists of four main components (Fig. 1): (1) the land-based source module, which models the fate and transport of constituents in OPW used for irrigation through the soil column; (2) the farm food chain module, which models the distribution and uptake of the constituents by plant roots, potential accumulation in edible fruits or seeds; (3) the human exposure module, which estimates human exposure due to consumption of the crops considered and soil consumed incidentally with the crops; and (4) the human health module, which estimates human health impacts (in the form of noncancer hazard or cancer risk). The source module is based on the peer-reviewed U.S. Environmental Protection Agency (EPA) land application unit model developed as part of the multipathway, multimedia, multireceptor risk assessment modeling system (also known as 3MRA) (US EPA, 2003). The food chain, exposure, and human risk algorithms were based on the USEPA's Human Health Risk Assessment Protocol (HHRAP) for Hazardous Waste Combustors.(US EPA, 2005) The model components and the Monte Carlo framework are described briefly here;

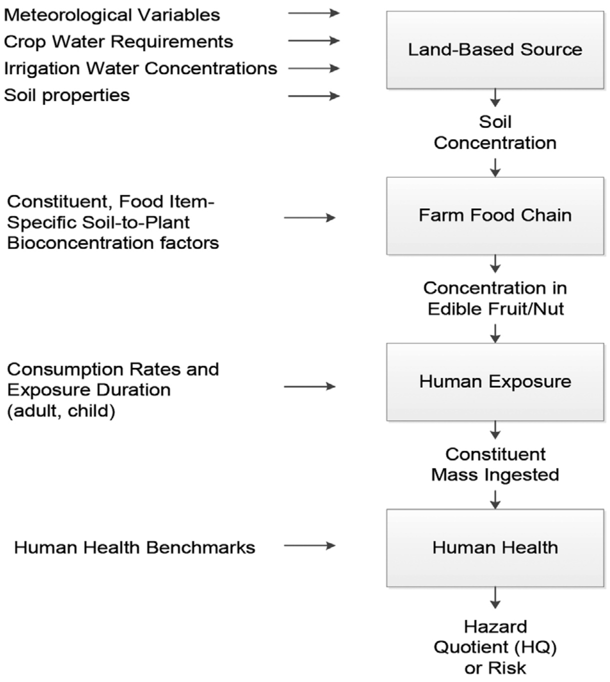


**Fig 1.** Overview of OPW crop irrigation risk modeling framework.

the Supporting Information includes an expanded methods section that provides more detail.

### 2.3.1. *Land-Based Source Module*

This model uses concentrations of the constituents of interest in OPW along with a variety of inputs characterizing irrigation practices and the environmental setting to estimate soil concentrations of the constituents resulting from the use of OPW for crop irrigation. The key inputs to the source model, in addition to the constituent concentrations in OPW, include a geospatial characterization of the agricultural setting for the study region, soil, and climate conditions at the agricultural fields, soil sorption coefficients for the constituents, crop characteristics and water requirements, and daily meteorological data.

For this assessment, we adapted the 3MRA land application unit model to simulate the application of OPW for irrigation of common perennial tree crops (citrus, almonds, and pistachios), grapes, and root vegetables using drip or microsprinklers, which are typically used for irrigation in the study region. Use of OPW was simulated only when the crop-specific daily demand for water was greater than daily precipitation during the period of interest. The model uses dissolved concentration in OPW to estimate mass transfer rates, and accounts for losses through erosion and runoff, percolation, and leaching.

The output of the source module is annual average soil concentrations in the field. Additional information on the source model is available in the Supporting Information.

### 2.3.2. *Farm Food Chain Module*

This module uses the soil concentrations from the source module to simulate uptake of the constituents from soil to crops. This simple algorithm relies on constituent-specific soil-to-plant uptake factors that relate soil concentrations to concentrations in different parts of the plant (roots, vegetative parts, and reproductive parts such as fruits. The output is constituent concentrations in different types of crops. Additional information on the farm food chain model is available in the Supporting Information.

### 2.3.3. *Human Exposure Module*

This component estimates the potential exposure to inorganic constituents that can occur when a person consumes crops grown on fields irrigated with OPW. The exposure pathways evaluated include consumption of crops (based on crop concentrations from the farm food chain module) as well as incidental ingestion of soil (based on soil concentrations from the source module). For incidental soil ingested, because the soil concentration may vary with different crops due to different irrigation water needs, we estimated those exposures separately for each crop. We evaluated risk for both an adult and a child, to account for differences in consumption relative to body weight and age.

Estimates of exposure relied on distributions of exposure parameters reflecting the physical characteristics (e.g., body weight) and behavior patterns (e.g., consumption rates) of the adult and child receptors. Continuous distributions for each exposure parameter were created in @Risk based on percentile data representative of the U.S. population presented in the EPA's *Exposure Factors Handbook* (EFH) (US EPA, 2011) and *Child Exposure Factors Handbook* (US EPA, 2008). The crops were assumed to be eaten as is (i.e., reflecting no preparation losses such as washing) to conservatively evaluate exposure risk.

The outputs of the exposure module are the average daily dose (used for noncancer hazard) or lifetime average daily dose (for cancer risk) from the consumption of crops and the incidental consumption of soil. Additional information on the exposure model, including the equations for calculating average and lifetime average daily dose and exposure factor distributions, is available in the Supporting Information.

#### *2.3.4. Human Risk Module*

This component combines the dose estimates from the exposure module with human health toxicity benchmarks to estimate noncancer hazard quotients (HQs) and cancer risks associated with predicted exposure levels. For noncancer hazard, we used the chronic Reference Dose (RfD) as the toxicity benchmark, and for cancer risks, we used the oral cancer slope factor (CSF).

We calculated hazard or risk for consumption of each crop individually (almonds, citrus fruits, grapes, pistachios, and root vegetables) and for incidental soil ingestion (ingesting soil after OPW irrigation) associated with each individual crop. We also combined risks across crops to reflect what a vegetarian diet might include by summing the risks for citrus, grapes, root vegetables, and whichever of the two nut crops had the higher risk (vegetarian scenario). The cumulative impacts of risks from multiple constituents were not estimated. Additional information on the risk model and the toxicity benchmarks used is available in the Supporting Information.

#### *2.3.5. Monte Carlo Framework*

The above model components were run in sequence many times within a Monte Carlo framework to account for different patterns of variability in space and time. Each model run (for a specific scenario, such as adult, noncancer hazard associated with arsenic in grapes) includes 10,000 iterations. For each iteration, inputs and parameters were selected from a distribution, loaded, and the modules run for the duration of the 100-year timeframe considered. The outputs of each iteration were aggregated to produce distributions of risk or hazard for the scenario. The input data and parameters were derived from the literature, publicly available databases, and expert opinions.

For the concentration of constituents in irrigation water, because of the high degree of variability in the data set, we started with the maximum concentration in OPW from the data collected as a conservative assumption, and did not vary this in the Monte Carlo iterations, planning to reevaluate the need to fully characterize the distribution based on the results. See Section 3 (Results) and Section 4 (Discussion) for further discussion.

The Monte Carlo framework addressed variability only in environmental settings (e.g., soil properties and meteorological conditions), farm operating conditions (e.g., frequency of irrigation, soil management), and human exposure patterns (e.g., food intake rates). Variability in those parameters was characterized using a combination of site-specific and published data. In the absence of site-specific data, parameters were obtained from regional or national databases.(NOAA, 2020; US EPA, 2011; USDA, 2005, 2017) More information on the Monte Carlo framework is available in the Supporting Information.

## 3. RESULTS

### 3.1. Concentrations in Irrigation Water

We analyzed 29 inorganic constituents found in groundwater, OPW, and blended groundwater/OPW mixtures used for irrigation (Table A3). For most constituents, there is considerable variability in the data, with the minimum and maximum concentrations in OPW separated by two to four orders of magnitude (Fig. 2). Constituents with low variability were typically based on very small sample sizes (Table II).

The maximum OPW concentrations were compared to the National Primary or Secondary Drinking Water Standards (Table II). The National Primary Drinking Water Regulations maximum contaminant levels (MCLs) are legally enforceable standards under the Safe Drinking Water Act; the secondary standards are nonmandatory water quality standards. Arsenic concentrations in the low-saline OPW from Kern County (Fig. 3) shows nonnormal distribution, with two peaks at concentrations of 10–20 g/L and 60–80 g/L and a max of 91 $\mu$g/L with a mean of 37 $\mu$g/L. In contrast, groundwater samples from the same region contained As in a range of 1–15 $\mu$g/L with a mean concentration of 3.4 $\mu$g/L (Fig. 3).

### 3.2. Probabilistic Risk Assessment Results

Risk assessment results are presented here for the constituents with a maximum concentration in

**Fig 2.** Concentrations of 27 inorganic constituents in OPW, plotted on a log scale and showing the range (minimum to maximum; shaded bars) and mean (points). The boxes show the 25–75th percentile values (median range shown by horizontal line within boxes); the lower line shows the 0–25th percentile values and the upper line shows the 75–100th percentile values. The dots are outliers. There were no detections in OPW for thorium and uranium. Three significant outliers were eliminated, one each for aluminum, total chromium, and zinc.

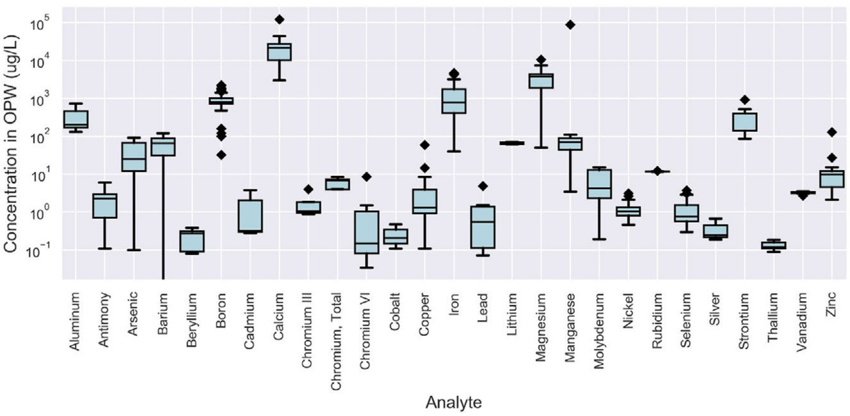
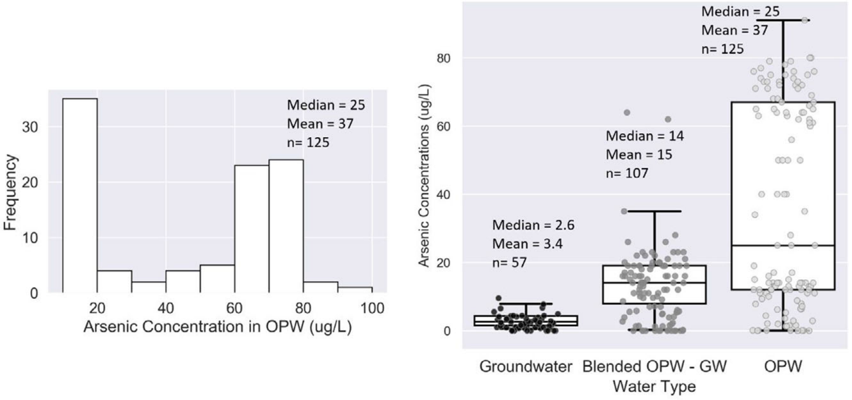


**Fig 3.** Arsenic concentrations in Kern county. (a) arsenic concentrations from low-saline OPW in Kern County, California showing a bimodal distribution of As concentrations and (b) arsenic concentrations in Kern County compared to local groundwater, blended OPW and groundwater, and OPW only.



OPW that exceeds the drinking water standard (aluminum, antimony, arsenic, iron, and manganese; Table II) and for all carcinogens (arsenic, chromium VI, and lead). Results for all other constituents are presented in the Supporting Information.

A level of concern was defined as (1) a noncancer HQ greater than 1 or (2) an excess individual lifetime cancer risk greater than 1 chance in 1,000,000 (i.e., $10^{-6}$); for cancer risk, the commonly used, slightly less conservative threshold of $10^{-5}$ is also shown. These levels of concern are consistent with the range EPA recommends in practice (2019). Additional information on human health is presented in the Supporting Information.

### *3.2.1. Noncancer Hazard*

The probabilistic risk assessment model did not identify noncancer hazards above levels of concern due to consumption of any crops, either individually or collectively as part of a vegetarian diet (i.e., high-end consumption of OPW-irrigated tree nuts, fruits, and root vegetables), for any of the inorganic constituents evaluated in this study. This finding applied to both adults and children. Fig. 4 shows box and whisker plots of the noncancer HQ results, plotted on a log scale) for consumption of crops for six selected noncarcinogens (the results for the additional noncarcinogens are provided in Fig. S2). Each panel is one constituent; the horizontal red line shows an HQ of 1 (the level of concern). Child (lighter boxes) and adult (darker boxes) results are plotted for each crop or the "vegetarian" scenario (i.e., a person eating citrus, grapes, root vegetables, and either almonds or pistachios, whichever had a higher HQ).

The model presented in this study shows that all noncancer hazards for crop consumption were far below the level of concern; the highest maximum HQ seen across all results was less than 0.2. Noncancer hazards for incidental soil ingestion were even lower (Fig. S3 for selected noncarcinogens and Fig. S4 for additional noncarcinogens).

**Table II.** Mean and Maximum Concentrations in OPW Samples for All Data Used in the Study and National Drinking Water Standards for comparison ($\mu$g/L)

| | OPW Concentration | | | | | |
|---|---|---|---|---|---|---|
| Constituent | *n* | Mean | 95th Percentile | Maximum | Standard Deviation | Drinking Water Standard |
| Aluminum | 3 | 350 | 670 | 720 | 323 | 50 |
| Antimony | 18 | 2.3 | 6 | 6 | 2 | 6 |
| Arsenic | 125 | 37 | 77 | 91 | 29 | 10 |
| Barium | 31 | 59 | 110 | 120 | 39 | 2,000 |
| Beryllium | 5 | 0.23 | 0.37 | 0.39 | 0 | 4 |
| Boron* | 281 | 880 | 1,300 | 2,200 | 286 | – |
| Cadmium | 3 | 1.4 | 3.4 | 3.7 | 2 | 5 |
| Calcium* | 167 | 19,000 | 31,000 | 120,000 | 11,860 | – |
| Chromium VI | 7 | 1.6 | 6.5 | 8.6 | 3 | – |
| Chromium (Total) | 5 | 6.4 | 8.2 | 8.4 | 2 | 100ˆ |
| Cobalt | 8 | 0.25 | 0.44 | 0.48 | 0 | – |
| Copper | 15 | 6.7 | 28 | 59 | 15 | 1,300 |
| Iron* | 72 | 1,200 | 3,600 | 4,600 | 1,161 | 300** |
| Lead | 6 | 1.3 | 4.0 | 4.8 | 2 | 15 |
| Lithium | 5 | 66 | 71 | 71 | 5 | – |
| Magnesium* | 148 | 3,200 | 5,900 | 10,000 | 1,791 | – |
| Manganese* | 68 | 1,300 | 100 | 87,000 | 10,542 | 50** |
| Molybdenum* | 22 | 6.7 | 13 | 15 | 5 | – |
| Nickel* | 20 | 1.2 | 2.6 | 3.1 | 1 | – |
| Rubidium | 5 | 12 | 12 | 12 | 0 | – |
| Selenium* | 16 | 1.3 | 3.3 | 3.7 | 1 | 50 |
| Silver | 3 | 0.37 | 0.63 | 0.67 | 0 | 100** |
| Strontium | 39 | 250 | 510 | 910 | 177 | – |
| Thallium | 6 | 0.13 | 0.185 | 0.19 | 0 | 2 |
| Vanadium | 4 | 3.2 | 3.5 | 3.5 | 0 | – |
| Zinc* | 18 | 16 | 42 | 130 | 29 | 5,000** |

All sampling data and publicly available monitoring data are from Kern County, CA.

Drinking Water Standards are the National Primary Drinking Water Standard, if available, or Secondary Drinking Water Standard (if no primary). Secondary standards are denoted by**.

*Nutrients or trace nutrients;

**= Secondary drinking water standard,

ˆ= 100 $\mu$g/L national standard, 50 $\mu$g/L MCL in CA.

### *3.2.2. Cancer Risk*

Cancer risk was evaluated for the three constituents with oral cancer slope factors: arsenic, chromium VI, and lead. Chromium VI and lead do not appear to pose cancer risks even when multiple crops are consumed, but the 90th percentile risk for arsenic in the vegetarian scenario just reaches the $10^{-6}$ level of concern (Fig. 5). When food consumption across food groups (fruits, vegetables, and vegetarian protein) is not summed and lower consumption patterns are present, the cancer risk falls below the threshold level of concern (Fig. 5). Lifetime cancer risks from incidental soil ingestion were lower than crop-based risks (Fig. S5).

## 4. DISCUSSION

The widespread production of oil in California generates large volumes of OPW in productive agricultural regions, such as Kern County. Based on our probabilistic human health risk assessment results evaluating trace inorganics in low-saline OPW that is currently used for irrigation in Kern County in Central Valley, we found that the use of OPW for crop irrigation is unlikely to cause accumulation of metals in soil and products and thus have low human health risks. Our study found that the accumulation of arsenic in soil and crops presents the greatest risk to human health. For example, a 180-pound adult whose diet is based on solely consumption of around 1

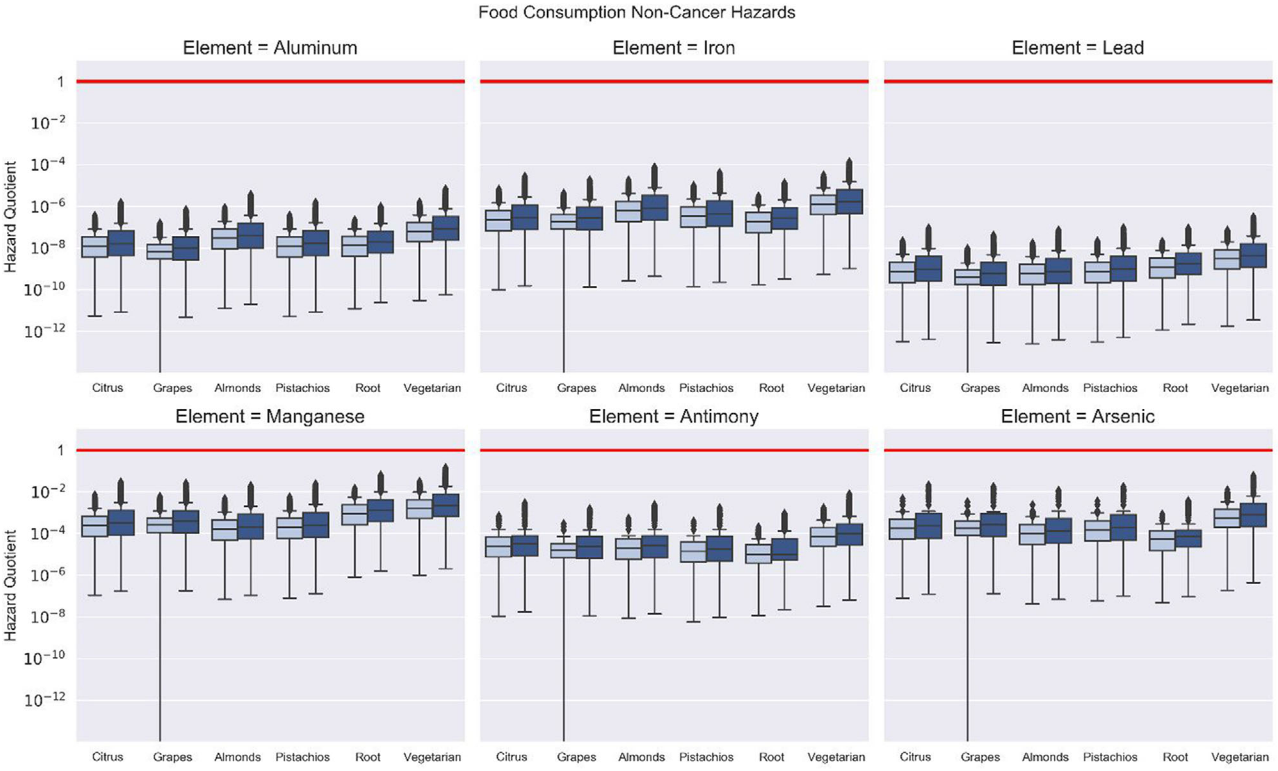


**Fig 4.** Crop ingestion noncancer hazards for selected constituents for children (lighter bars) and adults (darker bars). The red line indicates the screening HQ of 1. The "vegetarian" data is a person eating fruits (both citrus and grapes), root vegetables, and one of the nuts for protein (whichever has a higher HQ).

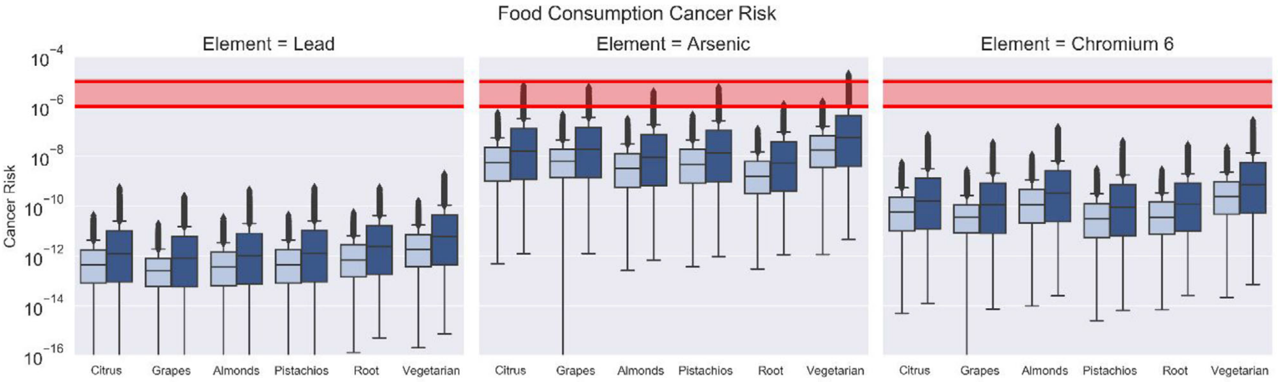


**Fig 5.** Crop ingestion cancer risks for lead, arsenic, and hexavalent chromium in children (lighter bars) and adults (darker bars). The red line indicates the screening risk level of $10^{-6}$. The "vegetarian" data is a person eating fruits (both citrus and grapes), root vegetables, and one of the nuts for protein.

pound of citrus, one-fourth pound of root vegetables, half pound of grapes, and 1 pound of nuts from fields irrigated with OPW every day (which, while possible, is not likely to be the case for many consumers), and assuming the irrigation water contains the maximum arsenic concentration seen in our data set, the 90th percentile cancer risk is $10^{-6}$. Measured samples of groundwater contained an average arsenic concentration of 3.4 $\mu$g/L while blended OPW and groundwater contained an average arsenic concentration of 15 $\mu$g/L (Table A3), which is 7× lower than our maximum observed As concentration in OPW, highlighting the importance of blending this water. The level of concern for cancer risks is typically set to $10^{-5}$ or $10^{-6}$, so this risk meets the more conservative $10^{-6}$ level of concern only. Thus, any lower concentrations of arsenic, whether due to blending with low-As surface or groundwater or OPW representing the first, lower peak of As observed in our data set (Fig. 3), would put that risk below the more conservative level of concern. We modeled the maximum concentrations in OPW initially to be conservative and reevaluated variability in the concentration data used for modeling. However, given the striking lack of hazards near levels of concern for noncarcinogens and this single cancer risk right at the lower level of concern, we determined that developing a rigorous distribution of concentrations for use in the Monte Carlo analysis was unnecessary.

With respect to arsenic, however, consumers may be exposed to additional arsenic through other pathways, particularly drinking water (Smith, Knight, & Fendorf, 2018). Arsenic occurs naturally in groundwater in California, with certain populations at elevated risk from drinking water exposure, especially those on private wells or drinking from municipal supplies reliant on groundwater (Ayotte, Nolan, & Gronberg, 2016). It is possible that the combined exposure to arsenic in drinking water and crops irrigated with OPW containing high levels of arsenic may in some cases further exceed levels of concern for human health. In certain instances, water treatment has been instituted to reduce arsenic levels in municipal drinking water (CAWB, California Water Boards, 2019; The Tribune, 2019). However, similar treatment for OPW with high arsenic levels is likely economically infeasible because of high operations and maintenance costs, and the per unit cost of irrigation water is much lower than drinking water (US EPA, 2000).

Despite maximum concentrations of antimony, lead, aluminum, iron, and manganese in OPW exceeding drinking water standards, no other inorganic constituents accumulated enough in crops and soil to pose significant risks to human health (Figs. 4, 5, and S2–5).

The multidisciplinary risk-based methodological approach applied in this study can provide a useful framework for other applied studies in complex systems at the nexus of energy, water, and food production, such as other nontraditional irrigation and food process water sources. To our knowledge, only one other study has evaluated the trace metals in low-saline OPW using a risk assessment framework, but the study methodology and findings were not peer-reviewed. The 2016 risk assessment by ERM (Navarro et al., 2016) completed a deterministic screening by back-calculating risk-based concentrations in OPW using a smaller subset of metals. These calculations used age-weighted exposure factors averaging out differences between child and adult receptors. Additionally, the study used single values for climate variables, irrigation rates, and environmental parameters, making it difficult to generalize the results to other environmental settings, even within California's Central Valley, with any confidence. A key limitation of the ERM approach is that the back calculation and presentation of risk-based concentrations (instead of risks) can obscure the embedded assumptions made about the level of concern and risk estimates. This makes it difficult to evaluate risks from the use of OPW as irrigation water in the context of other exposures; an example of this can be seen with arsenic, where ERM suggests an RBC risk-based concentration of 100 $\mu$g/L. In our data set, we observe a maximum As concentration of 91 $\mu$g/L, close but below the ERM RBC. Under our "vegetarian consumption scenario," this level of arsenic would meet the level of concern for the cancer risk level of $10^{-6}$ for adults, especially when considered in conjunction with other possible sources of arsenic exposure. While the likelihood of having As concentration of approximately 100 $\mu$g/L in the low-saline OPW is small (3 out of 125 or 2.4% of samples had As above 80 $\mu$g/L), our model indicates that the current allowable irrigation standard of 100 $\mu$g/L could result in cancer risk at or above the $10^{-6}$ level for the "vegetarian consumption scenario," and this risk does not incorporate the potential for additional arsenic exposure from naturally occurring drinking water sources in CA. (Ayers & Westcot, 1976) Enviro-Tox Services Inc. also prepared an irrigation water quality assessment for the Cawelo Water District in Kern County, CA, which reviewed concentrations of organic compounds found commonly in OPW, including acetone, benzene, pyrene, and others (Robles, 2016b). The report used water, soil, and plant data from samples collected by the Cawelo Water District and analyzed at a third-party laboratory using standard analytical methods. However, inorganic chemistry data in the laboratory reports was not evaluated or presented in the published Enviro-Tox Services water quality assessment report. Additionally, concentrations of oil and grease and organic compounds reported in the study did not apply a systematic or probabilistic risk assessment framework. Crop samples for test crops (irrigated with blended OPW) were compared to samples from control crops (irrigated with groundwater only) for acetone, diesel range organics, and methyl chloride, but most other constituents were not included in the analysis because concentrations were below detection limits or not included.

### 4.1. Limitations

This analysis makes use of a robust publicly available data set to supplement a limited collection of field data to evaluate the risks of using low-saline OPW for irrigation in Kern County, California. While reported concentrations in the publicly available data set match or exceed concentrations found in samples collected and analyzed during our study, future studies would benefit greatly from additional support from farmers and water districts to collect OPW, soil, and crop samples. Our study also focused on human exposure to metals associated with irrigation of low-saline OPW in Central California but not organic constituents, which are being evaluated by the California Food Safety Expert Panel (Robles, 2016a). It is important to emphasize that this analysis examined the use of low-saline OPW that is currently used for irrigation in Kern County. Across the United States there is interest in reusing higher salinity OPW for irrigation, and while this modeling framework could be useful in understanding the human health impacts of that irrigation, the potential for significantly different salinity, along with organic and inorganic chemical concentrations, need to be accounted for prior to applying this modeling framework elsewhere.

### 4.2. Recommendations

This is the first probabilistic risk assessment completed evaluating trace metals exposure from low-saline OPW used for crop irrigation. Overall, our findings suggest that with careful management and monitoring, low-saline OPW can be beneficially reused to augment regional water availability, in particular for the agricultural sector, especially with standardized regulations, monitoring and best management practices, as further described.

#### *4.2.1. Current Regulations and Policies*

The first agreement to supply OPW to water districts was signed in 1994, with the water district responsible for monitoring and managing water (CA RWQCB CVR, 2012). Permits have been issued on a case-by-case basis, with the Basin Plan placing limits on the levels of salinity, chloride, and boron in OPW used for irrigation (CA RWQCB CVR, 2018) Additional limits on arsenic concentrations of 10 $\mu$g/L (national MCL) have been added to limit supply of arsenic within distribution canals, and 90 $\mu$g/L daily maximum discharge into the Cawelo mixing basin (CA RWQCB CVR, 2007, 2012). In 2006, SOC Resources, Inc. was issued a permit to store OPW in an unlined surface impoundment, where a large portion of the wastewater was transferred from the impoundment through the Schaefer Pipeline (CA RWQCB CVR, 2006). The pipeline transfers the wastewater from the impoundment to the Cawelo Water District, where it is blended with fresh water and distributed for irrigation (CA RWQCB CVR, 2006). The 1994 Texaco (Chevron) deal was renewed in 2006, then again in 2012. The 2012 renewal granted Chevron permission to pipe 33.5 million gallons per day to the Cawelo Water District to be used to help meet irrigation demand (CA RWQCB CVR, 2012). The water supplied to the district is treated with mechanical separation, sedimentation, air floatation, and filtration to meet Basin Plan standards and delivered to the Cawelo district (CA RWQCB CVR, 2012). Other permits were issued to Valley Waste Disposal Company in 2007 (CA RWQCB CVR, 2007), E&B Natural resources in the Jasmin Mutual Water District (Jasmin Oil Field) in 1998 (CA RWQCB CVR, 1998), and California Resources Production Corporation in the North Kern Water Storage District (Kern Front Oil Field) in 2015 (CA RWQCB CVR, 2015).

In addition to following the Basin Plan's water quality control plan, districts also aim to follow set water quality standards outlined in *A Compilation of Water Quality Goals (17th Edition, January 2016)* (Marshack, 2016), setting guidelines for water quality associated with various reuse options. For agricultural water, suggestions from Ayers & Westcot's *Water Quality for Agriculture* (Ayers & Westcot, 1976) are used. These guidelines line up closely with those outlined in the Basin Plan and the Water Boards' stated goals and limits for chloride, boron, and arsenic in irrigation water.

#### *4.2.2. Recommended Safeguards to Reduce Arsenic Exposure*

The level of arsenic in OPW can lead to increased cancer risk for highly exposed subpopulations eating a vegetarian diet high in nuts, as well as fruits and root vegetables, that are irrigated with

OPW. While more study should be completed to characterize specific food consumption patterns on the farm-to-fork continuum, our findings indicate that for crops irrigated with OPW there is a small but potential increase in cancer risk, especially for highly exposed residents of California or other regions already exposed to elevated arsenic in their drinking water. Blending OPW with other lower arsenic water sources could reduce arsenic to levels below the level of concern.

### 4.2.3. *Recommended Monitoring Updates*

A number of parameters that can affect crop health (and are mentioned in the agricultural water quality thresholds) are omitted from the basin plan and water district-oil company agreements. These include aluminum (5,000 $\mu$g/L), beryllium (100 $\mu$g/L), cadmium (10 $\mu$g/L), total chromium (100 $\mu$g/L), cobalt (50 $\mu$g/L), copper (200 $\mu$g/L), fluoride (1,000 $\mu$g/L), iron (5,000 $\mu$g/L), lead (5,000 $\mu$g/L), manganese (200 $\mu$g/L), molybdenum (10 $\mu$g/L), nickel (200 $\mu$g/L), selenium (20 $\mu$g/L), and vanadium (100 $\mu$g/L) (Ayers & Westcot, 1976; Marshack, 2016). We recommend that these constituents, along with sodium adsorption ratio, are also added to the current regulations on water quality for agricultural usage.

It is important that both used OPW and groundwater quality will be monitored along with food safety on a regular (monthly, quarterly or semiannual) basis to detect possible changes in concentrations across growing seasons, geographic areas, and used OPW over time. OPW discharge into Cawelo reservoirs and being sent to farms is monitored for arsenic, boron, and chloride on a monthly basis (2012). Priority pollutants, including many of the inorganics mentioned in the water quality thresholds above, are only required to be monitored every five years. In comparison, recycling of other wastewater is monitored at a higher frequency and for a larger spectrum of constituents. For example, the U.S. EPA's Guidelines for Water Reuse (CA RWQCB CVR, 2012) allowing municipal wastewater recycling "was preceded by an intensive, 11-year pilot study to determine whether or not the use of disinfected filtered recycled water for irrigation of raw-eaten food crops would be safe for the consumer, the farmer, and the environment." Additionally, monitoring should be expanded to include inorganic and organic contaminants regularly. To foster transparency and thereby improve potential use of OPW, we recommend creating and maintaining a publicly available OPW database to house these data. This database should be continuously updated as publicly available laboratory reports are made available to facilitate public access to these data.

### 4.2.4. *Best Management Practices*

In addition to monitoring, standardization of OPW pretreatment and water blending protocols should be completed for transparency and to consider the long-term safety and sustainability of OPW usage (Kondash et al., 2020). Additionally, greater transparency and cooperation with both water districts and farmers on future studies in the region will help foster a greater understanding of the risks and mutual trust between consumers and farmers.

Future research should evaluate how the Sustainable Groundwater Management Act and California's net carbon zero plans may affect usage of OPW (CA Senate Bill No. 100, 2018, 2015). Overall uncertainty surrounding the sustainability and safety of using OPW may affect future regulations and permitting, leaving farmers without a lifeline source of alternative irrigation water during periods of water stress and leading to food insecurity concerns.

## 5. CONCLUSIONS

Beneficial use of certain low-saline OPW from Kern County in the Central Valley of California for irrigation is a promising example of a high-potential synergy among the energy, water, and food industries to sustainably use natural resources. This is the first study evaluating how trace metals in low-saline OPW used for crop irrigation in California may affect food safety and human health risks using a probabilistic risk modeling framework. This study was designed to model and quantify the risk associated with the consumption of crops and soil irrigated with low-saline OPW using available concentration data for inorganic compounds. Our scientific investigation shows low risk from consumption of crops irrigated within this area using low saline OPW. Results show that vegetarians or other adults that eat a significant amount of protein in their diet from nuts, plus high consumption of fruits and root vegetables, could have increased cancer risk associated with arsenic exposure, assuming the consumption of foods are irrigated with the higher arsenic concentrations (90 g/L relative to mean value of 30 g/L OPW). The noncancer hazards are far below levels of concern, and cancer risks for all other constituents evaluated are below levels of concern. The model used in this study applies for unique low-saline OPW that is clearly characterized by low salinity (Kondash et al., 2020). If the constituents in OPW vary in other regions, the study results may not apply, even though all other environmental parameters were considered across the Central Valley of California. Other oilfield formations, especially those with higher salinity, may contain higher inorganic and organic constituents in OPW and would therefore require additional testing and risk modeling to evaluate the potential human health effects of prospective irrigation use. With oilfield production (and thus, OPW volume) projected to increase in some basins in the United States long-term, the reuse of OPW has the potential to make a critical difference in the water budgets of drought-stressed watersheds. There is clear demand for increased access to OPW in this highly productive but water-stressed agricultural region, provided adequate water quality is monitored, regulations address human health and crop health concerns, and best management practices are followed. This article expands the limited body of literature on the human health impacts of using OPW for irrigation. Through the use of collected water samples and a rigorous modeling and risk assessment we have begun the process of filling in this literature gap.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**Table A1**. Oil Production (MMbbl) from the Top 10 Producing Formations in California
**Table A2**. Summary of the Five Identified OPW Supply Agreements
**Table A3**. Mean and Maximum Concentrations in Groundwater, OPW, and Irrigation Water Samples for All Data Used in the Study
**Fig. S1**. Map of 24 meteorological zones in California's Central Valley
**Fig. S2**. Crop ingestion noncancer hazards for additional constituents for children (lighter bars) and adults (darker bars)
**Fig. S3**. Incidental soil ingestion noncancer hazards for selected constituents for children (lighter bars) and adults (darker bars).
**Fig. S4**. Incidental soil ingestion noncancer hazards for additional constituents for children (lighter bars) and adults (darker bars)
**Fig S5**. Incidental soil ingestion cancer risks for lead, arsenic, and hexavalent chromium in children (lighter bars) and adults (darker bars)