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Article

Experimental Analysis of Heavy Metal Uptake in Soil and Citrus Plants from Irrigation Water

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Abstract: Oilfield produced water (OPW) is used to boost freshwater sources for crop irrigation in California's agriculturally important Central Valley. OPW is known to contain salts, metals, hydrocarbons, alkylphenols, naturally radioactive materials, biocides, and other compounds from drilling and production processes. Less is known about the potential uptake and accumulation of these compounds in crops and soil irrigated with OPW. In this study 23 potted mandarin orange plants were irrigated 2-3 times weekly (depending on season) with water containing three different concentrations of the known OPW heavy metals barium, chromium, lead, and silver. Seven sets of samples of soil and leaves and all fruits were collected and processed using microwave-assisted digestion (EPA Method 3051A). Processed samples were analyzed using ICP-OES. ANOVA, ANCOVA, and Tukey's honest significant difference test were used to examine the effects of metal concentrations in the irrigation water, sample number, and number of watering days on the metal concentrations in the soil, leaf, and fruit samples. Accumulation of barium in soil and leaves was strongly positively associated with sample and number of watering days, increasing nearly 2,000-fold. Lead also showed an upward trend, increasing up to 560-fold over baseline level. Chromium showed an increase in the soil that tapered off, but less consistent results in the leaves and fruit. The silver results were more volatile, but also indicated at least some level of accumulation in the tested media. The smallest absolute accumulation was observed for chromium. Concentrations in the fruit were highest in the peel, followed by pith and juice. Accumulation of all heavy metals was generally highest in the soil and plants that received the highest irrigation water concentration. Considering the potential for adverse human health effects associated with ingesting soluble barium contained in food and drinking water, and to a lesser extent chromium and lead, the study signals that it is important to conduct further research into whether OPW contaminants can enter the food chain and pose risks to consumers.

Keywords: oilfield produced water; wastewater; heavy metals; irrigation; bioaccumulation; soil health; California

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1. Introduction

California is still the third-largest oil-producing state in the United States.[1] During the oil production process, substantial volumes of oilfield produced water (OPW, also referred to as oilfield brine, connate water, or formation water) are typically generated, especially as the well and oilfield matures. The origins of the briny water include flow from above, within and below the targeted hydrocarbon zone as well as flow from injected fluids and additives employed during the production process.[2] OPW is the largest waste stream by volume in the exploration and extraction of oil, and over the lifespan of an oilfield the total volume of produced water can exceed tenfold the volume of hydrocarbons produced.[3] In 2012, for example, California generated an estimated 21 billion barrels of OPW, i.e., approximately 15 barrels of OPW for every barrel of oil.[4]

In general, OPW is high in salts and dissolved solids and may also contain metals, alkylphenols, trace elements, hydrocarbons, polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOC), benzene, toluene, ethylbenzene and xylenes (collectively known as BTEX), naturally radioactive materials (NORM), biocides, and other compounds used during the production process.[3] Concentrations of total dissolved solids (TDS) in OPW range from the low thousand mg/L to several hundred thousand mg/L.[2] In the Western U.S., including several California oilfields, measured concentrations range from 1,000 mg/L to 400,000 mg/L.[5] A case study analyzing the composition of OPW from 630 producing oil and gas wells in California that were stimulated through hydraulic fracturing found that the average concentration of Cr(VI) in the OPW was 8.5 µg/L, while the average concentrations of Sb was 1,100 µg/L, As 1,100 µg/L, Cd 40 µg/L, Pb 420 µg/L, Se 1,900 µg/L and Zn 420 µg/L.[4] Many of the elements and compounds used in oil well drilling and production can have varying adverse health effects on the gastrointestinal tract, the nervous system, and the reproductive system when ingested.

Although the most common method for managing OPW in California is deep-well injection and disposal in evaporation-percolation pits, accounting for 60% and 18% of total OPW disposal, respectively, a small fraction of California's OPW is applied to land surface.[6] The Clean Water Act stipulates effluent guidelines for on-shore oil and gas extraction facilities that prohibit the discharge of pollutants into surface waters, except for wastewater that is of good enough quality for use in agricultural and wildlife propagation for onshore facilities located in the continental United States and west of the 98th meridian. This creates the possibility for reusing OPW in agricultural crop irrigation, as is the case in California's Central Valley.

Although OPW has been reused in surface applications for more than 20 years, it gained wider prominence and interest during the exceptional drought that gripped California between 2011-2016 as a means to supplement heavily constrained agricultural freshwater supplies.[7,8] However, the question of whether it can be done safely for consumers, agricultural workers and communities living near OPW application sites, has not been sufficiently answered to date.[9] Among the concerns voiced by public health and environmental groups is whether toxic OPW compounds, such as heavy metals, may become bioavailable and accumulate in parts of the crops intended for human consumption.[9] Concerns about long-term soil health and productivity have also been raised.[9] There is a substantial body of literature, involving field and laboratory studies, regarding the origins, environmental and health effects, and remediation of soil contamination with heavy metals, including Ba, Cd, Pb, and As.[10-16] Studies by Fliessbach et al. (1994) and Khan et al. (2000) show the negative effects on soil productivity resulting from heavy metal contamination.[17-19] While soil accumulation has been widely documented, Toze (2009) found evidence that the seeds and leaves of flax, cotton and rice report store only a small percentage of the heavy metals compared to soils.[20] However, even small concentrations may pose health risks if the crop is consumed frequently, such as rice, or in larger amounts over a short period of time, such as seasonal crops like mandarin oranges. A study in Tongzhou District, Bejing, China in 2007 examined wastewater-irrigated soils used to grow radish, maize, spinach, green cabbage, cauliflower, turnip, and lettuce.[21] It found significant correlations between heavy metal concentration in soils and the edible parts of plants for Cd, Cu, Pb, and Zn. In particular, the concentrations of Cd, Cr, and Ni exceeded regulatory limits set by the State Environmental Protection Administration.[21] Similar issues are known to arise in the proximity of metal ore mines. For example, the soil and corn, jujube, perilla, red pepper, soybean, and spring onions grown near a copper-tungsten mine in South East Korea were found to have elevated concentrations of Cu, Zn, Cd, and Pb.[22] Concentrations varied with crop species and higher concentrations were found in the leafy material of the crops compared with the fruit and seeds. It was also determined that the most dominant factor affecting metal uptake in plants was the metal content in the surface soil, which may be problematic in the long-term application of OPW wastewater.[22]

While the existing literature demonstrates the potential for plant uptake of metals through soil and irrigation water, it is of specific interest to look into the potential soil and crop impacts of OPW reuse in agriculture in California's Central Valley. As of now, water quality monitoring involving OPW is limited and not federally regulated.[5] In response to concerns raised by environmental and public health organizations, the Central Valley Regional Water Board initiated a Food Safety Expert Panel tasked with examining the available evidence and conducting studies for testing the risk involved in OPW reuse in the region's agricultural operations, primarily citrus, almond, pistachio, and table grape farming and to a lesser extent garlic, carrot and tomato plantings.[9] The panel commissioned sampling campaigns in the spring and summer of 2017 for table grapes, citrus, almonds, garlic, and pistachios and tested the edible fruit for over 100 organic, inorganic and metal analytes. A total of 16 compound or elements were detected, among them the metals Ba, Cu, Mo, Ni, Sr, and Zn, although at mostly low concentrations.[23]

The present study complements the work of the Food Expert Panel with an observational, controlled study of heavy metal accumulation of Ba, Cr, Pb, and Ag in the soil, leaves and fruit of mandarin orange plants. The goal of the study is to identify if and to what extent the tested heavy metals accumulate in the soil, leaves, and/or fruit in response to sampling time and the concentration of heavy metals used in the irrigation water.

2. Materials and Methods

A total of 23 mandarin orange trees, representing six varieties found in California's Central Valley and residential gardens, were purchased in 5 gallon pots from the same local nursery in late spring 2017. The plants were semi-randomly assigned to receiving irrigation water with three different concentration levels of Ba, Cr, Pb, and Ag (see Table 1) reflecting measurements reported in the OPW literature.[2,24] Nitrate salts were used due to their high solubilities and the absence of deleterious effects. The high concentration level was selected to test for substantial plant effects such as growth decline and mortality. The procedure was semi-random, because fruit-bearing plants were allocated such that each concentration level had at least two plants with fruits. The tested metals are found in OPW and are known for their risks to human health and soil productivity.

Table 1: Range of concentrations observed in produced water for the tested elements.

Metal salt	low concentration [mg metal/L]	# of plants	medium concentration [mg metal/ L]	# of plants	high concentration [mg metal/L]	# of plants	conc reported in literature [mg metal/L]
Barium nitrate	25.0	7*	1,500	8	3,000	8	9.65 - 1,740
Chromium(III) nitrate	0.01		0.03		0.10		ND - 0.03
Lead nitrate	5.0		10.0		30.0		<0.2 - 10.2
Silver nitrate	1.0		7.0		15.0		0.047 - 7.0

Note: low concentration levels were well above the LOD of the ICP-OES instrument. *A temporary, region-wide shortage in citrus plants meant that only 23 instead of 24 plants could be purchased within a reasonable timeframe.

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Baseline concentrations of the metals in the soil and leaves were determined before watering began. Plants were watered twice (cold season) or three times (hot season) weekly. During August and mid-December through mid-January the plants were watered with freshwater due to breaks in the academic calendar. Samples of soil and leaves were taken every two weeks during the active experimentation period. The fruit was harvested for analysis at the end of the experiment in March, 2018. Watering solutions were prepared on the days of irrigation. The soil and leaf samples were then processed by microwave-assisted digestion using EPA Method 3051A. Method blanks were run for each analysis. Specifically, in a typical procedure, 0.300 grams of soil or leaf were dried at 60° C for 3 days, digested with 12 mL of (3:1 HNO_3:HCl, A.C.S. reagent grade, Spectrum Chemical Mfg. Corp.) and filtered through a 2-μm glass fibre filter (Millipore Sigma AP2501300). The supernatant solution was diluted to 50.0 mL and stored in polypropylene test tubes. The samples were then analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). A PerkinElmer 8300 ICP-OES was used to construct calibration curves over the range of 0 – 400 mg/L Ba; 0 – 5.0 mg/L Cr; 0 – 50 mg/L Pb; and 0 – 0.25 mg/L Ag. The plasma operated at 1500 W RF power with argon gas flows of 10 L/min, 0.4 L/min, and 0.6 L/min in plasma, auxiliary, and nebulizer supplies, respectively. The oranges were analyzed in three parts: the juice, the pith, and and the peel. The pith and peels were dried at 60° C for 3 days prior to being processed as described above.

3. Results

A total of 7 sampling times t=(0,1,2, …,6) for soil and leaves were analyzed, with t=0 representing the baseline sample. While t is a discrete measure of the passage of time, another means to capture the exposure of the plants to the metal-tainted irrigation water is to consider the number of days that plants were watered with the metal solutions between the start of the experiment and the day the respective sample was collected. This watering vector is w=(0, 20, 26, 31, 35, 39, 43), with w=0 representing the baseline measurement day. Two types of analysis were conducted to model the change in measured metal concentrations over the course of the experiment. First, analysis of variance (ANOVA) was carried out to determine the effect of *treatment* (low, medium and high metal concentration in irrigation water) and *time* (using the discrete vector t) on the measured concentration of the metal in the soil and leaves. Second, an analysis of covariance (ANCOVA) was run for each metal using the same *treatment* factor and the watering vector, w, as a continuous variable. Since the sampling design was not fully balanced (the low concentration level had only 7 replicates), type II and III sums of squares were used.[25] Tukey's honest significant difference test (Tukey HSD) was applied to identify differences in means between factor level combinations. All analyses were carried out in the R statistical language and computing environment, version 3.4.3.[26] Results are presented by metal.

3.1. Barium

Of the tested metals, Ba shows the most pronounced and consistent pattern of increase in accumulation in soil and the leaves for t and w, respectively (see Figure 1). The increase was largest for the high concentration water, followed by the medium and low concentration water, respectively. Concentrations increased from an average baseline level of 17.6 mg/L (sd=11.4 mg/L) to an average of 48,086.5 mg/L (sd=9,270 mg/L) for the high concentration water at time t=6. For the low watering concentrations the increase was from 57.6 mg/L (sd=61.8 mg/L) at baseline to 3,674.5 mg/L (sd=2,737.6 mg/L) at t=6.

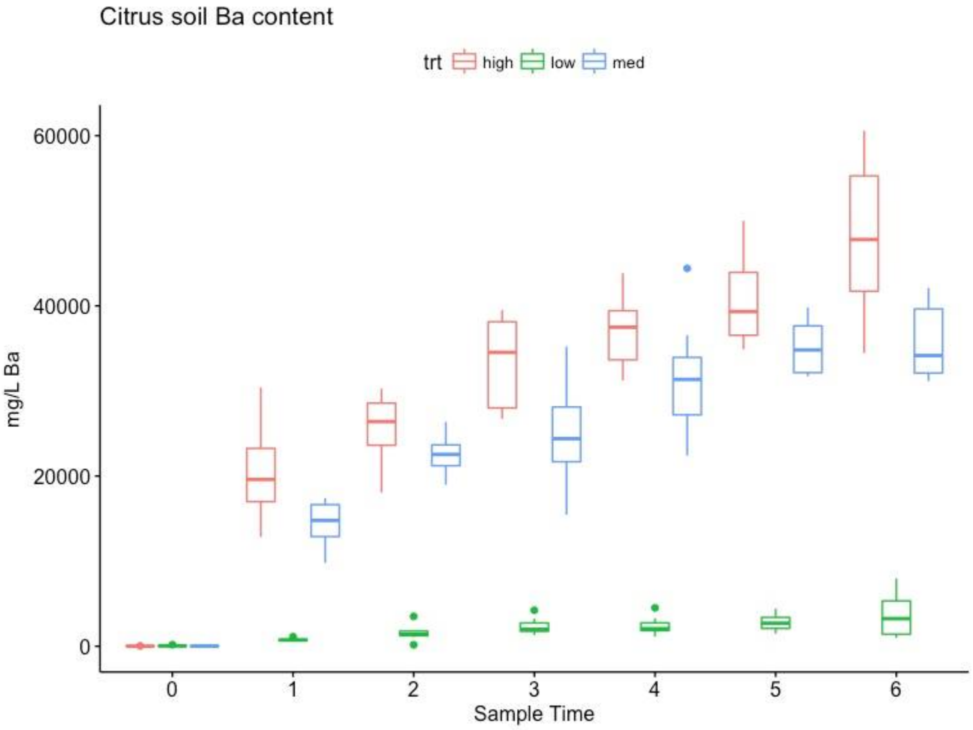

Figure 1: Boxplots of measured concentrations of Ba in the soil as a function of Ba concentration in the irrigation water (low, medium, high) and sampling time, t.

The results for the ANOVA are shown in Table 1; both treatment and time factors are statistically significant as is their interaction, which means that the slopes for the time effects differ across treatments. Specifically, the higher the Ba concentration in the irrigation water, the faster the soil accumulates occurs the metal.

Table 1: Summary of ANOVA for Ba concentrations in the soil samples.

Factor	F-value	p-value
treatment	444.960	<0.0001
time	135.221	<0.0001
treatment:time	19.669	<0.0001

A similar pattern presents for the leaves (see Figure 2 and Table 2), although at a slower rate and with concentrations leveling off at t=2. No significant accumulation occurs at the low watering concentration and there is not enough evidence for significant interactions between treatment and time. The ANOVA results for the leaves are shown in Table 2.

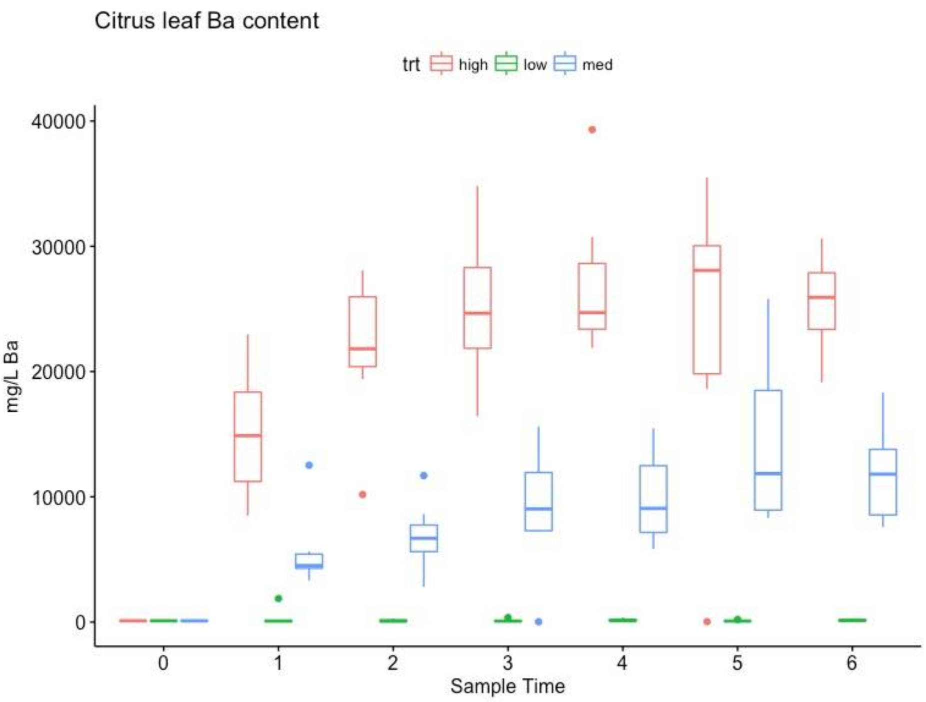

Figure 2: Boxplots of measured concentrations of Ba in the leaves as a function of Ba concentration in the irrigation water (low, medium, high) and sampling time, t.

Table 2: Summary of ANOVA for Ba concentrations in the leaf samples.

Factor	F-value	p-value
treatment	187.356	<0.0001
time	5.3329	0.0002
treatment:time	1.7141	0.0613

When considering watering as a continuous time metric, the results are similar, but the interaction is now statistically significant and indicates different accumulation rates for the three tested concentrations (see Table 3).

Table 3: Summary of ANCOVA for Ba concentrations in the soil and the leaf samples.

Factor	F-value	p-value
Soil		
treatment	465.40	<0.0001
waterings	845.11	<0.0001
treatment:waterings	105.95	<0.0001
Leaves		
treatment	182.00	<0.0001

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waterings	35.02	<0.0001
treatment:waterings	7.72	<0.0001

Ba concentrations in the fruit are highest for the peel (mean=1,014.2 mg/L, sd=1,654.1 mg/L) and pith (mean=834.0 mg/L, sd=1,193.2 mg/L). At the high watering concentration, the peel has a mean concentration of 4,544.3 mg/L (sd=315.5 mg/L), and the pith a mean of 3,318.4 mg/L (sd=16.8 mg/l). Concentrations of Ba in the juice remain low regardless of the concentration of Ba in the irrigation water (mean=52.8 mg/L, sd=56.1 mg/L). The ANOVA of the effect of Ba watering concentrations and fruit type (peel, pith, and juice) show that both are highly significant and that the effect of treatment depends on the type of fruit analyzed.

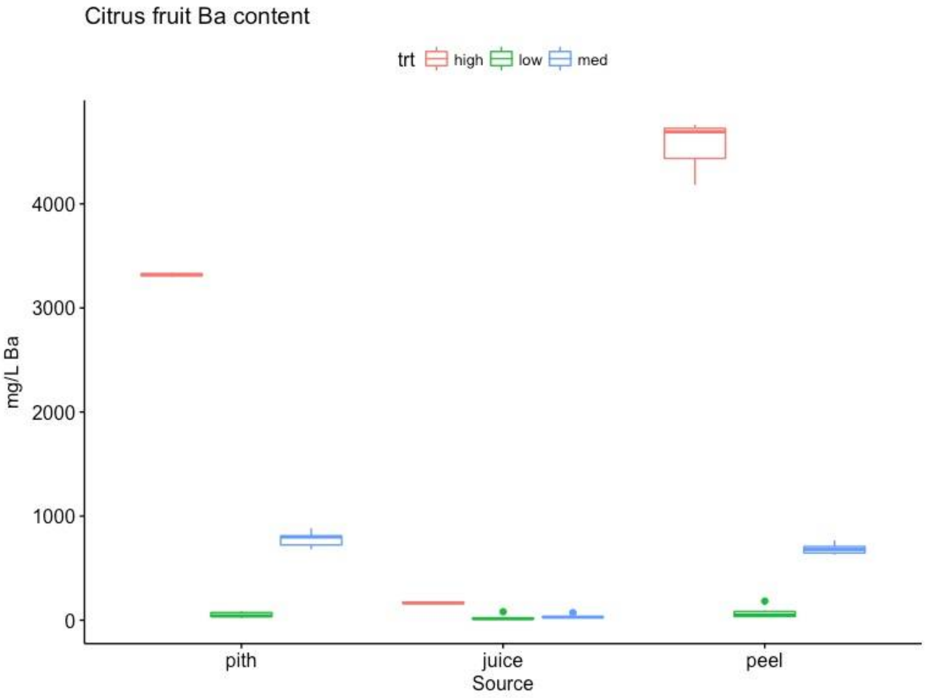

Figure 3: Boxplots of measured concentrations of Ba in the pith, juice and peel portions of the harvested mandarin oranges as a function of Ba concentration in the irrigation water (low, medium, high).

Table 4: Summary of ANOVA for the concentrations of Ba in the fruit samples.

Factor	F-value	p-value
treatment	2,469.77	<0.0001
type	735.67	0.0002
treatment:type	603.81	0.0613

3.2 Chromium

The measurements for Cr in the soil show an increase with time, *t*, that levels off at *t*=2. As the boxplots in Figure 4 illustrate, the variation in measured concentrations also increases with time ($sd_{t=0}$=1.2 mg/L and $sd_{t=6}$=5.7 mg/L). There is little to no differentiation in soil accumulation between the three tested irrigation water concentrations. The results of the ANOVA are shown in Table 5.

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The results for Cr in the leaves (see Supplementary Material Figure S1) are more volatile with initial increase up to *t*=3, followed by a sharp drop at *t*=4, substantial rise at *t*=5, and smaller decline at *t*=6.

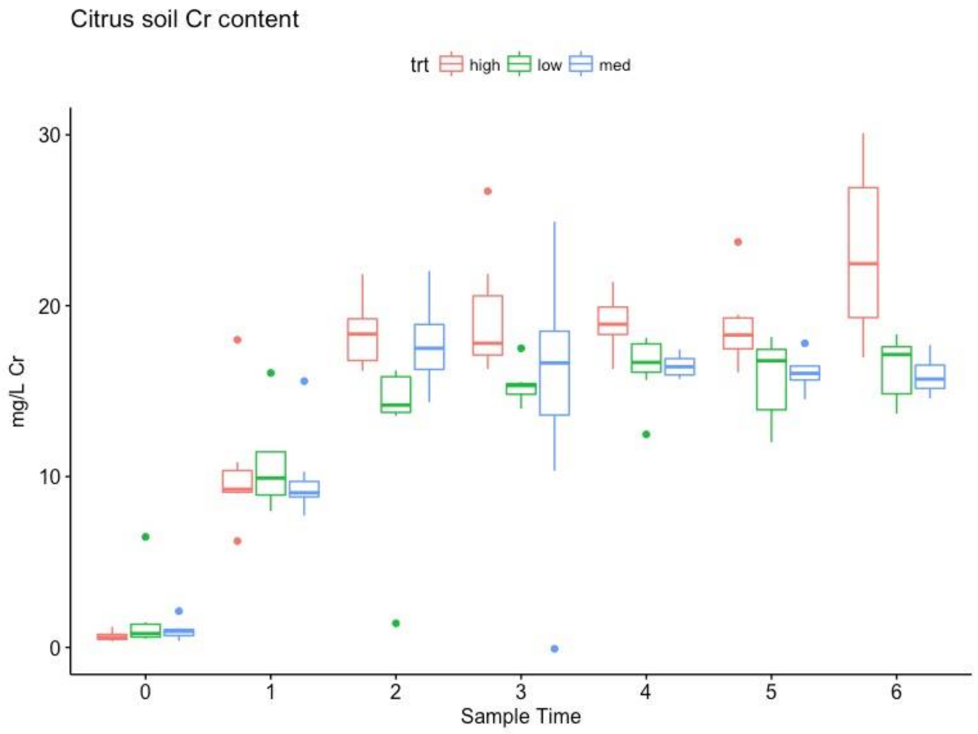

Figure 4: Boxplots of measured concentrations of Cr in the soil as a function of Cr concentration in the irrigation water (low, medium, high) and sampling time, *t*.

Table 5: Summary of ANOVA for Cr concentrations in the soil samples.

Factor	F-value	p-value
treatment	44.102	<0.0001
time	99.645	<0.0001
treatment:time	3.524	<0.0001

The results for the ANCOVA with watering days as the continuous variable are shown in Table 6.

Table 6: Summary of ANCOVA for Cr concentrations in the soil and the leaf samples.

Factor	F-value	p-value
Soil		
treatment	28.69	<0.0001
waterings	359.05	<0.0001
treatment:waterings	5.667	<0.001
Leaves		

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treatment	3.76	0.0129
waterings	2.88	0.0924
treatment:waterings	0.60	0.6181

For the harvested oranges, the highest Cr concentrations are measured in the peel (mean=0.66 mg/L, sd=0.44 mg/L), followed by the pith (mean=0.30 mg/L, sd=0.08 mg/L) and the juice (mean=0.20 mg/L, sd=0.11 mg/L) (see Figure 5 and Table 7). These differences are statistically significant. While average concentrations increase with the level of watering concentrations for the pith (not for the peel and juice), F-tests in the ANOVA and Tukey's HSD tests reveal no statistically significant differences for treatment and treatment:type interaction.

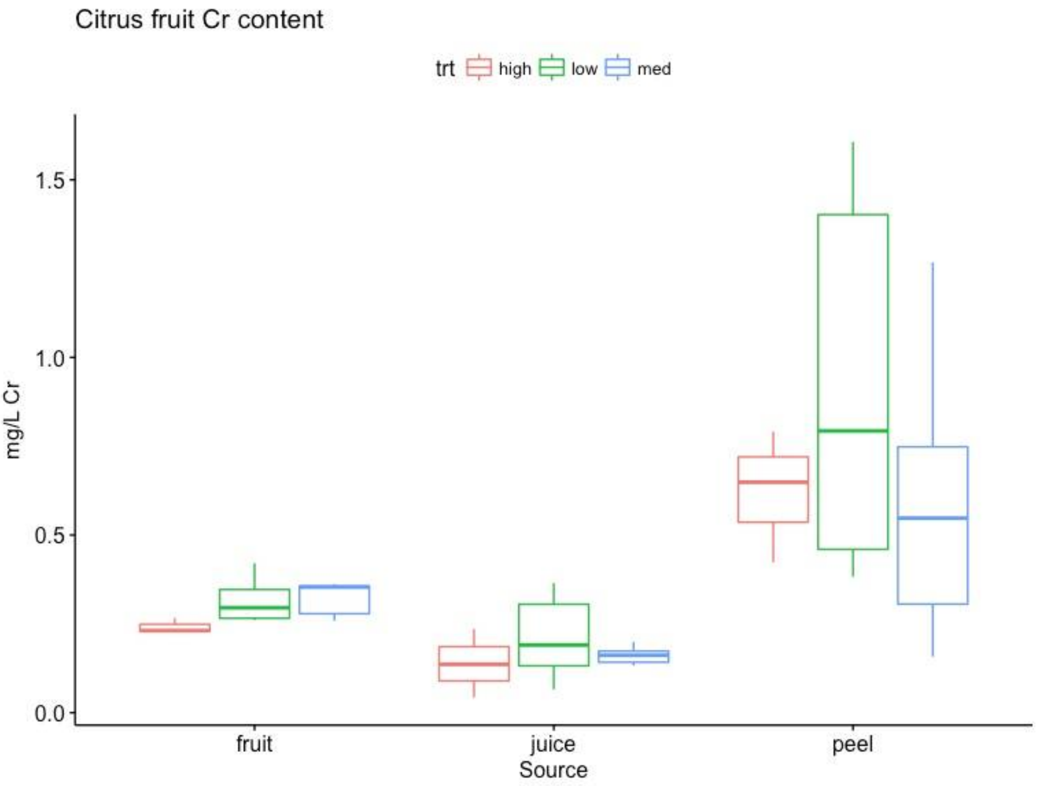

Figure 5: Boxplots of measured concentrations of Cr in the pith, juice and peel portions of the harvested mandarin oranges as a function of Cr concentration in the irrigation water (low, medium, high).

Table 7: Summary of ANOVA for Cr concentrations in fruit samples.

Factor	F-value	p-value
treatment	1.3142	0.2831
type	15.176	<0.0001
treatment:type	1.4861	0.2077

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3.3 Lead

The results for Pb indicate that accumulation in the soil is associated with time, t, watering days, w, and the concentration of Pb in the irrigation water (see Figure 6). At low and medium irrigation water concentrations, the soil concentration of Pb increases slowly and steadily (mean_{low}=194.0 mg/L, sd_{low}=212.8 mg/L, mean_{med}=309.8 mg/L, sd_{med}=382.9 mg/L), while for the high concentration water the slope of accumulation is larger, but also subject to greater variation (mean=866.8 mg/L, sd=943.5 mg/L,). The leaves (see Supplementary Material Figure S2) show little accumulation up to t=3. Beyond this time point, concentrations in the leaves rise but at a markedly increased between-plant variance. No systematic differences between low, medium and high irrigation water concentrations are detected using Tukey's HSD test. ANOVA results are shown in Table 8. As with Ba, the slopes for the soil concentrations for time vary based on treatment.

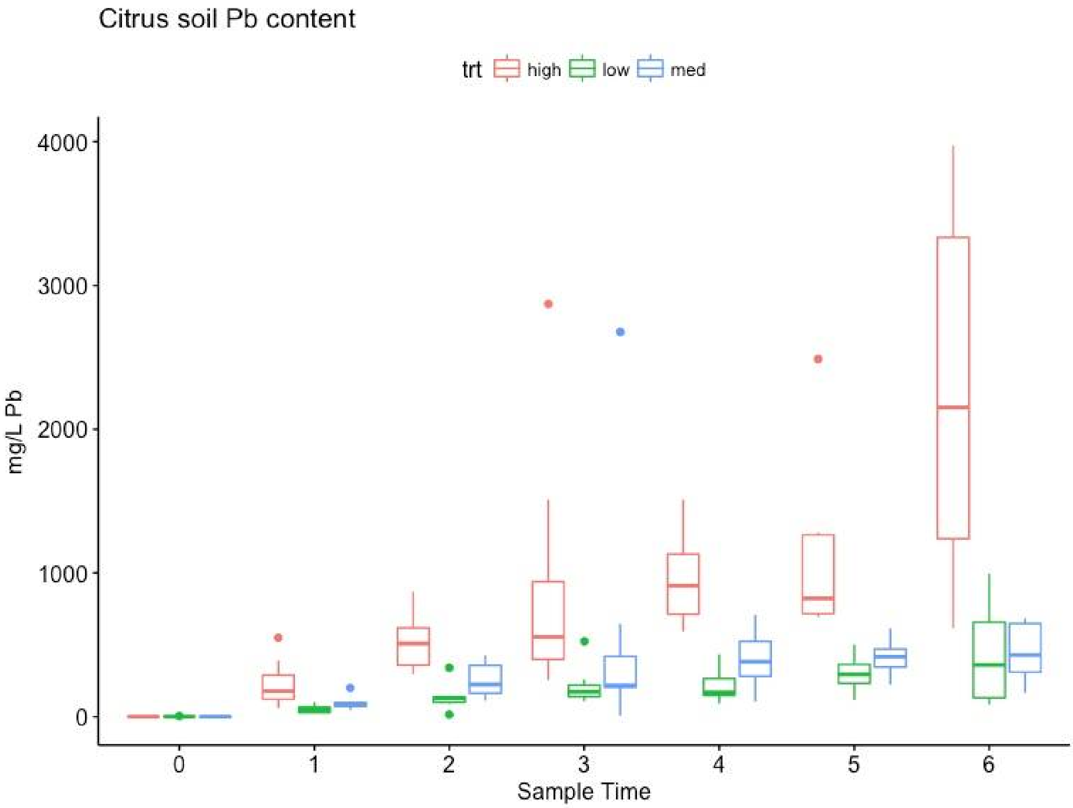

Figure 6: Boxplots of measured concentrations of Pb in the soil as a function of Pb concentration in the irrigation water (low, medium, high) and sampling time, t.

Table 8: Summary of ANOVA for Pb concentrations in soil samples.

Factor	F-value	p-value
treatment	23.4233	0.2831
type	13.2193	<0.0001
treatment:type	3.3416	0.2077

ANCOVA results are shown in Table 9.

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Table 9: Summary of ANCOVA for Pb concentrations in the soil and the leaf samples.

Factor	F-value	p-value
Soil		
treatment	21.208	<0.0001
waterings	57.288	<0.0001
treatment:waterings	9.857	<0.0001
Leaves		
treatment	3.26	0.0238
waterings	11.43	0.001
treatment:waterings	0.87	0.4572

Comparatively high levels of variation mark the Pb concentrations in the pith, juice and peel for all three tested watering concentrations (see Supplementary Material Figure S3). Average concentrations are highest for the fruit material, but were not statistically significant.

3.4 Silver

Silver concentrations show little in terms of clear detectable patterns over time or watering concentrations (see Supplementary Material Figures S4 and S5) for both soil and leaves. While baseline soil and leaf concentrations are low and subsequent sampling times detect significant increases, they remain approximately steady over time. Furthermore, the results for the medium and high watering concentrations are indistinguishable, while low watering concentrations on average yield lower Ag soil concentrations.

For the harvested mandarin oranges, Ag concentrations appear to increase with watering concentrations in the pith, but not in the juice nor the peel, where they remain well below 1 mg/L (see Supplementary Material Figure S6).

4. Discussion

The study presents the result of a controlled experiment of the accumulation of four heavy metals (Ba, Cd, Pb, Ag) in the soil, leaves and fruit of 23 mandarin orange trees that were irrigated with water containing three different concentrations of these elements that are representative of OPW conditions. The study's goals were to detect the soil and plant (leaves, fruit) concentrations of these elements, which are frequently found in similar concentrations in oilfield produced water (OPW), and to examine if there are detectable trends over time and as a function of the metals' concentration in the irrigation water. In the absence of federal (and state) regulations on the permissible concentrations of these and other compounds found in OPW, it is of interest to learn about their fate when OPW is reused for agricultural crop irrigation on a frequent basis as is the case in several water districts in California's agriculturally important Central Valley.

The results indicate that soils can accumulate several of the tested elements, in particular Ba, but to a lesser extent also Pb and Cr, and that generally the accumulated amounts are higher when these heavy metals are supplied in high concentrations in the irrigation water. The results for Ag were inconclusive.

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Compared with the soil samples, the leaf material showed consistently lower concentrations of the tested elements. The most significant uptick was observed for Ba at the high concentration level. This finding is supported by reports in the literature that green, leafy material, with the exception of leafy produce such as spinach and lettuce, tends to store little to no heavy metals.

All tested metals have known adverse human health effects that range from mild discomforts to serious organ damage and even death. For example, Ba (in soluble form), Cr and Pb ingested in small to moderate concentrations can impact the digestive and respiratory tracts, the musculoskeletal and neurological systems, and the reproductive organs. The effects depend on the exposure route, frequency and magnitude of exposure, as well as the chemical formulation of the metal (e.g., soluble versus insoluble Ba). Although the OPW in this study is used for crop irrigation and does not directly enter drinking water sources, it is illustrative to compare the measured concentrations with applicable drinking water standards, because of the risk of exposure to consumers of the edible crop. For Ba, the federal Maximum Contaminant Level (MCL) is 2.0 mg/L, for Pb the EPA specified an Action Level of 0.015 mg/L. The MCL for total Cr is 0.1 mg/L, and for Ag the federal Secondary Drinking Water Standard is 2.0 mg/L.[27] The soil, leaf, and fruit concentrations measured for the four metals frequently exceeded these thresholds, noticeably at the medium and high watering concentrations.

The exceedance of public health standards is especially concerning for the fruit measurements. The pith appears to be the most likely to accumulate the tested metals at concentrations potentially endangering the health of the consumer with concentrations for Ba ranging from 21.57 mg/L to 4,758.25 mg/L, for Cr from 0.13 mg/L to 1.61 mg/L, for Pb from 0.43 mg/L to 8.36 mg/L, and for Ag from 0.10 mg/L to 0.91 mg/L. It is noted, however, that the concentrations measured are for total Ba, Cr, Pb, and Ag and do not distinguish between soluble and insoluble fractions, although the heavy metals were applied in the watering solutions as the soluble species.

The study has a few additional limitations. The sample size of 23 citrus plants is relatively small and the experiment was conducted on potted plants and not in an orchard in the Central Valley with actual OPW-supplemented irrigation water. Thus, the typical conditions, including soil cycling, soil types and hydrological movements of irrigation water could not be fully replicated and no soil characterization was done. The study also had a limited duration (June 2017 through March 2018) and was interrupted by two periods of watering with freshwater only. However, this watering, and a small number of precipitation events in the winter months, are assumed to have flushed out some of the metals that had accumulated in the soil as opposed to further enrich it. Finally, due to the time limits on the study, mandarin oranges could only be harvested and tested once.

Despite these constraints, the study allows the following conclusions. First, the elevated concentrations of Ba, Cr, and Pb indicate that further research on the potential risks associated with the reuse of OPW in agricultural crop irrigation is needed. The field sampling conducted by the Food Safety Expert Panel for citrus, almonds, pistachios, table grapes and garlic tested for 108 elements and chemical compounds and detected 16 in the fruit and seed samples, among them Ba, Cu, Mo, Ni, Sr, and Zn. In several cases, concentrations of these metals in the treated crop were statistically higher than in the controls, but were still judged to be “non-alarming.” The present study indicates that field sampling should be continued at least for the citrus fruit to reaffirm that there is no risk for consumers. The results further signal the need to conduct a systematic soil study to assess the risk of heavy metal accumulation for soil and crop health. The Regional Water Quality Control Board is in the process of planning additional studies for the new growing season to supplement the existing data. These studies aim to include root vegetables such as garlic, potatoes and carrots, which may have a higher propensity to store heavy metals and other contaminants than tree crops. The present study suggests that soil analysis should be included as well.

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The question of whether OPW use in agriculture poses risk to consumers of the impacted crops also requires testing the long-term effects of OPW application, because crops with very low to low concentrations of compounds with known adverse health effects may pose risks if the crop is consumed in large-enough quantities by consumers (e.g., the increase in consumption of mandarin oranges between October – February).

Since OPW chemical composition can change over time, often within short time periods, it remains advisable that OPW water quality testing continues for at least key contaminants that carry substantial health risks at even small concentrations such as heavy metals, BTEX, and radioactive isotopes.

Adding more advanced treatment of OPW to regular OPW, crop, and soil quality monitoring can further ensure that harmful and toxic elements and chemicals do not reach agricultural products, especially those aimed for human consumption. With sufficient safeguards in place OPW could be considered a supplemental water resource for California's Central Valley farms and hence make for a mutually beneficial partnership between the oil and agricultural industry in the region.

Supplementary Materials: The following are available online at www.mdpi.com/link:
R Markdown Scripts for Ag, Ba, Cr, and Pb.
Data files for Ag, Ba, Cr, and Pb.
Figure S1: Boxplots of measured concentrations of Cr in the leaves as a function of Cr concentration in the irrigation water (low, medium, high) and sampling time, *t*.
Figure S2: Boxplots of measured concentrations of Pb in the leaves as a function of Pb concentration in the irrigation water (low, medium, high) and sampling time, *t*.
Figure S3: Boxplots of measured concentrations of Pb in the pith, juice and peel portions of the harvested mandarin oranges as a function of Pb concentration in the irrigation water (low, medium, high).
Figure S4: Boxplots of measured concentrations of Ag in the soil as a function of Ag concentration in the irrigation water (low, medium, high) and sampling time, *t*.
Figure S5: Boxplots of measured concentrations of Ag in the leaves as a function of Ag concentration in the irrigation water (low, medium, high) and sampling time, *t*.
Figure S6: Boxplots of measured concentrations of Ag in the pith, juice and peel portions of the harvested mandarin oranges as a function of Ag concentration in the irrigation water (low, medium, high).

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