On the Reuse of Oil Field Produced Water for Irrigation of Food Crops In Central Kern County, California



8 September 2021

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#### Acknowledgements

Staff of the California Regional Water Quality Control Board, Central Valley Region, (Central Valley Water Board) prepared this Food Safety Project White Paper (White Paper) on behalf of the Food Safety Expert Panel (Panel). The Central Valley Water Board would like to thank the Panel (listed below) for their time, expertise, and contributions to this Food Safety Project.

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Draft versions of this White Paper were circulated to the Panel for review and input throughout the Food Safety Project. Also, the Panel developed and approved (via consensus) twelve recommendations based on the work and findings of the Food Safety Project (discussed in Section 8 of this White Paper). This version of the White Paper has undergone a review by the Panel, GSI, Science Advisor, and public, and comments have been incorporated, as appropriate.

This White Paper also summarizes the work completed by GSI Environmental, Inc., (GSI) as a part of the Food Safety Project. The work completed by GSI was broken into three tasks. Throughout the Food Safety Project, GSI presented its proposed methodology and findings to the Panel for review and input. The Panel, Science Advisor, and Central Valley Water Board staff have reviewed the Task 1 Report, Task 2 Report, and Task 3 Report.

The Central Valley Water Board would like to thank Dr. William T. Stringfellow who began this project as a member of the Panel and then filled the role of Science Advisor to the Central Valley Water Board. His expertise, assistance, and dedication to this project is greatly appreciated by Central Valley Water Board staff and Board members.

The Central Valley Water Board members instrumental in the preparation of this document include Board Members Dr. Karl Longley, Denise Kadara, and Raji Brar for representing a sub-committee of the Board and being involved in the Food Safety Project. Central Valley Water Board staff involved throughout the Food Safety Project and preparing this White Paper include Joshua G. Mahoney, W. Dale Harvey, and Rebecca T. Asami.

## Food Safety Project White Paper (White Paper)

## On the Reuse of Oil Field Produced Water for Irrigation of Food Crops In Central Kern County, California

**Food Safety Project** 

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## Food Safety Project White Paper Food Safety Project

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#### **List of Abbreviations**

AB1328 – Assembly Bill 1328

AEC – Advanced Environmental Concepts, Inc.

APPL - Agricultural and Priority Pollutants Laboratories, Inc.

ATSDR – Agency for Toxic Substance and Disease Registry

CALEPA – California Environmental Protection Agency

CalGEM – California Geologic Energy Management Division

CASRN – Chemical Abstract Service Registry Number

CEBS - Chemical Effects in Biological Systems

CICAD – Concise International Chemicals Assessment Document

DOGGR - Division of Oil, Gas, and Geothermal Resources

EC – Electrical Conductivity

ECHA – European Chemicals Agency

ELAP – Environmental Laboratory Accreditation Program

EPA - Environmental Protection Agency

EPI – Estimation Programs Interface

FWER - Family-Wise Error Rate

FDR = False Discovery Rate

GSI – GSI Environmental, Inc.

HBSL - Human Based Screening Levels

HSDB – National Library of Medicine's Hazardous Substances Database

HEAST – Health Effects Assessment Summary Table

HHBP - Human Health Benchmarks for Pesticides

IPS-INCHEM – International Programme on Chemicals Safety from Intergovernmental Organizations

IRIS – Integrated Risk Information System

MADL - Maximum Allowable Dose Level

MCL – Maximum Contaminant Level

mg/L – Milligrams per Liter

mg/kg/d – Milligrams per Kilogram per Day

MOU – Memorandum of Understanding

MRP – Monitoring and Reporting Program

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MTBE – Methyl-Tert-Butyl-Ether

NAWQA – National Water Quality Assessment

NIEHS – National Institutes of Environmental Health

NIH – National Institutes of Health

NIFA - National Institute for Food and Agriculture

NOEL - No Observed Effect Level

NOAEL - No Observed Adverse Effect Level

NSRL – No Significant Risk Level

NTP - National Toxicology Program

OECD – Organisation for Economic Co-operation and Development

OEHHA - California Office of Environmental Health Hazard Assessment

OSPAR – Oslo and Paris Commission

PAH – Polycyclic Aromatic Hydrocarbons

pCi/L - Picocurie per Liter

PPRTV - Provisional Peer-Reviewed Toxicity Values

REACH – Registration, Evaluation, Authorization and Restriction of Chemicals

RfD - Reference Dose

SAP - Sampling and Analysis Plan

SDS – Safety Data Sheets

SVOC – Semi-Volatile Organic Compound

TCE – Tricholorethylene

TDI – Tolerable Daily Intake

TOXNET – Toxicology Data Network

ug/L – Micrograms per Liter

umhos/cm - Micromhos per Centimeter

USDA – United States Department of Agriculture

USEPA – United States Environmental Protection Agency

USGS – United States Geological Survey

VOC - Volatile Organic Compound

WDRs – Waste Discharge Requirements

WHO – World Health Organization

#### **1.0 Executive Summary**

Concern that severe drought may become more common in the future has increased interest in using unconventional water sources for irrigation. Oil and gas "produced water" is an unconventional water source that has potential for agricultural use because of the proximity of some oil and gas fields to agricultural lands. However, environmental advocacy groups and other members of the public have raised questions regarding the safety of reusing produced water as a source of irrigation. Crops grown with produced water are regulated under waste discharge requirements (WDRs) adopted by the California Regional Water Quality Control Board, Central Valley Region, (Central Valley Water Board). Staff of the Central Valley Water Board initiated a Food Safety Project and commissioned a panel of experts, the Food Safety Expert Panel (Panel), to help the Central Valley Water Board evaluate the safety of reusing produced water for irrigation of crops grown for human consumption.

The Panel provided technical guidance and recommendations on components of the Food Safety Project. These components included:

- Identifying chemicals used in oil production in areas that currently use produced water for irrigation. This includes known oil field additives used in the oil fields from which this water is produced;
- Determining the ingestion toxicity of each chemical, to the extent possible given the available data;
- Using ingestion toxicity ranking to eliminate chemicals of low toxicity and identify chemicals with higher toxicity or unknown toxicity, creating a Chemicals of Interest list;
- Determining the potential for Chemicals of Interest to persist in the agricultural environment, persist in soils, transfer into plants, and transfer to the edible portion of the crop;
- Evaluating the efficacy of the water quality monitoring program regarding the safety of reusing produced water for agriculture; and
- Implementing a crop monitoring program in cooperation with the permitted produced water providers and users to address questions about the quality of crops grown with produced water.

The Food Safety Project included three main studies (Tasks 1-3) conducted by an independent consultant:

 Task 1: Identify chemicals that have the potential to be in produced water and conduct a preliminary hazard evaluation to identify which of these were worthy of further evaluation, creating a Chemicals of Interest list.

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- Task 2: Conduct a rigorous evaluation of the Chemicals of Interest in a literature review that considers potential hazards from ingestion, persistence in agricultural ecosystems, and the potential for plant uptake.
- Task 3: Evaluate the chemical composition of crops irrigated with produced water (treated crops) in comparison to crops that were irrigated with conventional sources of water (control crops).

The results of these studies are in Task Reports 1, 2, and 3. In this Food Safety Project White Paper (White Paper), the results of the Food Safety Project are summarized and discussed. In Section 8 of this paper, the final conclusions and recommendations from the Food Safety Panel are presented.

Under Task 1 of the Food Safety Project, almost four-hundred chemicals and constituents were identified as having the potential to occur in produced water reused for irrigation in the Central Valley. The complete list includes chemicals and constituents that make-up oil field additives (such as surfactants, solvents, and biocides) used for oil exploration, production, and treatment, and naturally occurring chemicals (such as metals, hydrocarbons, and radionuclides). Chemicals and constituents were examined for potential ingestion toxicity and persistence in the environment. As the result of Task 1, 143 chemicals were designated as "Chemicals of Interest" and selected for further evaluation in Task 2.

Under Task 2 of the Food Safety Project, a rigorous and thorough review of the available literature related to the environmental fate and health risks associated with the Chemicals of Interest was conducted. The literature review investigated the Chemicals of Interest and considered: chronic ingestion toxicity, potential alternative environmental and industrial sources, ambient levels in the environment, levels in marketplace foods, environmental fate and transport characteristics, degradation and transformation products, and known plant uptake properties. The Task 2 investigation found that many Chemicals of Interest were expected to either biodegrade or sorb to soils, which would inhibit or prevent uptake of the Chemicals of Interest into plants. Some of the Chemicals of Interest were found to have the potential for plant uptake, especially elemental metals. Since metals are persistent in the environment and under some conditions can be taken up by plants, metals were identified as important Chemicals of Interest. Understanding the long-term effects of produced water derived metals on soil quality (e.g., increased metal concentrations over time) was identified as a data gap. Understanding of how organic compounds generally are taken up from the soil and water by plants was also identified as a data gap. Data gaps identified under Task 2 and the Food Safety Project are discussed in more detail in Section 6 of this White Paper.

Under Task 3 of the Food Safety Project, crop samples from areas that irrigate using at least some produced water and areas that do not use any produced water were collected over three years (2017, 2018, and 2019). Samples of known food crop-types grown with produced water in Kern County (treated samples) were collected, analyzed, and compared to crops grown without produced water (control samples). Crop groups

evaluated as part of Task 3 include root and tuber vegetables, bulb vegetables, fruiting vegetables, citrus, pome and stone fruit, berry and small fruit, and tree nuts.

The Task 3 study showed that some of the Chemicals of Interest were found in crops irrigated with produced water; however, in most cases the concentration of these chemicals in treated crops did not exceed the concentration found in comparable control crops. Chemicals of Interest that were found at a higher concentration in treated crops than control crops were the elements barium and zinc in almonds, and strontium in garlic, grapes, and lemons. Barium, strontium, and zinc occur naturally in food and the concentrations measured in crops are within the range of normal concentrations reported from surveys and studies examining food nutrition and safety. It is not certain that the elevated concentrations of barium, strontium, or zinc can be attributed to the use of produced water for irrigation. Concentrations of these elements in plants are generally a function of the concentration of these elements in soils and concentrations of these elements can vary widely even over small distances in this region. A better understanding of the soils in areas irrigated with produced water was identified as a data gap.

Based on the work and findings of the Food Safety Project and other scientific evidence presented to the Panel, the Panel made the following twelve recommendations, which are discussed in greater detail in Section 8 of this White Paper:

## Part 1 – Findings and recommendations concerning current produced water reuse program:

- 1. Crop sampling should be discontinued at this time.
- 2. Current produced water quality monitoring program should be continued.
- 3. The Central Valley Water Board should continue to require the disclosure of oil field additives used in oil exploration, production, or treatment that supply produced water for agriculture.
- 4. The Central Valley Water Board should evaluate new proposals for reuse of produced water in irrigation (and expanding projects that need new WDRs) based upon experience with existing produced water reuse projects and using the information and recommendations developed in the Tasks 1, 2, and 3 Reports and this White Paper.

### Part 2 – Findings and recommendations concerning management of potential hazards from additives:

5. The Central Valley Water Board should periodically review the list of additives, identify new additives, and evaluate the potential human health risks associated with new chemicals.

- 6. The Central Valley Water Board should consider requiring the disclosure of the mass amount of each additive used, as well as the frequency of use.
- 7. The Central Valley Water Board should consider publishing a list of oil field additives that have been evaluated as a low human or environmental hazard in the context of produced water reuse for irrigation.
- 8. The Central Valley Water Board should take steps to acquire missing hazard and water-concentration information for oil field additives and associated chemical constituents.

## Part 3 – Findings and recommendations concerning studies or actions needed to close identified data gaps

- 9. The Central Valley Water Board should conduct or sponsor (and encourage other regulatory agencies to conduct or sponsor) environmental studies on the effects of produced water on the fate and transport of chemicals associated with oil development in agricultural systems.
- 10. The Central Valley Water Board should examine the effect of produced water use on soils.
- 11. The Central Valley Water Board should evaluate temporal and spatial variability in the quality of produced water reused for irrigation.
- 12. The Central Valley Water Board should evaluate and consider incorporating emerging monitoring approaches for their applicability to the reuse of produced water.

#### 2.0 Introduction and Overview

This Food Safety Project White Paper (White Paper) summarizes the Food Safety Project that involved Central Valley Water Board staff, the Science Advisor to the Central Valley Water Board, GSI Environmental, Inc., (GSI), and a Panel of Experts (Panel) in food safety. The Food Safety Project consisted of three tasks which evaluated whether there is an increased risk of a detrimental impact to human health associated with human consumption of crops irrigated with produced water.

Panel members were selected based on their expertise in toxicology, risk assessment, agriculture, public health, and/or wildlife. Using the experience of the Panel, Science Advisor, and the technical contractor GSI, Central Valley Water Board staff oversaw the Food Safety Project in order to answer the following general questions:

 Are there immediate threats to human health related to the reuse of produced water for irrigation of crops for human consumption?

- Are the monitoring requirements in the waste discharge requirements (WDRs) adequate?
- Are oil field additives a problem of concern?
- Are there long-term risks related to crop safety and/or human health as a result of the reuse of produced water for irrigation of crops for human consumption?
- What are next steps with regard to the reuse of produced water for irrigation of crops for human consumption?
- Should there be conditions related to the reuse of produced water for irrigation?

With input from the Panel and the Science Advisor, Central Valley Water Board staff developed a Memorandum of Understanding (MOU) that outlined the objectives and work to be completed under the Food Safety Project. The MOU also required the development of Scopes of Work for the work to be completed under the Food Safety Project. The final Scopes of Work outline three tasks (Tasks 1 through 3), which are briefly described below:

- Task 1 Completion of a preliminary hazard assessment of chemicals and constituents that are: (1) associated with oil field additives used during oil exploration, production, or treatment; (2) naturally occurring in produced water; or (3) otherwise identified as having the potential to be in produced water based on the literature review. Chemicals and constituents that are toxic or have no or insufficient toxicity data were designated as Chemicals of Interest and were further evaluated in Task 2.
- Task 2 Completion of a comprehensive literature review to identify the potential threat to human health and crop safety of the Chemicals of Interest based on: degradation potential, surrogate toxicity data (where applicable), fate and transport, and plant uptake.
- Task 3 Comparison of crop sample results from cropland irrigated with produced water (treated samples) versus cropland irrigated with conventional sources (control samples).

Under the MOU, a neutral, third-party consultant, GSI, was awarded a contract to complete the work for Tasks 1 through 3. Sections 3 through 5 of this White Paper summarize the work and findings completed by GSI related to Tasks 1 through 3 of the Food Safety Project.

This White Paper was prepared by Central Valley Water Board staff and Dr. William Stringfellow on behalf of the Panel. The Panel has reviewed this White Paper and reached a consensus regarding the recommendations discussed in Section 8 of this White Paper. This White Paper includes an overview of the work and findings of

Tasks 1 through 3, recommendations of the Panel, and conclusions of the Food Safety Project.

#### 2.1 Background

California's Central Valley is one of the leading agricultural areas in the world and produces a multitude of commodities on over 7 million acres of irrigated land. In the southern part of the Central Valley, the San Joaquin Valley, surface water supplies are often limited and much of this land relies on imported surface water and groundwater. Surface water sources in California have been significantly impacted during the droughts of 1928-34, 1987-92, and 2012-16 (USGS 2018). These conditions have resulted in a concern that available water supplies may not be sustainable and led some farmers in the southern San Joaquin Valley to look to unconventional sources of water for irrigation. One of these sources is produced water.

Produced water, or oil field produced water, is a byproduct of oil production. Production fluid, extracted from the ground via oil wells, generally consists of oil and water. The water fraction is called "produced water."

Under State policy, recycling of water is encouraged to supplement California's water supply, if the water is suitable for the intended use. Due to the quality of produced water currently reused for irrigation, this practice is approved and regulated under WDRs adopted by the Central Valley Water Board.

#### 2.2 Waste Discharge Requirements (WDRs)

Farmers in Kern County have been using low salinity produced water to irrigate crops for human consumption for over 30 years. The Central Valley Water Board regulates parties that reuse produced water for irrigation through WDRs, which conditionally authorize the practice and stipulate groundwater and effluent limits for the discharge of produced water to land for irrigation. Included in new WDRs is language that prohibits the reuse for irrigation of produced water from wells that contain well stimulation treatment fluids (as defined by the California Code of Regulations, title 14, section 1761). Also included in the WDRs are Monitoring and Reporting Programs (MRP), which require parties (identified as "Dischargers" in WDRs) to complete specific monitoring of the discharge and groundwater at specific monitoring locations and frequencies.

#### 2.3 Irrigators

Produced water is transferred from oil companies to water management companies (also referred to as "irrigators") through pipelines and canals. Upon receiving the produced water, irrigators typically blend the produced water with surface water and/or groundwater prior to delivering the water to farmers for irrigation. Currently, there are five irrigators, regulated under WDRs, that receive produced water for irrigation. Under the WDRs, approximately 95,000 acres of farmland in east Kern County are irrigated

with produced water. A map of the farmland authorized for the reuse of produced water for irrigation is shown in Figure 1.

#### 2.4 Oil Field Additives

Oil field additives consist of chemicals, compounds, and other materials that are used by oil producers for oil exploration, production, or treatment. Oil field additives are used for a variety of purposes and vary depending on an individual oil operator's operating procedure. In the Central Valley, oil field additives can be used for the following:

- Sealing the borehole to reduce the volume of fluid lost in a formation;
- Reducing the swelling of clay in the borehole;
- Reducing or preventing the corrosion of pipes, casing, equipment, and tanks;
- Controlling microbial activities in the subsurface environment;
- Separating oil and solids from produced water; and
- Removing oil coating in water softeners; and
- Other production and maintenance activities.

#### 2.5 Additional Information Related to the Food Safety Project

For additional information related to the introduction or overview of the Food Safety Project, see the *General Information and Operating Guidelines of the Food Safety Project* memorandum in Appendix A of this White Paper.

#### 3.0 Task 1 – List of Chemicals of Interest

Task 1 consisted of a preliminary hazard assessment of potential chemicals and constituents that could be found in produced water reused for irrigation. In order to be included in this preliminary hazard assessment, chemicals and constituents needed to be naturally occurring in produced water; introduced to the system through oil field additives used during oil exploration, production, or treatment; identified as potentially present in produced water based on the available literature; or having been detected during water quality monitoring. Chemicals or constituents that satisfied at least one of these criteria were included in a Task 1 list prepared by GSI. The GSI Task 1 list included chemicals from the *Central Valley Water Board Oil Field Additive List* (Oil Field Additive List), which identified chemicals and constituents that are in oil field additives used during oil exploration, production, or treatment. The comprehensive Task 1 list generated by GSI identified 399 chemicals and constituents, all of which were included in a preliminary hazard assessment in Task 1 that identified the subset of chemicals and constituents that were placed on the Chemicals of Interest list. The Chemicals of Interest were further investigated in an extensive literature review under Task 2.

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The work and findings for Task 1 are summarized in a report prepared by GSI, referred to as the *Final Task 1 Report*. The Panel, Science Advisor, and Central Valley Water Board staff have reviewed the work and findings of the report. The following sections provide an overview of the work and findings completed by GSI for Task 1. For more information related to Task 1, see the *Final Task 1 Report* in Appendix C of this White Paper.

#### 3.1 Values Used for Toxicity Evaluation

Toxicity or health-risk screening values are derived from studies that identify an adverse effect threshold or a health-risk increment based on a specific route of exposure. As the focus of the Food Safety Project was to identify potential impacts to human health from the consumption of crops irrigated with produced water, GSI focused on chronic ingestion toxicity.

In the Task 1 evaluation, GSI used two types of toxicity values. The first type is associated with non-cancer outcomes and represents the dose level at which an adverse health outcome is unlikely to occur. A "reference dose" is an example of a toxicity value related to a non-cancer outcome. The second type of toxicity value used in this evaluation is related to cancer outcomes based on a cancer slope factor. Cancer slope factors are used to estimate the incremental risk associated with a lifetime of exposure to a substance. For this evaluation, toxicity values related to cancer outcomes were defined as the risk specific dose associated with an incremental additional cancer risk of 1 in 100,000, based on a lifetime of exposure to a substance.

#### 3.2 Preliminary Hazard Assessment Process

GSI combined the Oil Field Additive List, the list of chemicals that are naturally occurring in produced water, and chemicals that have the potential to be in produced water based on a literature review. This combination generated GSI's new list of chemicals and constituents that have the potential to be present in produced water reused for irrigation. GSI addressed duplicative chemicals resulting in a comprehensive list of 399 chemicals and constituents that were subsequently used in the preliminary Task 1 hazard assessment by GSI.

For many of these chemicals and constituents, toxicological data were available and used in the preliminary hazard assessment. For the remaining chemicals and constituents, the preliminary hazard assessment yielded limited, incomplete, or no information related to chronic toxicity. For some of the chemicals and constituents that did not have published toxicological data available, GSI developed surrogate toxicity values for comparative purposes only, using peer reviewed literature related to human or animal testing.

While toxicity was the primary factor in the selection of the Chemicals of Interest, GSI also considered the biodegradability (by OECD biodegradability tests) for screening and identifying chemicals and constituents for consideration of the Chemicals of Interest list.

#### 3.3 Chemicals of Interest

The preliminary hazard assessment completed by GSI resulted in 143 of the 399 chemicals and constituents being assigned to the Chemicals of Interest list. Table 1 of this White Paper identifies the 143 chemicals and constituents of the Chemicals of Interest list by chemical name and Chemical Abstract Service Registry Number (CASRN). The Chemicals of Interest were further examined in the literature review under Task 2.

Using the methodology and toxicity values described in the *Final Task 1 Report*, GSI assigned 395 of the 399 chemicals and constituents to one of six categories. The categories were based on the available toxicological data for each chemical or constituent. An overview of the categories is provided below:

- Category 1 Are non-toxic or of low concern for chronic toxicity:
  - o 71 chemicals and constituents were assigned to Category 1; and
  - 0 of the 71 chemicals and constituents were designated as Chemicals of Interest.
- Category 2 Have insufficient toxicity data available:
  - o 59 chemicals and constituents were assigned to Category 2; and
  - 59 of the 59 chemicals and constituents were designated as Chemicals of Interest.
- Category 3 Have low chronic toxicity:
  - o 69 chemicals and constituents were assigned to Category 3; and
  - 0 of 69 chemicals and constituents were designated as Chemicals of Interest.
- Category 4 Have incomplete or inconclusive toxicity data:
  - o 15 chemicals and constituents were assigned to Category 4; and
  - 15 of the 15 chemicals and constituents were designated as Chemicals of Interest.
- Category 5 Have agency derived or peer-reviewed toxicity values:
  - 130 chemicals and constituents were assigned to Category 5; and
  - 53 of the 130 chemicals and constituents were designated as Chemicals of Interest.
- Category 6 Surrogate toxicity values were derived by GSI:
  - o 51 chemicals and constituents were assigned to Category 6; and
  - 12 of the 51 chemicals and constituents were designated as Chemicals of Interest.

In addition to the Chemicals of Interest identified in Categories 1 through 6, GSI also designated the radionuclides as Chemicals of Interest. The 143 chemicals and

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constituents assigned to the Chemicals of Interest list include the 139 chemicals [102 organic and 37 inorganic] and constituents from Categories 1 through 6 and four additional radionuclides (excludes uranium since this was included in Category 5) that have the potential to be in produced water based on the literature review. The final Chemicals of Interest list is shown in Table 1.

#### 4.0 Task 2 – Literature Review

Task 2 consisted of a rigorous and thorough review of the available literature related to the health risks associated with the Chemicals of Interest with regard to the reuse of produced water for irrigation. GSI performed the literature review and investigated the Chemicals of Interest for potential alternative sources (e.g., agriculture), ambient levels in the environment and marketplace foods, environmental fate and transport characteristics, degradation and transformation products, and known plant uptake properties. In conducting the work under Task 2, GSI utilized peer reviewed literature, government publications, scientific letters, and industry reports.

The work and findings for Task 2 are summarized in a report prepared by GSI, referred to as the *Final Task 2 Report*. The Panel, Science Advisor, and Central Valley Water Board staff have reviewed the work and findings of the report. The following sections provide an overview of the work and findings completed by GSI for Task 2. For more information related to Task 2, see the *Final Task 2 Report* in Appendix D of this White Paper.

#### 4.1 Known Ambient Levels in the Environment

To help understand the likelihood that sources other than produced water could be the source of chemicals in crops irrigated with produced water, GSI researched the levels of Chemicals of Interest in environmental media, including air, soil, surface water, and food. The literature review of ambient levels in the environment yielded information related to the range of concentrations of Chemicals of Interest in each media. The collection of data on the ambient levels of the Chemicals of Interest was prioritized based on their proximity to the San Joaquin Valley, which resulted in ambient levels relevant to the San Joaquin Valley being the highest priority, followed by California in general, and lastly the United States (US).

Ambient levels of the Chemicals of Interest in food were primarily found in the *Total Diet Study* published by the US Food and Drug Administration (FDA). The *Total Diet Study* is an ongoing program that examines major chemicals and components based on the average diet of an individual in the US. GSI summarized the available data in Table 10 of the *Final Task 2 Report*, which is used in GSI's evaluation of produced water quality (available in the Section 4.2 of this White Paper).

#### 4.2 Review of Produced Water Quality

Task 2 examined the quality of produced water and irrigation water, blended with produced water, prior to reuse for irrigation. The goal of this analysis was to compare

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crop sample results, water quality results, and Chemicals of Interest to identify any potential relationships or correlations that could be associated with the reuse of produced water for irrigation.

Central Valley Water Board staff compiled and posted (on the Central Valley Water Board's Food Safety web page) produced and blended water quality data related to the reuse of produced water for irrigation. The data were from 16 sample locations and ranged in date from 1967 through September 2019. Tables 7 and 8 of the *Final Task 2 Report* summarize the water quality data and include the following: minimum, mean, and maximum concentrations for each listed chemical; total number of sample results available; percentage of detections; and percentage of results above available irrigation goals and/or water quality standards / goals. Of the 143 chemicals and constituents that were designated as Chemicals of Interest, 52 have been analyzed in produced water either directly or as the metal of a salt, oxide, or carbonate (e.g., total zinc include zinc chloride). The list of the 52 Chemicals of Interest analyzed in produced water is available on Table 5 in the *Final Task 2 Report*.

#### 4.3 Plant Uptake

GSI reviewed the available literature related to the uptake of organic and inorganic chemicals by food crops. GSI noted that plant uptake of inorganic chemicals occurs at the roots while the uptake of organic chemicals can occur at the roots and leaves. The mechanism for and amount of chemical uptake depends on a variety of factors, which include, but are not limited to, the following: (1) chemical and physical properties of the chemical or constituent; (2) environmental conditions (e.g., ambient temperature and organic content of the soil); and (3) plant species.

Although plant uptake of chemicals is required for crop development, the uptake of specific chemicals can result in: (1) toxic levels of chemicals entering a plant and/or (2) a chemical accumulating to a concentration that exceeds the natural toxicity limit for a plant. As a defense mechanism by the plant, many chemicals that may pose a threat to crop health are compartmentalized in certain cellular structures. The compartmentalization or sequestration of these chemicals removes them from key plant areas responsible for cell division and respiration. This process and other factors have the potential to result in the accumulation of chemical(s) in different parts of the crop (i.e., roots, stems, leaves, or fruit). Research obtained during the literature review yielded some information related to plant uptake of inorganics and organics.

In the literature review, GSI found that inorganic chemicals generally concentrate in the roots, stems, and/or leaves, rather than the edible portion of the plant. For root crops, inorganic chemicals are primarily observed in the leaves or skin, and not as heavily concentrated in the center of the edible portion of the crop. For the majority of crop types, the edible portion of the crop appears to have lower concentrations of inorganics than the skin, roots, stems, or leaves.

For organic chemicals, the primary method for plant uptake of lipophilic chemicals is foliar (through the leaves), while water soluble chemicals may be taken up through the

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roots. However, there are a limited number of published studies examining organic chemical uptake by plants and the transfer of organic chemicals from roots to other parts of the plant. The potential for organic chemicals taken up by the roots to occur in crops grown for human consumption is unknown. Therefore, GSI felt there was insufficient information to make generalizations regarding organic chemical uptake by food plants, except that root uptake appears to be the dominant route by which plants could potentially accumulate chemicals from irrigation water. The Task 2 report identified knowledge of organic chemical uptake by plants as a data gap. Although limited information is available concerning plant uptake of organic chemicals, the fate of organic chemicals in water and soil has been investigated in numerous scientific studies (see the Task 2 Report and Sections 4.4 and 4.5, below). In addition, the chemical composition of crops was examined directly in Task 3 (see Section 5.3, below).

#### 4.4 Fate and Transport

GSI examined the potential for chemicals to persist and move through the environment, potentially reaching the root zone of crops. Utilizing fate and transport data, chemicals in irrigation water that do not have the potential to reach the root zone of crops would have a greatly diminished likelihood of accumulating in irrigated crops. Under this evaluation, the fate and transport of chemicals considered two pathways: (1) irrigation water distribution system and (2) soil. GSI evaluated these two pathways separately. The degradation and transformation potential of the Chemicals of Interest is discussed in Section 4.5 of this White Paper. Section 4.3 discusses plant uptake if a chemical has persisted in the soil and reached the root zone of a crop.

The literature review completed by GSI highlights the complexity associated with the fate and transport of the Chemicals of Interest. The analysis by GSI indicated that organic chemicals that possessed the following traits had the greatest potential to reach the root zone of crops: (1) soluble, (2) limited volatility, (3) low adsorptive potential to organic matter in water and soil, and (4) limited biodegradability. Of the 45 organic chemicals that had sufficient data to be evaluated, GSI confirmed that the 45 chemicals possessed at least one these traits that would make them less likely to be available for plant uptake.

For inorganic chemicals, GSI considered additional factors due to the nature of inorganic chemicals and their potential fate and transport pathways in soil and water. Factors that were considered for inorganic chemicals were pH, humic/fulvic acid content, and soil clay content. In soil, the pH and clay content have major impacts that can result in inorganic chemicals being locked in the soil and not being available for plant uptake. Of the 16 inorganic chemicals, GSI found that there are factors that can attenuate the movement of many of the metals in soil and water. Although three of the inorganic chemicals are mobile in soil, GSI notes that mobility is greatly dependent on the site conditions.

GSI notes that to make an accurate assessment regarding the presence of the Chemicals of Interest at the root zone, a complete understanding of the agricultural

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setting is needed. Research results show that specific soil pH, soil saturation, redox potential, cation exchange capacity, soil organic content, soil mineral content, and mixture of compounds present are needed to obtain a better understanding of the availability of chemicals in the root zone. While GSI did find specific information related to the fate and transport of the Chemicals of Interest, there are too many variables and uncertainties to support an accurate prediction of the availability and plant uptake of the Chemicals of Interest by crops irrigated with produced water.

#### 4.5 Degradation and Transformation Products

Chemicals that are naturally occurring or that are present from the use of oil field additives have the potential to degrade or transform into new chemicals downhole in the well, at the surface after production, in the irrigation distribution system, or in the soil. GSI evaluated the potential degradation and transformation of the Chemicals of Interest as part of Task 2.

GSI found limited information regarding the degradation and transformation products related to chemicals expected to be present in produced water. Most studies of degradation and transformation products focused on hydraulic fracturing, which produces downhole conditions that differ from those associated with conventional oil extraction methods. The oil companies that generated produced water reused for irrigation do not use hydraulic fracturing practices, however they may use biocides and surfactants that have the potential to contain similar chemicals as those used for hydraulic fracturing. The literature suggests that degradation products of biocides do not appear to pose additional health risks, while those from some of the surfactants have the potential to include endocrine disrupting chemicals. Based on the biodegradability of these compounds and the concentrations observed in the produced water and crop samples, endocrine disrupting chemicals are not judged likely to be present at levels that would impact human health or crop safety, however a better understanding of degradation products was identified as a data gap.

GSI's research of *in vivo* and *in vitro* toxicity testing methods identified potential hazards associated with the direct human contact with produced water and chemicals associated with hydraulic fracturing. These findings concerning direct contact with produced water are not directly comparable to irrigation with blended produced water, as the fate and transport processes discussed above affect the chemicals in produced water and alter the composition of the chemical mixture reaching the root zone. The concentration of many of the components of produced water would be reduced and/or removed by the time the produced water reaches the root zone. As part of the degradation and transformation evaluation, high-throughput toxicity testing was discussed to provide potential options for obtaining data in the future. GSI noted that the USEPA, National Toxicology Program (NTP), and National Institutes of Health (NIH) through the "Toxicology in the 21st Century" (Tox21) program, are researching and developing test methods for more rapid assessments of chemical toxicity. Methods such as high-throughput testing using zebrafish embryo may prove to be a valuable resource for the assessment of chemical toxicity in produced water in a future study.

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GSI notes that some of the organic chemicals detected in the crops are potential degradation and transformation products of Chemicals of Interest. However, these chemicals were not observed at significantly higher concentrations than in the control group, nor were the levels higher than background levels expected for each crop type.

#### 4.6 Radionuclides

Under Task 1, five radionuclides were assigned to the Chemicals of Interest list. While researching radionuclides under Task 2, GSI identified additional radionuclides that are naturally occurring in produced water. GSI's evaluation of the radionuclides that have the potential to be in produced water reused for irrigation is summarized in this section.

Uranium-238 (uranium) and radium are potentially naturally occurring in produced water. GSI identified that the most common forms of radium found in produced water generally are radium-226 and radium-228, which are decay products of uranium and thorium-238 (thorium). Since radium-226 and -228 are generated from the mutual decay of uranium and thorium, thorium was added to the list of radionuclides to evaluate as part of Task 2.

In a study specific to the Central Valley of California, produced water samples were collected from various phases of oil production (e.g., tanks, oil, and produced water post treatment) and analyzed for radionuclides. Of the 18 produced water samples, eight samples had detectable concentrations for radium-228. For uranium and thorium, the samples were non-detect. The study reported that thorium is relatively insoluble, which likely limited the ability of thorium to be brought to the surface through the production fluid. GSI also noted that the samples of produced water were collected from the west side of the Central Valley, where produced water is of significantly poorer quality than the produced water reused for irrigation. In addition, findings by the California Geologic Energy Management Division (CalGEM) (formerly the Division of Oil, Gas, and Geothermal Resources (DOGGR)) state that there appears to be a correlation between the elevated concentrations of radionuclides in higher salinity produced water. The results of this study indicate that produced water on the east side of the San Joaquin Valley (location where produced water is being reused for irrigation) has a lower risk of containing high levels of radionuclides due to low salinity. Analysis of monitoring data in Task 2 shows these produced waters have low radioactivity.

The radionuclides krypton-85 (krypton) and xenon-133 (xenon) have the potential to be in produced water due to their use as oil field additives. Krypton and xenon are noble gasses and the mode of decay for both radionuclides is through beta decay. Krypton has a half-life of 10.8 years and decays to stable rubidium. Xenon has a half-life of 5.25 days and decays to cesium, which is stable. Since rubidium and cesium are relatively non-toxic, GSI did not consider rubidium or cesium for further evaluation in Task 2 as they are unlikely to cause adverse health effects at low level chronic exposures. The toxicities of krypton and xenon are related to beta radiation, which is monitored in produced water.

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GSI's evaluation of radionuclides examined radium-226, radium-228, uranium, thorium, krypton, and xenon. Based on consideration of their fate and transport in water and soil, krypton and xenon were not considered to have the potential to reach the root zone of the crop. In contrast, radium, uranium, and thorium behave like other metals in soil and water in that their mobility is affected by the same fate and transport factors. Evidence suggests that the mobility of these radionuclides in soils are attenuated by fate and transport factors and that food crops are unlikely to bioaccumulate these radionuclides to a significant degree. Due to the low concentrations of radionuclides in produced water and the fate and transport factors limiting their phytoavailability, GSI determined that the concentrations of radionuclides in the produced water reused for irrigation does not appear to pose a significant risk to human health or crop safety.

#### 4.7 Other Sources of Chemicals of Interest

GSI found that 83 of the 143 Chemical of Interest are also used in agrochemicals and are found as natural components of soil. Other Chemicals of Interest are used widely in industry: 112 chemicals were identified in processing materials or products ranging from food, plastics, dyes, pharmaceuticals, and sanitizers. Of the 143 Chemicals of Interest, 22 chemicals did not have information available regarding potential sources of the chemical in the environment. For the complete list of the Chemicals of Interest and potential sources in the environment, see Tables 2 and 3 in the *Final Task 2 Report*. Table 2 summarizes the findings for conventional oil production and Table 3 summarizes the findings for agricultural and general uses.

#### 4.8 Other Places that Reuse Produced Water for Irrigation

GSI identified a peer reviewed article that examines the reuse of produced water for irrigation in dry areas across the world (Echchelh et al. 2018). The article states that during a review of over 474 produced water quality samples across the United States, Australia, Africa, and Qatar, approximately 8.4% of the samples met agricultural requirements for electrical conductivity and sodium adsorption. The article states that the most practicable methods for treating produced water for salts is dilution with low-salinity freshwater or desalination with reverse osmosis. Within the United States, research regarding this practice and practical treatment methods has occurred in California and Wyoming. In Monterey and Los Angeles Counties, California, treatment plants have been successfully designed to generate produced water of adequate quality for reuse for irrigation. In Wyoming, a pilot study demonstrated that untreated produced water could be used for aquaculture and hydroponic crops. Currently, the Central Valley is the only place in the United States implementing the practice of reusing untreated (with regard to water quality) produced water for irrigation. This is mostly due to the quality of the produced water, which is exceptionally low in mineral salts.

Outside the United States, case-studies in Mexico, Brazil, Oman, Qatar, and Yemen have been completed related to the reuse of produced water for irrigation. According to these case-studies, produced water from these areas yields electrical conductivity results that are three to six times higher than produced water reused for irrigation in the

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Central Valley. Electrical conductivity is one indicator of salt content. The case-studies show that crops have been successfully grown using produced water in the following areas: tomatoes in Northern Mexico, sunflowers in Brazil, cotton and hemp in Yemen, and alfalfa, barley, and Rhodes grass in Oman. Commercial farming operations using produced water in these countries do not appear to exist at this time, although case studies demonstrate that crops have been successfully grown using produced water significantly higher in salinity than produced water being used for irrigation in the Central Valley.

#### 4.9 Summary of Findings for Task 2

Consistent with the scope of work for Task 2, GSI completed a comprehensive review of the available literature for the Chemicals of Interest that may be in produced water reused for the irrigation of food crops. GSI examined:

- The concentrations of the Chemicals of Interest in produced water and blended produced water;
- The ambient levels of the Chemicals of Interest in air, soil, water, and food;
- Other potential sources of the Chemicals of Interest, including agricultural and general uses;
- The potential fate and transport pathways of the Chemicals of Interest to identify chemicals or constituents that have limited availability for uptake by crops;
- Potential degradation and reaction products related to the presence of the Chemicals of Interest;
- The potential for plant uptake of the Chemicals of Interest; and
- The potential for radionuclides to accumulate in the edible portion of the crop.

GSI also completed a comparison between produced water, blended produced water, and water from other sources. This comparison found that there were no significant differences in the levels of chemicals in blended produced water from other sources of water. Many chemicals found in the blended produced water may have originated from local agricultural activities or other environmental sources.

GSI searched several sources to obtain pertinent information related to the Chemicals of Interest. While there is reliable literature about fate and transport, plant uptake, and comparison of produced water quality to ambient levels, there is currently no known method to reliably predict the concentrations and health risks of chemicals in crops based on the concentrations observed in irrigation water. While there are unanswered questions and data gaps, the information available does not indicate that there are concerns related to the presence of Chemicals of Interest at either background concentrations or elevated levels in blended produced water. Also, while it has been

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demonstrated that some of the Chemicals of Interest have the potential for plant uptake, the available evidence does not indicate that this has or will occur at particularly higher rates than plants using conventional sources of irrigation water. In addition, GSI demonstrated that some of the Chemicals of Interest have characteristics which will attenuate their presence or mobility in soil and thereby reduce their availability for plant uptake.

#### 5.0 Task 3 - Crop Sampling and Analysis

Task 3 consisted of the collection, analysis, and comparison of food crop samples. Crop samples were collected from two area types: (1) farmland irrigated with produced water (treated sites), and (2) farmland irrigated with conventional sources of water (control sites). To ensure the validity of the crop sample results, Sampling and Analysis Plans (SAPs) were developed that outlined general sampling procedures, sample locations, and analyses. The SAPs were reviewed and approved by the Panel, Science Advisor, and Central Valley Water Board staff. Crop samples were collected from 2017 through 2019 and sample results were distributed to the Panel, Science Advisor, and GSI for review.

The work and findings for Task 3 are summarized in a comprehensive report prepared by GSI, referred to as the *Final Task 3 Report*. The Panel, Science Advisor, and Central Valley Water Board staff have reviewed the work and findings in the *Final Task 3 Report*. The following sections provide an overview of the work and findings completed by GSI for Task 3. For more information related to Task 3, see the *Final Task 3 Report* available in Appendix E of this White Paper.

#### 5.1 Overview of Sampling

From 2017 through 2019, crop samples were collected in accordance with the approved SAPs. During this period, there were 26 sampling events for the collection of 13 crop types. A sampling event is a single day in which a third-party consultant went into the field and collected at least one crop sample. Crop samples collected include: almonds; apples; carrots; cherries; garlic; grapes; lemons; mandarins; Navel oranges; Valencia oranges; pistachios; potatoes; and tomatoes. Crop samples were collected and immediately stored in ice chests under the oversight of Central Valley Water Board staff. At the conclusion of each sampling event, the ice chest(s) were either driven by Central Valley Water Board staff or shipped (via overnight delivery) to a laboratory for analysis, maintaining the chain of custody.

#### 5.2 Sample Results (Overview)

Crops collected under Task 3 were analyzed for 113 analytes. The 113 analytes include 13 metals and 95 organic chemicals (listed in Table 2 of this White Paper). GSI reviewed the analytical results and determined that 89 analytes were non-detect for all crop samples and 24 analytes had detectable concentrations in at least one or more of the crop samples irrigated with produced water. The majority of the 24 analytes were determined by GSI to have likely originated from natural sources. Table 3 in this White

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Paper identifies the analytes, the number of detections and percent detections observed in crop samples, and a classification determined by GSI. As shown in Table 3, 18 of the 24 analytes are commonly found in fruit and vegetables. In addition, the analytes that had the greatest number of detections appear to be common in fruit and vegetables. Analytes with the lowest number of detections appear to be associated with the environment or farming.

#### **5.3 Sample Results (Treated versus Control Comparison)**

To identify potential trends between control and treated sites, GSI examined differences between the analytical results for crops irrigated with produced water (treated sites) versus crops irrigated with conventional sources of water (control sites). The analysis and comparison of treated versus control sites consisted of the following:

- Calculation of the frequency of detections;
- Calculation of the arithmetic mean and median of chemical concentrations;
- Evaluation of normal distribution curves using a graphical analysis (Q-Q Plot) and statistical analysis (Shapiro-Wilks test);
- Box and whisker plots;
- Bar charts and stiff plots;
- Correlation matrix charts: and
- Statistical analysis methods that include Wilcoxon-Mann-Whitney, Fishers Exact Test, and Welch-Satterthwaite Test.

The above described analyses were completed by GSI for the 24 analytes that had detectable concentrations in crops. Based on the confidence levels and ratios using the statistical analytical methods and graphical representations, GSI concluded that the overall chemical profile for treated and control samples appear to be similar.

Apples were the only crop type that did not have a control sample group for comparison. Control samples for apples were not collected, since there were no apples being grown using conventional sources of irrigation water in the area. In lieu of completing a statistical comparison for apples, GSI compared the observed concentrations to toxicity screening levels for apples published by the US EPA and World Health Organization (WHO). GSI found that the detectable concentrations in apples were within the acceptable range and that there does not appear to be a threat to human health from the ingestion of apples irrigated with produced water.

#### 5.4 Summary of Findings for Task 3

Based on crop sample results, statistical analyses, and national food survey and chemical profile data, GSI found the following:

- Levels of metals and organics detected in crops irrigated with produced water are within ranges expected for food supplies in the United States;
- While there are some specific crop/chemical combinations for which chemical results are different, the overall chemical profiles in crops are the same for crops irrigated with blended produced water and crops irrigated with conventional sources; and
- The chemical profiles are very similar for several groups of crops, which may help to establish baseline conditions and guide future studies with similar objectives.

#### 6.0 Data Gaps

Throughout the Food Safety Project, the Panel, Science Advisor, and GSI have identified data gaps related to the work and findings of Tasks 1 through 3. These data gaps describe items of interest that (1) have limited data available by private or public entities, (2) would require an extensive study to evaluate, or (3) pertain to specific information that was not available to the Panel and GSI due to industry claims of trade secret. Data gaps identified by the Panel, Science Advisor, and GSI include:

- Mass Data of Chemicals Mass data with regard to the make-up of oil field additives would provide pertinent information related to specific chemicals and constituents that may influence the Chemicals of Interest designated under Task 1.
- Chemical Uptake in Plants Limited information is available concerning plant
  uptake of organic chemicals. There is a limited understanding of plant physiology
  concerning the uptake and translocation of both organic and inorganic chemicals
  in crops used for food. A better understanding of how Chemicals of Interest and
  plants interact would reduce uncertainty and improve evaluation of irrigation
  practices.
- Potential Long-Term Impacts to Soil and Plants The potential accumulation
  of Chemicals of Interest in the soil was not evaluated in the Food Safety Project
  and the potential for recurring reuse of produced water for irrigation to adversely
  impact the soil and / or plants is not known.
- Chemicals with No Toxicity Data or Analytical Method Chemicals or constituents that do not have toxicity data or an approved analytical method may have the potential to pose a threat to crop safety and human health. Since these chemicals or constituents cannot be analyzed or do not have a known toxicity

threshold, there are potentially significant unknowns associated with these chemicals or constituents. Section 8 of this White Paper includes more information regarding this data gap.

• Transformation Products of Chemicals – A thorough assessment of all potential transformation and daughter products was not completed under the Food Safety Project due mostly to the scale of work needed to accomplish this task. Therefore, there is some potential for additional chemicals and constituents to be present in the produced water, reused for irrigation, that may not be included in the 399 chemicals and constituents identified in Task 1.

The data gaps identified here are discussed in more detail in the *Data Gaps Related to the Food Safety Project* memorandum available in Appendix B of this White Paper. As discussed in the memorandum, the purpose of identifying analytical data gaps is to acknowledge the limitations of the study and highlight potential areas of interest for future studies.

The data gaps identified in the Food Safety Project were not investigated further due to:

- Technology or analytical methods are not currently available,
- Scope and funding far exceeds that of the Food Safety Project, or
- Scientific information needed to close the data gap is not available at this time.

The work and findings of the Food Safety Project are based on the scientific information available as of the date of this White Paper. As part of the objectives of the Food Safety Project, the work and findings were completed based on available science to reach a conclusion that is scientifically defensible.

#### 7.0 Conclusions of the Food Safety Project

This White Paper was prepared by Central Valley Water Board staff and the Science Advisor on behalf of the Panel. The Panel and GSI have reviewed the content of this White Paper. In addition, the Panel, Science Advisor, and Central Valley Water Board staff have reviewed the work completed by GSI under the Food Safety Project. The work and findings of the Food Safety Project were also presented to the Panel during numerous public meetings that included opportunities for comments and/or questions by the Panel and members of the public.

The work under the Food Safety Project answered important questions related to human health and food safety and resulted in numerous findings that are discussed in detail in the Task Reports (available in Appendices D – F of this White Paper). Some major findings include the following:

 A complete list of 399 chemicals that could be potentially found in produced water in this region was developed.

- The preliminary hazard assessment designated 143 of the 399 chemicals identified in produced water as Chemicals of Interest that were studied in depth.
- Many Chemicals of Interest are naturally occurring chemicals or are used in agriculture, as well as for oil and gas production.
- Radionuclides occur at very low levels in produced waters of this region.
- The literature review identified data gaps related to some Chemicals of Interest, including the absence of analytical methods for a sub-set of chemicals and, thereby, characterized uncertainty concerning study outcomes.
- Crop sample analyses indicated that the Chemicals of Interest that were measured in crops were all with in the normal range of concentrations for food.
- The current monitoring required for produced water used for irrigation by the Central Valley Water Board is sufficiently rigorous.
- The majority of 399 chemicals and constituents routinely monitored in produced water used for irrigation were below drinking water standards established by the California Department of Public Health.
- The crop sampling program was not shown to be superior to a water monitoring program for ensuring public health and safety in the context of using produced water for irrigation water.
- The disclosure of oil field additives and monitoring and reporting requirements of the produced water and the blended produced water provided critical data for this study.
- Although some organic chemicals may have the potential to be taken up by plants, the literature review found evidence that organics are not likely to be available for plant uptake due to adsorption in the water and soil and potential degradation.
- When comparing the findings of the literature review and comparison of crop sample results, GSI noted that the findings did not conflict with each other and are expected based on the best available science.
- Tasks 1 through 3 did not yield any evidence that the reuse of produced water for irrigation poses an elevated threat to human health or crop safety.

These findings, the Task 1, 2, and 3 Reports, and other information presented in public meetings were used by the Panel to develop recommendations for the Central Valley Water Board regarding how to move forward with regulating new and expanding projects that propose the reuse of produced water for irrigation (Section 8).

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The results and findings of the Food Safety Project have been supported by an independent study in the same region conducted by researchers at Duke University and their collaborators (Kondash et al., 2020). This independent study found that produced water reused for irrigation by Cawelo Water District is of comparable quality to the local groundwater and that the majority of chemicals do not exceed irrigation or drinking water standards (except for arsenic which is also observed in local water sources). The independent study also states that the preliminary results do not show evidence for metals accumulating in pistachios (the only crop sampled as part of that study) from fields that are irrigated with produced water.

#### 8.0 Findings and Recommendations from the Food Safety Expert Panel

The Panel has reviewed and has reached a consensus regarding the following recommendations:

## 8.1 Findings and Recommendations Concerning Current Produced Water Reuse Program

#### 1. Discontinue Crop Sampling

The Panel recommends that crop sampling be discontinued at this time.

There were no findings from crop sampling to indicate a food safety or public health concern related to the reuse of produced water for irrigation in this region. However, crop analysis for crude oil constituents and associated additives is complicated by many factors that introduce uncertainty, including chemical inputs to agricultural systems (i.e., fertilizers, pest control chemicals); interference from natural organic compounds in foods; and limitations of approved and verified methods to analyze chemical contaminants in food crops. Given these uncertainties and limitations, crop sampling is less productive/informative than soil and water sampling, controlled plant-uptake studies, and other data-collection efforts discussed in the recommendations below.

#### 2. Continue Produced Water Quality Monitoring

The Panel recommends that the current produced water quality monitoring program be continued.

Monitoring and reporting programs issued by the Central Valley Water Board for produced water reuse require quarterly sampling and analysis of a broad suite of organic and inorganic compounds related to oil production that can be measured using State and Federally approved analytical methods. The Board should use an adaptive management approach – in which it continuously and systematically incorporates new information for risk-based decision making – to maintain a current and up-to-date analytical program for monitoring of produced water. For example, as new water quality monitoring and analytical methods are approved, they can be incorporated, and the list of analytes can be adjusted as appropriate.

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Similarly, as new water quality monitoring and testing approaches emerge for regulatory use, these should be incorporated into monitoring requirements as well. The Central Valley Water Board should continue the produced water monitoring requirements at quarterly frequencies unless water quality variability indicate more frequent sampling is needed.

#### 3. Continue Disclosure of Additives

The Panel recommends that the Central Valley Water Board continue to require the disclosure of additives used in oil production that supply produced water for agriculture.

The disclosure of additives that are used during petroleum exploration and production, including chemicals used in the treatment of produced water, enabled the review completed by the Panel. Continued chemical disclosure will support risk management in the face of changing oil and gas production practices. Additives should be disclosed with their corresponding Chemical Abstract Services Registry Numbers (CASRN). The use of additives that lack sufficient characterization to undertake a hazard evaluation or risk assessment should be discouraged.

## 4. Consider New Information Developed by the Food Safety Project When Evaluating WDRs for Produced Water Reuse Projects

The Central Valley Water Board should evaluate new proposals for reuse of produced water in irrigation (and also WDR renewals) based upon experience with existing produced water reuse projects and using the information and recommendations developed in the Tasks 1, 2, and 3 Reports and this White Paper.

Additional monitoring and analyses should be considered to reduce the data gaps identified in this White Paper and the task reports, and projects should be rejected if significant data gaps cannot be addressed. Factors to consider in granting WDRs include, but are not limited to, the type of crops being irrigated, adequate characterization of water quality, demonstration that the project would not negatively impact water quality, and identification and toxicity of additives and transformation products associated with petroleum exploration, petroleum production, and the treatment of produced water.

### 8.2 Findings and Recommendations Concerning Management of Potential Hazards from Additives

## 5. Continue Evaluation of New Additives Used in Oil Operations that Provide Produced Water for Irrigation

The Panel recommends that the Central Valley Water Board periodically review the list of additives, identify new additives, and evaluate the potential human health risks associated with new chemicals.

The Food Safety Project evaluated the hazard potential of additives associated with oil production in the context of using produced water for irrigation. The Task 1 and 2 reports describe the methods, results, and limitations of this work. Additives not previously evaluated in these reports should be subjected to a similar level of review. Characteristics to consider in a hazard assessment include, but are not limited to, abiotic and biotic degradability, plant uptake, persistence in the environment, and toxicity of the parent compounds and known transformation products. The review should be conducted by experts in evaluation of chemical impacts to food safety and human health. Findings for new chemicals should be made available for review and consideration by the public.

#### 6. Consider Requiring the Disclosure of Mass Data for Additives

The Panel recommends that the Central Valley Water Board consider requiring the disclosure of the mass amount of each additive used, as well as the frequency of use.

The disclosure of additives used in oil exploration, production, or treatment (and their CASRNs) enabled the Panel to evaluate the hazard characteristics of these substances and to develop the Chemicals of Interest list (see the Task 1 Report). However, the Chemicals of Interest list contains many chemicals that may be used in small or large amounts or infrequently or frequently during oil operations. In addition to toxicity and other factors, the hazard associated with a chemical is related to the mass of the chemical used. As such, disclosure of the mass amount and frequency of chemicals used would allow a more context-specific evaluation of potential hazards. Although there are trade-secret issues, it should be noted that programs governing hydraulic fracturing and well stimulation in the State of California require the reporting of mass data.

#### 7. Develop a List of Additives Designated as "Low Hazard"

The Panel recommends that the Central Valley Water Board consider publishing a list of oil additives that have been evaluated as of low human and environmental hazard in the context of produced water reuse for irrigation.

The Task 1 and 2 reports could be used as the basis for the development of a list of additives that were evaluated to be of low human and environmental hazard in the context of produced water reuse for irrigation. Compounds that exhibit low chronic toxicity and/or are found to be easily biodegradable could be considered candidates for this list. Chemicals on the list must meet criteria based on toxicity, persistence, mutagenicity, and transformation products. Oil producers should be encouraged to use additives from the low hazard list, which would reduce the uncertainty regarding the quality of produced water used for irrigation. If there is a new chemical to be considered for the list, it should be subjected to a standardized review process. The list could be a deliverable for a subsequent study, or the product from a group of experts from fields of toxicology, environmental science, public health, and industry.

#### 8. Work to Close Data Gaps Concerning Oil Additives

The Panel recommends that the Central Valley Water Board take steps to acquire missing hazard and water-concentration information for oil additives and associated chemical constituents.

The Panel notes that the Task 1 and 2 reports identified 91 disclosed chemicals additives (23% of all additives) that cannot be measured in produced water samples due to a lack of established analytical methods. The reports also found that 74 disclosed chemical additives (19% of total) had insufficient toxicity information with which to carry out an initial hazard assessment. The Panel has further noted that environmental fate and transformation product information is lacking for many chemical additives.

Actions recommended to close data gaps include identifying or developing new analytical methods and continued effort to identify or develop new toxicity and environmental fate information on data-poor chemicals. The Central Valley Water Board should work with other agencies in these matters and identify data gap priorities. Assistance from outside experts may also be required, as well as working with chemical suppliers.

## 8.3 Findings and Recommendations Concerning Studies or Actions Needed to Close Identified Data Gaps

#### 9. Conduct Environmental Studies on Produced Water Reuse for Irrigation

The Panel recommends that the Central Valley Water Board conduct or sponsor (and encourage other regulatory agencies to conduct or sponsor) environmental studies on the effects of produced water on the fate and transport of chemicals associated with oil development in agricultural systems.

The Panel identified data gaps in the available information on the persistence of oil production chemicals and their transformation products in irrigation water and the fate of these chemicals in agriculture (e.g., rates of degradation and

accumulation in soil, and plant uptake). The Central Valley Water Board should promote the development of a coherent scientific program to examine outstanding issues concerning the use of produced water for the irrigation of food crops. In doing so, the Central Valley Water Board may need to partner with other state or federal agencies, as well as experts outside of government.

Such a program could address knowledge gaps by employing field or laboratory studies to examine the fate and transport of oil and gas development-related chemicals potentially found in the irrigation water or if indicated by other information. Studies could include the uptake of these chemicals in crops and their impact upon irrigated soils. This should be accomplished by undertaking well-designed, controlled studies using comparable soils, agricultural practices, and documented irrigation histories, and using the best available scientific approaches. Techniques that are currently under review by other agencies, such as isotope geochemistry and non-targeted bioanalytical tests, should be considered for their suitability in this research.

#### 10. Conduct a Soil Study

The Panel recommends that the Central Valley Water Board examine the effect of produced water use on soils.

A poor understanding of the effects of long-term produced water reuse on soil condition (i.e., physical, biological, and chemical) was identified as a data gap by the Panel. Either as part of the studies described above or as an independent effort, the Central Valley Water Board should sponsor a study to investigate the potential accumulation of produced water constituents in the soil or changes in soil characteristics. The study could include, but not be limited to, an examination of how produced water use may affect the concentration of metals and persistent organic chemicals, sodium adsorption ratio, soil salinity, soil microbiology, and fertility.

#### 11. Evaluate the Variability of Produced Water Quality Used for Irrigation

The Panel recommends that the Central Valley Water Board evaluate temporal and spatial variability in the quality of produced water reused for irrigation.

The Panel identified a data gap concerning the temporal and spatial variability in the quality of produced water being used for irrigation. Water quality variability is important to understand when conducting water management oversight activities. Variability can be evaluated, in part, by continuously monitoring parameters such as specific conductance (EC) or fluorescence (for hydrocarbons), or by reviewing historical water quality data (where data are available). The Central Valley Water Board should consider water quality variability when establishing monitoring programs and should require that dischargers demonstrate that produced water being reused for irrigation has a consistent water quality (i.e., has low variability).

#### 12. Examine the Utility of Emerging Water Quality Monitoring Methods

The Panel recommends that the Central Valley Water Board evaluate and consider incorporating emerging monitoring approaches for their applicability to the reuse of produced water.

The current monitoring plans include the majority of constituents known to be associated with oil production. The lack of validated analytical methods for some additives and likely many transformation products has been identified as a data gap by the Panel. However, several new test methods for recycled municipal wastewater are under development and may be applicable to monitoring produced water. For example, cellular biological assays may soon be used to test for so-called "emerging contaminants" in municipal wastewater. The Central Valley Water Board should evaluate bioanalytical screening tools and other nontargeted analyses as an approach to measure the hazard of transformation products and other compounds that are not included in current monitoring programs. This evaluation could include participation in or support of method development studies.

#### 9.0 References

- Echchelh, A., Hess, T. and Sakrabani, R., 2018. Reusing oil and gas produced water for irrigation of food crops in drylands. Agricultural Water Management, 206, pp.124-134.
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- <u>USGS. 2018. California Drought</u>. [https://ca.water.usgs.gov/california-drought/california-drought-comparisons.html]. Accessed 07/24/2019

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#### 10.0 List of Tables

Table 1: Chemicals of Interest List

Table 2: List of Chemicals for Crop Analysis

Table 3: Detected Analytes in Crop Samples

**Table 1: Chemicals of Interest List** 

CASRN	Name	CASRN	Name
479-66-3	1H, 3H-Pyrano (4,3-b)(1)benzopyran-9-carboxylic acid, 4,10-dihydro-3,7,8 trihydroxy-3-methyl-10-oxo (fulvic acid)	68527-49-1	Thiourea, polymer with formaldehyde and 1-phenylethanone
100-73-2	Acrolein dimer	64114-46-1	Triethanolamine homopolymer
No CASRN	Aromatic amine	53-70-3	Dibenzo(a,h)anthracene
38011-25-5	Disodium ethylenediaminetetraacetate	50-32-8	Benzo(a)pyrene
No CASRN	Heavy catalytic reformed naptha	111-44-4	Bis (2-chloroethyl) ether
1415-93-6	Humic acids	7440-38-2	Arsenic
85-01-8	Phenanthrene	56-55-3	Benzo(a)anthracene
19019-43-3	Polycarboxlate salt	205-99-2	Benzo(b)fluoranthene
74-84-0	Polyethylene	193-39-5	Indenopyrene
9038-95-3	Polyglycol ether	218-01-9	Chrysene
91-63-4	Quinaldine	123-91-1	1,4 Dioxane
NP- SMO3_U1240	Sorbitan ester	7440-43-9	Cadmium
65996-69-2	Steel mill slag	7439-97-6	Mercury
8052-41-3	Stoddard solvents	7440-48-4	Cobalt
64-02-8	Tetrasodium ethylenediaminetetraacetate	7439-92-1	Lead
27646-80-6	2-Methylamino-2-methyl-1-propanol	7440-36-0	Antimony
67990-40-3	2-Propen-1-aminium, N,N-dimethyl- N-2-propenyl-, chloride, polymer with 2-hydroxypropyl 2-propenoate and 2-propenoic acid	7440-41-7	Beryllium

CASRN	Name	CASRN	Name
145417-45-4	2-Propenoic acid, 2-methyl-, polymer with methyl 2-methyl-2- propenoate, octadecyl 2-methyl 2 propenoate and 2propenoic acid, sodium salt	7439-93-2	Lithium
9033-79-8	2-propenoic acid, polymer with sodium 2-propenoate	554-13-2	Lithium carbonate
130800-24-7	2-Propenoic acid, telomer with 2-methyl-2-(1-oxo-2-propenyl)-1-propanesulfonic acid, sodium salt	13453-71-9	Lithium chlorate
300-92-5	Aluminum distearate	1310-65-2	Lithium hydroxide
No CASRN	Amide surfactant acid salt	13840-33-0	Lithium hypochlorite
No CASRN	Amides, non-ionics	7440-47-3	Chromium
61791-24-0	Amine derivative	7440-61-1	Uranium
67924-33-8	Amine salt	7439-98-7	Molybdenum
NP-U2856	Amine salt	7782-49-2	Selenium
64346-44-7	Amine sulfate	7440-22-4	Silver
68239-30-5	Bis (HDMA) EPI copolymer hydrochloride	7440-50-8	Copper
69418-26-4	Cationic acrylamide copolymer	7758-99-8	Copper sulfate pentahydrate
44992-01-0	Cationic acrylamide monomer	7553-56-2	lodine
54076-97-0	Cationic polymer	7440-02-0	Nickel
681331-04-4	Causticized lignite	7786-81-4	Nickel sulfate
64743-05-1	Coke (petroleum), calcined	120-12-7	Anthracene
25987-30-8	Copolymer of acrylamide and sodium acrylate	108-90-7	Chlorobenzene

CASRN	Name	CASRN	Name
129828-31-5	Crosslinked polyol ester	129-00-0	Pyrene
2673-22-5	Diester of sulfosuccinic acid sodium salt	64742-95-6	Solvent naphtha, petroleum, light aromatic.
No CASRN	Drilling paper	206-44-0	Fluoranthene
61791-26-2	Ethoxylated amine	16984-48-8	Fluoride
9081-83-8	Ethoxylated octylphenol	7664-39-3	Hydrofluoric acid
5877-42-9	Ethyl octynol	83-32-9	Acenaphthene
63428-92-2	Formaldehyde, polymer with 2- methyloxirane, 4-nonylphenol and oxirane	7439-96-5	Manganese
30704-64-4	Formaldehyde, polymer with 4-(1,1-dimethylethyl) phenol, 2-methyloxirane and oxirane	14797-65- 0	Nitrite
30846-35-6	Formaldehyde, polymer with 4- nonylphenol and oxirane	2025884	Sulfur dioxide
No CASRN	Heavy catalytic reformed naptha	7440-62-2	Vanadium
61790-59-8	Hydrogenated tallow amine acetone	7727-43-7	Barite
68648-89-5	Kraton G1702H	7440-39-3	Barium
129521-66-0	Lignite	7440-42-8	Boron
PE-M2464	Methyl oxirane polymer	12179-04-3	Sodium tetraborate pentahydrate
No CASRN	Organic acid ethoxylated alcohols	7440-31-5	Tin
68171-44-8	Oxyalkylated alkylphenolic resin	7440-66-6	Zinc
68910-19-0	Oxyalkylated polyamine	7646-85-7	Zinc chloride
67939-72-4	Oxyalkylated polyamine	119-65-3	Isoquinoline

CASRN	Name	CASRN	Name
68123-18-2	Phenol, 4,4'-(1-methylethylidene) bis-, polymer with 2- (chloromethyl)oxirane, 2- methyloxirane and oxirane	1309-64-4	Antimony trioxide
68425-75-2	Phosphate ester salt	7447-41-8	Lithium chloride
9005-70-3	POE (20) sorbitan trioleate	29868-05-1	Alkanolamine phosphate
68938-70-5	Poly (triethanolamine.mce)	60-24-2	2-mercaptoethanol
68955-69-1	Polyamine salts	64742-53-6	Distillates, hydrotreated light naphthenic
26062-79-3	Polydimethyl diallyl ammonium chloride	126-97-6	Ethanolamine thioglycolate
68036-92-0	Polyglycol diepoxide	115-19-5	2-methyl-3-Butyn-2-ol
68036-95-3	Polyglycol diepoxide	68308-87-2	Cottonseed, flour
No CASRN	Polyhydroxyalkanoates (PHA)	26027-38-3	Ethoxylated 4- nonphenol
64741-71-5	Polymers (petroleum) viscous	2809-21-4	Hydroxyethylidenediphosphonic acid
36484-54-5	Polyoxyalkylene glycol	68439-70-3	Alkyl amine
61790-86-1	Polyoxyalkylenes	61790-41-8	Quaternary ammonium compound
9014-93-1	Polyoxyethylene dinonylphenol	No CASRN	Nonylphenol ethoxylates
12068-19-8	Polyoxyethylene nonyl phenyl ether phosphate	127087-87- 0	Nonylphenol polyethylene glycol ether
70142-34-6	Polyoxyl 15 hydroxystearate	68412-54-4	Oxyalkylated alkylphenol
42751-79-1	Polyquaternary amine	13983-27-2	Krypton-85
68609-18-7	Quaternized condensed alkanolamines	7440-14-4	Radium-226

CASRN	Name	CASRN	Name
No CASRN	Steranes or cyclopentanoperhydrophenanthrene	15262-20-1	Radium-228
68140-11-4	Tall oil, DETA/ midazoline acetates	14932-42-4	Xenon-133
72480-70-7	Tar bases, quinoline derivatives, quaternized benzyl chloride		

Table 2: List of Chemicals for Crop Analysis

	Table 2: List of Chemicals for Crop Analysis					
Analytical Method	Analyte	Analytical Method	Analyte			
EPA 6020	Antimony, Total	EPA 8260B	1,2-Dichloropropane			
EPA 6020	Arsenic, Total	EPA 8260B	1,3,5-Trimethylbenzene			
EPA 6020	Barium, Total	EPA 8260B	1,3-Dichlorobenzene			
EPA 6020	Beryllium, Total	EPA 8260B	1,3-Dichloropropane			
EPA 6020	Cadmium, Total	EPA 8260B	1,4-Dichlorobenzene			
EPA 6020	Chromium, Total	EPA 8260B	2,2-Dichloropropane			
EPA 6020	Cobalt, Total	EPA 8260B	2-Butanone			
EPA 6020	Copper, Total	EPA 8260B	2-Chloroethyl Vinyl Ether			
EPA 6020	Lead, Total	EPA 8260B	2-Chlorotoluene			
EPA 6020	Molybdenum, Total	EPA 8260B	2-Hexanone			
EPA 6020	Nickel, Total	EPA 8260B	4-Chlorotoluene			
EPA 6020	Selenium, Total	EPA 8260B	4-Methyl-2-Pentanone			
EPA 6020	Silver, Total	EPA 8260B	Acetone			
EPA 6020	Strontium, Total	EPA 8260B	Acrolein			
EPA 6020	Thallium, Total	EPA 8260B	Acrylonitrile			
EPA 6020	Vanadium, Total	EPA 8260B	Benzene			
EPA 6020	Zinc, Total	EPA 8260B	Bromobenzene			
EPA 6010B	Lithium, Total	EPA 8260B	Bromochloromethane			
EPA 8270C	2-Naphthylamine	EPA 8260B	Bromodichloromethane			
EPA 8270C	Bis(2-chloroethyl)ether	EPA 8260B	Bromoform			
EPA 8270C	Bis(2-ethylhexyl)phthalate	EPA 8260B	Bromomethane			
EPA 8270C	Carbazole	EPA 8260B	Carbon Tetrachloride			

Analytical Method	Analyte	Analytical Method	Analyte
EPA 8270C	Phenol	EPA 8260B	Chlorobenzene
EPA 8270C	Pyridine	EPA 8260B	Chloroethane
EPA 8270C-SIM	1-Methylnaphthalene	EPA 8260B	Chloroform
EPA 8270C-SIM	2-Methylnaphthalene	EPA 8260B	Chloromethane
EPA 8270C-SIM	Acenaphthene	EPA 8260B	Cis-1,2-Dichloroethene
EPA 8270C-SIM	Acenaphthylene	EPA 8260B	Cis-1,3-Dichloropropene
EPA 8270C-SIM	Anthracene	EPA 8260B	Dibromochloromethane
EPA 8270C-SIM	Benzo (a) anthracene	EPA 8260B	Dibromomethane
EPA 8270C-SIM	Benzo (a) pyrene	EPA 8260B	Dichlorodifluoromethane
EPA 8270C-SIM	Benzo (b) fluoranthene	EPA 8260B	Ethyl Acetate
EPA 8270C-SIM	Benzo (g,h,i) perylene	EPA 8260B	Ethylbenzene
EPA 8270C-SIM	Benzo (k) fluoranthene	EPA 8260B	Hexachlorobutadiene
EPA 8270C-SIM	Chrysene	EPA 8260B	Isopropylbenzene
EPA 8270C-SIM	Dibenzo (a,h) anthracene	EPA 8260B	m,p-Xylene
EPA 8270C-SIM	Fluoranthene	EPA 8260B	Methyl Tert-Butyl Ether (MTBE)
EPA 8270C-SIM	Fluorene	EPA 8260B	Methylene Chloride
EPA 8270C-SIM	Indeno (1,2,3-cd) pyrene	EPA 8260B	n-Butylbenzene
EPA 8270C-SIM	Naphthalene	EPA 8260B	n-Propylbenzene
EPA 8270C-SIM	Phenanthrene	EPA 8260B	o-Xylene
EPA 8270C-SIM	Pyrene	EPA 8260B	p-Isopropyltoluene
EPA 8260B	1,1,1,2-Tetrachloroethane	EPA 8260B	sec-Butylbenzene
EPA 8260B	1,1,1-Trichloroethane	EPA 8260B	Styrene

Analytical Method	Analyte	Analytical Method	Analyte
EPA 8260B	1,1,2,2-Tetrachloroethane	EPA 8260B	Tert-Butylbenzene
EPA 8260B	1,1,2-Trichloroethane	EPA 8260B	Tetrachloroethene
EPA 8260B	1,1-Dichloroethane	EPA 8260B	Toluene
EPA 8260B	1,1-Dichloroethene	EPA 8260B	Trans-1,2-Dichloroethene
EPA 8260B	1,1-Dichloropropene	EPA 8260B	Trans-1,3-Dichloropropene
EPA 8260B	1,2,3-Trichlorobenzene	EPA 8260B	Trichloroethene
EPA 8260B	1,2,3-Trichloropropane	EPA 8260B	Trichlorofluoromethane
EPA 8260B	1,2,4-Trichlorobenzene	EPA 8260B	Vinyl Chloride
EPA 8260B	1,2,4-Trimethylbenzene	EPA 8270M	1,4-Dioxane
EPA 8260B	1,2-Dibromo-3- Chloropropane	EPA 8316M	Acrylamide
EPA 8260B	1,2-Dibromoethane	EPA 8015B	Isopropyl alcohol
EPA 8260B	1,2-Dichlorobenzene	EPA 8015B	Methanol
EPA 8260B	1,2-Dichloroethane		

Table 3: Detected Analytes in Crop Samples

Analysta	No. of	%	Classification	
Analyte	Detections	Detections	Classification	
Strontium, Total	257	89.9%	Common in fruit and vegetables	
Copper, Total	232	81.1%	Common in fruit and vegetables	
Barium, Total	124	43.4%	Common in fruit and vegetables	
Acetone	122	42.7%	Common in fruit and vegetables	
Zinc, Total	111	38.8%	Common in fruit and vegetables	
Acrolein	76	26.6%	Common in fruit and vegetables	
Ethyl Acetate	75	26.2%	Common in fruit and vegetables	
p-Isopropyltoluene	46	16.1%	Common in fruit and vegetables	
Methanol	41	14.3%	Common in fruit and vegetables	
2-Butanone	22	7.7%	Common in fruit and vegetables	
Methyl-Tert-Butyl-Ether	22	7.7%	Chemical found in the environment	
Nickel, Total	17	5.9%	Common in fruit and vegetables	
Antimony, Total	16	5.6%	Common in fruit and vegetables	
2-Hexanone	8	2.8%	Common in fruit and vegetables	
Molybdenum, Total	8	2.8%	Common in fruit and vegetables	
Chromium, Total	5	1.7%	Common in fruit and vegetables	
Bis (2-ethylhexy) phthalate	4	1.4%	Chemical found in the environment	
Cadmium, Total	4	1.4%	Common in fruit and vegetables	
Arsenic, Total	3	1.0%	Common in fruit and vegetables	
Lead, Total	3	1.0%	Chemical found in the environment	
2-Chloroethyl Vinyl Ether	1	0.3%	Farming chemical	
Dibenzo (a,h) anthracene	1	0.3%	Chemical found in the environment	

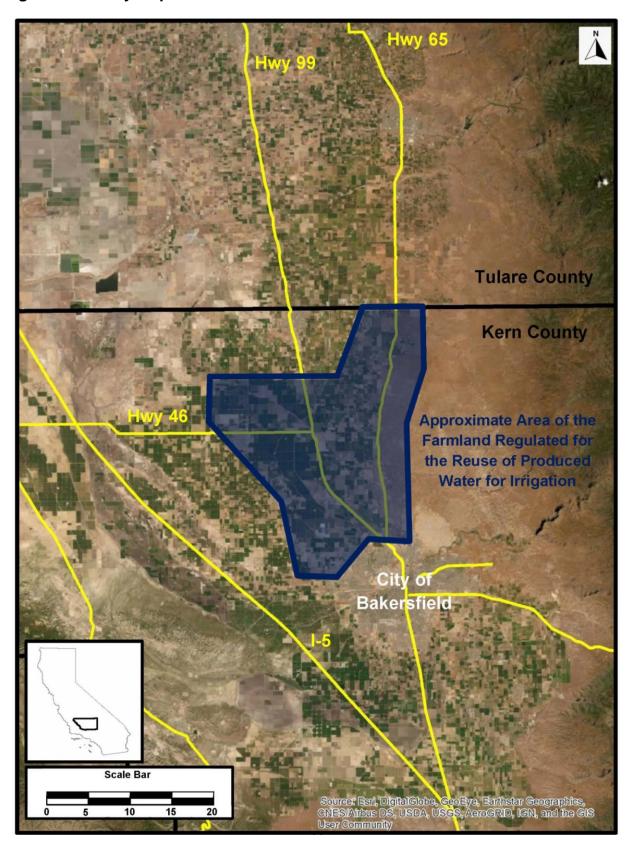
Analyte	No. of Detections	% Detections	Classification
sec-Butylbenzene	1	0.3%	Chemical found in the environment
Selenium, Total	1	0.3%	Common in fruit and vegetables

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### 11.0 List of Figures Figure 1: Vicinity Map

Figure 1: Vicinity Map



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#### **12.0 List of Appendices**

Appendix A – General Information and Operating Guidelines of the Food Safety Project

Appendix B – Data Gaps Related to the Food Safety Project

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Appendix D – Final Task 1 Report

Appendix E – Final Task 2 Report

Appendix F – Final Task 3 Report

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Appendix A – General Information and Operating Guidelines of the Food Safety Project

#### **MEMORANDUM**

Date: 8 September 2021

Prepared By: CA Regional Water Quality Control Board

(Central Valley Region) Staff

### GENERAL INFORMATION AND OPERATING GUIDELINES OF THE FOOD SAFETY PROJECT

This memorandum was prepared by staff of the California Regional Water Quality Control Board, Central Valley Region (Central Valley Water Board) to provide additional information related to the Food Safety Project. This memorandum focuses on general information and operating guidelines of the Food Safety Project, while also providing pertinent background information. Topics of discussion have been separated into sections, as shown below.

- 1. What is Produced Water
- 2. Background
- 3. Waste Discharge Requirements
- 4. Oil Extraction Methods
- 5. Irrigators
- 6. Treatment of Produced Water
- 7. Oil Field Additives
- 8. Quality of Produced Water
- 9. Food Safety Expert Panel
- 10. Memorandum of Understanding
- 11. Science Advisor
- 12. Technical Consultant
- 13. Food Safety Charter
- 14. Sampling Protocols Under Task 3
- 15. Analysis of Crops Under Task 3
- 16. Cawelo Water District's Crop Study

#### 1.0 What is Produced Water

Produced water, or oil field produced water, is a byproduct of oil production. Production fluid, extracted from the ground by oil wells, generally consists of oil and water. The ratio of oil to produced water varies between and within oil fields and oil extraction methods. In the Central Valley, typically 10-15 gallons of produced water is extracted with each gallon of oil.

#### 2.0 Background

The southern San Joaquin Valley is a major oil producing area. Approximately 150 million barrels of oil (42 gallons per barrel) are produced in California each year. Since oil develops primarily in source rock associated with marine geologic formations, produced water tends to be highly saline and is typically recycled back into the production system, discharged into underground injection wells, or discharged to surface ponds.

In some of the oil fields east and north of Bakersfield, oil has migrated far away from the source rock and accumulated in sediments containing low salinity water, when compared to most produced water. In these oil fields, the produced water is of sufficient quality (typically less than 1,000 milligrams per liter (mg/l) total dissolved solids, and less than 1.0 mg/l boron) that it can meet the effluent limits in the *Water Quality Control Plan for the Tulare Lake Basin, Third Edition, revised May 2018* (Basin Plan) without treatment beyond the removal of oil.

Farmers in Kern County have been using this low salinity water to irrigate crops for over 30 years. In 2019, four petroleum companies were sending produced water to four irrigation entities (the petroleum companies and irrigation entities are collectively referred to as "Dischargers"). The Central Valley Water Board regulates the Dischargers through waste discharge requirements (WDRs). Before it is distributed to irrigators for reuse, produced water is treated to remove sediments, hydrocarbons, and other chemicals. Typically, the irrigators receive the produced water in reservoirs where it is blended with other irrigation water and then applied to crops.

#### 3.0 Waste Discharge Requirements

Recycling of water is encouraged by State policy to supplement California's limited water supply, if the water is suitable for the intended use. The Basin Plan states that "blending of wastewater with surface or groundwater to promote beneficial reuse of wastewater may be allowed where the [Central Valley Water Board] determines such reuse is consistent with other regulatory policies set forth or referenced herein." The Basin Plan designates beneficial uses, establishes water quality objectives, contains implementation policies for protecting waters of the basin, and incorporates policies adopted by the State Water Resources Control Board (State Board).

The reuse of produced water for irrigation is regulated under WDRs that implement the Basin Plan requirements and conditionally authorize the practice and stipulate groundwater and effluent limits for the discharge of produced water to land. Included in the WDRs are Monitoring and Reporting Programs (MRPs), which require Dischargers regulated under WDRs to complete specific monitoring of the discharge and groundwater at specific monitoring frequencies. Water samples are collected at various points of discharge, including after treatment and before irrigation and analyzed for hundreds of chemicals associated with oil field activities, including: salts, metals, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), radionuclides, and oil field additives used during oil exploration, production, or treatment. Water

samples required under the MRP are sent to third-party laboratories certified under the State Board's Environmental Laboratory Accreditation Program (ELAP) for analyses.

#### 4.0 Oil Extraction Methods

In the White Paper, oil extraction methods are broken down into two categories: conventional and unconventional. Conventional oil extraction methods consist of using an oil well to pump production fluid from the oil formation to the surface for processing. In conventional oil extraction methods, additional enhanced oil recovery methods may be used. Enhanced oil recovery methods are used to increase the productivity of the oil formation, therefore, enabling the extraction of a greater volume of oil. Enhanced oil recovery methods include acidification, water and steam flooding, and cyclic steam.

Unconventional oil extraction methods are similar to conventional methods, with the exception that hydraulic fracturing is used in lieu of or in combination with enhanced oil recovery methods. Hydraulic fracturing or "fracking" is a method in which water, sand, and other chemicals are injected into an oil formation at a high pressure to fracture the formation and increase the oil production rate. Facilities that generate produced water for irrigation do not use hydraulic fracturing. Also, new WDRs that regulate the reuse of produced water for irrigation prohibit the discharge of produced water from wells that contain well stimulation treatment fluids (as defined by the California Code of Regulations, title 14, section 1761).

#### 5.0 Irrigators

Produced water from oil companies is transported to water management entities (also referred to as "irrigators") for reuse. Irrigators typically receive the produced water into reservoirs where it is blended with surface water and/or groundwater. In 2019, three water districts and two privately owned companies were regulated by the Central Valley Water Board to reuse produced water for the irrigation of crops grown for human consumption. The following is a brief overview of the irrigators:

**Cawelo Water District (Cawelo)** - Cawelo's water supply sources include the Kern River, State Water Project, groundwater, and produced water from the Kern River and Kern Front Oil Fields. Most of the crops grown in Cawelo are permanent crops (e.g., citrus, nuts, and grapes), but occasionally row crops are grown (e.g., carrots, potatoes, and garlic).

**Kern-Tulare Water District (Kern-Tulare)** – Kern-Tulare's water supply sources include the Kern River, Central Valley Project, groundwater, and produced water from the Jasmin Oil Field. Most of the crops grown in Kern-Tulare are permanent crops (e.g., citrus). Kern-Tulare's service territory spans parts of Kern and Tulare counties. Due to the use of isolated distribution networks, produced water is only available in the distribution network operating in Kern County.

Jasmin Ranchos Mutual Water Company (Jasmin Water Company) – The Jasmin Water Company's sources are groundwater, produced water from the

Jasmin Oil Field, and irrigation water from Kern-Tulare. The Jasmin Water Company is within the service territory of Kern-Tulare but maintains autonomy for distribution operations. Most of the crops grown in the Jasmin Water Company service area are permanent crops (e.g., citrus).

**North Kern Water Storage District (North Kern)** - North Kern's water supply sources include the Kern River, groundwater, and produced water from the Kern Front Oil Field. Most of the crops in North Kern are permanent crops (e.g., citrus and nuts), but row crops are grown in some years (e.g., tomatoes, beans, garlic, carrots, and others).

**Sherwood Hills, LLC (Sherwood)** – Sherwood's water supply sources are groundwater and produced water. Produced water from the Poso Creek Oil Field is pumped to Sherwood's Reservoirs. Blending of produced water with groundwater is not required prior to irrigation. The discharge of produced water for irrigation did not start until 2020. Produced water may be used to irrigate citrus, nuts, silage, oilseed, and/or grain crops.

#### 6.0 Treatment of Produced Water

The separation / treatment process for Dischargers that reuse produced water for irrigation generally consists of two phases. The first phase is the primary separation of the production fluid, which removes most of the oil from the produced water. In the Central Valley, this phase normally consists of wash tanks that are designed to separate fluids based on their specific gravity. Some operators heat the wash tanks for increased oil removal efficiency. Oil from the first phase is pumped to stock tanks (used as temporary storage prior to being transported to refineries) and produced water is pumped to the secondary phase.

The secondary phase of treatment is primarily used by Dischargers that reuse produced water for irrigation. The secondary phase varies for each operator and consists of one or more of the following:

- Dissolved Air Flotation Removes residual oil and solids using a mechanically induced dissolved air flotation system. Commonly referred to as WEMCOs by oil operators.
- Filters Removes residual oil and solids by passing produced water through a filtering media.
- Ponds Provides additional retention time that enables residual oil to coalesce and rise to the fluid surface. Skimming operations remove the oil from the fluid surface.

Residual oil captured using a dissolved air floatation system or pond is either transferred to an oil stock tank or re-injected into the first phase of the separation / treatment system. Used filters with recoverable wastes are transported to a permitted, third-party facility for disposal.

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The complete separation / treatment system configurations for each of the Dischargers are described in the WDRs that regulate each discharge. <u>The WDRs are available on the Central Valley Water Board's website</u>

(https://www.waterboards.ca.gov/centralvalley/board\_decisions/adopted\_orders/).

#### 7.0 Oil Field Additives

The types and mass of oil field additives that are used depend on a variety of factors, including the geology and the oil production facility. Through the use of oil field additives, new chemicals and constituents may be added to produced water that are not naturally occurring in oil bearing formations. Identification of these chemicals and constituents in produced water is challenging, as their presence depends heavily on the mass of the oil field additive used during oil operations. In addition, chemicals have the potential to: volatize in the soil or water, break down in the environment, absorb or adsorb to organics and/or clay rendering it unavailable for plant uptake, or are present in concentrations that are below the most stringent analytical methods available for water testing. Recognized by Central Valley Water Board staff as a potential concern, staff determined that the MRPs for Dischargers that reuse produced water for irrigation should require information regarding oil field additives used during oil exploration, production, or treatment.

On 13 October 2017, Governor Edmund Gerald Brown Jr., signed California Assembly Bill 1328 (AB 1328). AB 1328 states that when conducting an investigation regarding the quality of the waters of the state, a Regional Water Quality Control Board may require a discharger to furnish information related to chemicals in produced water. AB 1328 amends the Water Code by adding section 13267.5. From December 2017 to September 2018, Central Valley Water Board staff issued more than 50 Orders pursuant to sections 13267 and 13267.5 of the Water Code to Dischargers under WDRs, irrigators, manufacturers, and suppliers associated with oil field additives. The Orders required the submittal of information on oil field additives, their ingredients, and associated chemical abstract service registry numbers (CASRNs).

Information submitted to the Central Valley Water Board in response to the Orders was compiled by Central Valley Water Board staff. Due to issues regarding trade secret claims, not all the information contained in the responses to these Orders is available for review by the public or the Panel. In an effort to be transparent while maintaining trade secret claims, Central Valley Water Board staff generated a list of the chemicals and constituents that make-up the oil field additives used during oil exploration, production, or treatment. This list was posted on the Central Valley Water Board's website

(https://www.waterboards.ca.gov/centralvalley/water\_issues/oil\_fields/food\_safety/) and is referred to as the *Central Valley Water Board Oil Field Additive List* (Oil Field Additive List). The Oil Field Additive List identifies the names and CASRNs of chemicals and constituents that may be in produced water due to the use of oil field additives used during oil exploration, production, or treatment.

#### 8.0 Quality of Produced Water

The quality of produced water is highly variable and can change both between oil fields and within an oil field depending on a variety of factors. Kern County, California is the southernmost county in the Central Valley. Kern County is where most of the produced water is generated in California and the only county where produced water is reused for irrigation. In Kern County, there are approximately 76 oil fields and each have unique produced water quality. Due to the geology and migration of oil, produced water from oil fields along the east side of the San Joaquin Valley tends to be of higher quality than that from oil fields located along the west side. This difference in quality enables produced water from specific oil fields along the east side of Kern County to be reused for irrigation without removal of salts.

To illustrate the difference in produced water quality in Kern County, Central Valley Water Board staff calculated the average value for nine constituents (using available 2018 data) and summarized the results in Table I. Table I includes three data columns that identify the following: (1) the quality of produced water, prior to blending; (2) the quality of produced water discharged to a land disposal facility in the McKittrick Oil Field, along the west side of Kern County; and (3) some of the State drinking water standards (referenced in Title 22, Division 4, Chapter 15 of the California Code of Regulations) listed as a comparison for the first two data columns. Drinking water standards in Table I that have an asterisk are recommended secondary standards, which are designated as non-health threatening and are based on aesthetic (e.g., taste, odor, or color) or cosmetic properties (e.g., skin or tooth discoloration).

Table I: Produced Water Quality for Oil Fields in Kern County

Parameters	Units	Produced Water Reused for Irrigation	Produced Water from the McKittrick Oil Field	Drinking Water Standards
Total Dissolved Solids	mg/L	524	15,250	500 *
Electrical Conductivity	umhos/cm	751	20,333	900 *
Boron	mg/L	0.84	59.75	NA
Chloride	mg/L	94	8,325	250 *
Copper	ug/L	1.83	5.70	1,300
Sodium	mg/L	143	5,000	NA
Benzene	ug/L	0.88	2.21	1
Xylenes, Total	ug/L	2.39	10.10	1,750
Toluene	ug/L	1.29	89.25	150

mg/L = milligrams per liter.

umhos/cm = micromhos per centimeter.

ug/L = micrograms per liter.

<sup>\* =</sup> Secondary Drinking Water Standard.

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As shown in Table I, produced water reused for irrigation is of better quality than produced water from the McKittrick Oil Field. In Table I, water quality data compared between the east and west sides varies by 3 to 89 times, depending on the parameter being examined. This comparison highlights the difference in water quality across Kern County and between oil fields. For the constituents shown in Table I, produced water reused for irrigation is below the primary standards for drinking water and near or below recommended secondary standards for drinking water.

#### 9.0 Food Safety Expert Panel

Following increased public concern and resources made available by budget augmentation, Central Valley Water Board staff initiated the Food Safety Project. The primary objective of the Food Safety Project was to investigate the potential impacts to human health and crop safety from the reuse of produced water for irrigation, with the input of the Panel.

In the beginning of the Food Safety Project, Central Valley Water Board staff outlined a plan for investigating potential impacts to human health and crop safety. Since Central Valley Water Board staff are not experts in food safety, outside experts and representatives of state and federal agencies and private organizations with experience in food safety were enlisted to advise the Central Valley Water Board. The objective of enlisting experts in food safety was to ensure the Food Safety Project would be thorough and scientifically defensible. When selecting members of the Panel, the primary objective was to assemble a group of experts with diverse representation and the appropriate scientific background. Members of the Panel have expertise in toxicology, risk assessment, agriculture, public health, and/or wildlife. The Panel was a group of volunteers, and no financial compensation (excluding travel expenses) by the Central Valley Water Board was provided to any member of the Panel. Table II provides a list of the Panel members names, title, and affiliated organizations.

**Table II: Information Related to the Panel Members** 

Name Title		Organization
Andrew Gordus, PhD	Staff Toxicologist	CA Dept. of Fish and Wildlife (Retired on 30 December 2020)
Barbara Petersen, PhD, MPH	Principal Scientist	Exponent, Inc.
Bruce Macler, PhD	Regional Toxicologist	US EPA Region 9 (Retired on 31 July 2020)
David Mazzera, PhD	Chief, Division of Food, Drug, & Cannabis Safety	CA Dept. of Public Health
Gabriele Ludwig, PhD  Director, Sustainabilit Environmental Affairs		Almond Board of California
Kenneth Kloc, PhD, MPH Staff Toxicologist		CA Office of Environmental Health Hazard and Assessment
Mark Jones, MS Staff Toxicologist		US Army Corps of Engineers
Seth Shonkoff, PhD, MPH	Executive Director and Visiting Scholar	PSE Healthy Energy and UC Berkeley, Dept. of Environmental Science, Policy, and Development
Stephen Beam, PhD Branch Chief		CA Dept. of Food and Agriculture

#### 10.0 Memorandum of Understanding

In the beginning of the Food Safety Project, Central Valley Water Board staff and Dischargers under WDRs prepared a draft Memorandum of Understanding (MOU) to describe the roles, relationships, and responsibilities, as they relate to the Food Safety Project. In June 2017, Central Valley Water Board staff and the Dischargers under WDRs signed the final MOU, which described the following as it relates to the Food Safety Project:

- Identification of Parties to the MOU and Studies Covered by the MOU,
- Statement of Facts,
- Development of Scopes of Work,
- Roles and Responsibilities of the Parties to the MOU,
- Schedule and Performance of Work, and
- General Terms of the MOU.

#### 11.0 Science Advisor

To assist Central Valley Water Board staff in the review and approval of the work and findings of the Food Safety Project, the Central Valley Water Board contracted with a Science Advisor. Dr. William Stringfellow of Berkeley National Laboratory was selected

to fill that role. Because Dr. Stringfellow has over 35 years of experience in wastewater treatment and management and was a lead scientists on the Senate Bill 4 scientific study evaluating hydraulic fracturing in California, Central Valley Water Board staff and the Panel agreed his appointment was appropriate.

#### 12.0 Technical Consultant

Through the MOU between the Dischargers and the Central Valley Water Board, guidelines for the work completed under the Food Safety Project were established. Under the MOU, a neutral third-party consultant was awarded a contract to complete the work under the Food Safety Project. GSI Environmental, Inc., (GSI) was selected as the third-party consultant due to its background and experience in risk assessment, public health, crop sample analysis, and environmental science. The Panel, Science Advisor, Dischargers, and Central Valley Water Board staff agreed that the selection of GSI as the technical consultant was appropriate.

Under the MOU, the Dischargers were required to fund the work completed by GSI, but not allowed to design studies. To maintain separation between the Dischargers and GSI, Central Valley Water Board staff and the Science Advisor were responsible for overseeing and managing the technical work completed under the Food Safety Project.

#### 13.0 Food Safety Charter

The Food Safety Expert Panel Charter (Charter) was prepared by Central Valley Water Board staff. The Charter was approved by the Panel, Science Advisor, and Central Valley Water Board staff and outlines the following items for the Food Safety Project:

- Project purpose and scope:
- Project outcomes;
- Meeting schedule;
- Roles and responsibilities for participants;
- Communication guidelines;
- Values and principles;
- Decision making; and
- Operating guidelines.

Under the Project Outcomes section of the Charter, the document states that Central Valley Water Board staff will prepare a "White Paper" for the Food Safety Project. As required under the Charter, this White Paper has been prepared by Central Valley Water Board staff to summarize the work and findings for the Food Safety Project. For additional information related to the Charter, the document is available on the Central Valley Water Board Food Safety Page

(https://www.waterboards.ca.gov/centralvalley/water issues/oil fields/food safety/).

#### 14.0 Sampling Protocols Under Task 3

For the first sampling event, Enviro-Tox Services, Inc., prepared a Sampling and Analysis Plan (SAP) on behalf of Cawelo Water District (Cawelo) for the sampling of citrus within Cawelo. The SAP outlined sampling and handling procedures, sampling documentation, quality control procedures, and specific analyses. As additional crops were added to the sampling list and new analytes were considered for analysis, new SAPs were prepared for each crop type. The new SAPs were prepared by Enviro-Tox Services, Inc., and were submitted to the Panel and Science Advisor for review and consideration and presented during public and working meetings with the Panel. Feedback from the Panel and the Science Advisor were incorporated into the SAP(s), as appropriate.

As stated in the SAPs, the collection and handling of crops was completed by Advanced Environmental Concepts, Inc., (AEC), a third-party consultant with experience in crop sampling. AEC received copies of the SAPs prior to sampling events and were instructed to follow sampling and handling procedures in the SAP. General procedures implemented for sampling included the following:

- Samples were collected at least 100 feet into a field to minimize potential contamination from traffic or road sources;
- Samples were required to resemble the quality of fruit that would be expected to be found in a store;
- Samples were not collected from the ground; and
- Samples were immediately placed in sample containers and stored on ice.

To ensure AEC complied with the requirements of the SAPs, Central Valley Water Board staff oversaw the sampling events. From 2017 through 2019, 26 crop sampling events occurred. Of the 26 sampling events, AEC was not able to collect crop samples for 3 sampling events due to the following:

- The harvest date for two sampling events of tomatoes was pushed forward requiring the immediate collection of tomatoes before the farmer's crew picked the fields. Due to insufficient notification time, AEC was not able to attend these two sampling events for tomatoes. In AEC's absence, Central Valley Water Board staff oversaw Cawelo Water District personnel while they collected tomato samples, to ensure compliance with the SAP.
- Cawelo personnel collected potatoes at a Smart and Final Grocery Store in Bakersfield and had them sent to the laboratory as a control sample. The potatoes were collected from a local grocery store since Cawelo personnel was not able to find a control potato sample in the area. Central Valley Water Board staff and AEC were not present for this sampling event.

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To ensure the integrity of the sample results, Central Valley Water Board staff retained possession of the samples throughout the sampling events (excluding the control potato sample). Central Valley Water Board staff was in possession of the samples until the ice chests (that contained the samples) were mailed to the laboratory for analysis. Chain of custody documents were maintained for each sampling event and are available in the laboratory reports.

#### 15.0 Analysis of Crops Under Task 3

Crop samples from 2017 through 2019 were mailed, by FedEx, to Weck Laboratories (Weck) in City of Industry, California. In July 2019, crop samples were transported by Central Valley Water Board staff to Agricultural and Priority Pollutants Laboratories Inc., (APPL) in Clovis, California. These laboratories were approved by the Panel, Science Advisor, and GSI based on the experience each laboratory had associated with the analysis of fruit and other food samples. Due to delays in receiving complete laboratory reports, Central Valley Water Board staff (with approval of the Science Advisor and GSI) determined that crop samples collected after May 2019 would be submitted to APPL for analysis.

Crop samples received by the laboratory were cleaned and stored in temperaturecontrolled cooling units until laboratory technicians were ready to process the samples. Processing of crop samples consisted of removing the non-edible portion of the crop and homogenizing the edible portion of the crop for analysis within a reasonable time of receiving the samples, as not to exceed holding times for specific analyses. Depending on the crop type and necessary volume of the sample, multiple sample containers may have been used for a single sample location. For example, only one sample container of oranges was needed where two containers of nuts were required to get the appropriate sample size. In these cases where multiple crops were needed for a sample, the edible portion of the crop from multiple sample containers were homogenized together to produce a single sample. Duplicate samples were also collected for each crop type and irrigation source (e.g., control samples versus treated samples). Duplicate samples were analyzed independently and were labeled so that the laboratory could not identify duplicate, treated, or control samples. Duplicate samples were used to determine whether the crops on the trees, vines, etc., for a sample location were homogenous, not to assess the reproducibility of the analytical methods.

In 2017, the crop sample analyses consisted of approximately 108 chemicals. The analyses included primarily metals, VOCs, and semi-volatile organic compounds (SVOCs). As the Food Safety Project progressed, additional chemicals were added to the list of analytes based on water quality data, the Central Valley Water Board Oil Field Additive List, and recommendations by the Panel, Science Advisor, and GSI. In 2019, the crop analysis list consisted of 113 chemicals.

#### 16. Cawelo Water District's Crop Study

In 2015, before the Food Safety Project was initiated by the Central Valley Water Board, Cawelo hired a third-party consulting firm (Enviro-Tox Services, Inc.) to conduct three

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independent evaluations of Cawelo's crops and irrigation water (Cawelo's Crop Studies). The purpose of Cawelo's Crop Studies was to evaluate whether petroleum production related constituents were present in Cawelo's irrigation water and subsequently accumulating in the crops. Citrus, almonds, grapes, carrots, and pistachios grown in Cawelo were analyzed for volatile organic compounds and polycyclic aromatic hydrocarbons. Enviro-Tox Services, Inc., (Enviro-Tox) also collected and analyzed crop samples from treated and control sites. From the results, Enviro-Tox concluded that the constituents detected in crops grown with Cawelo's irrigation water were also found in crops grown with traditional irrigation water. According to Cawelo's Crop Studies the consumption of crops irrigated with Cawelo's water does not appear to pose a threat to crop safety or human health.

When the Central Valley Water Board initiated the Food Safety Project, Cawelo provided their analytical results and other pertinent data from Cawelo's Crop Studies to the Panel and Central Valley Water Board for review. Cawelo's Crop Studies were one of the first items discussed during public meetings of the Panel. Cawelo's Crop Studies are available on Cawelo Water District's website.

8 September 2021

Appendix B – Data Gaps Related to the Food Safety Project

#### **MEMORANDUM**

Date: 8 September 2021

Prepared By: CA Regional Water Quality Control Board

(Central Valley Region) Staff

#### DATA GAPS RELATED TO THE FOOD SAFETY PROJECT

This memorandum was prepared by staff of the California Regional Water Quality Control Board, Central Valley Region (Central Valley Water Board) to provide interested parties with additional information related to data gaps of the Food Safety Project. Data gaps in this memorandum are items that have been discussed during the Food Safety Project as a potential concern related to the Food Safety Project or items that need to be considered in future studies (as appropriate). The data gaps identified below were identified by the Panel, Science Advisor, Central Valley Water Board staff, and GSI:

- Mass data of chemicals;
- Chemical uptake in plants;
- Potential long-term impacts to soil and plants;
- Chemicals with no toxicity data or analytical method; and
- Transformation products of chemicals.

The data gaps identified in this memorandum are intended to highlight potential areas of interest for future studies. These data gaps may not have been investigated further due to one or more of the following:

- Analytical methods for chemicals, that may be present in produced water and crops, have not been approved by state or federal agencies for regulatory use:
- Limited information or peer reviewed literature currently available in both public and private sectors;
- Scope and funding needed to close data gaps far exceeds that of the Food Safety Project; or
- Data not available to the Panel and Science Advisor for review.

The work and findings of the Food Safety Project were based on the available science and data at the date of this Food Safety Project White Paper (White Paper). As such, the findings are generally limited to the subset of oil and gas related chemicals for which adequate toxicity, concentration, and environmental fate information was available. Sections 3 – 5 of this White Paper provide a summary of the work and findings of Tasks 1 through 3.

#### **Mass Data of Chemicals**

The collection and review of mass data would enable the Panel and GSI to prioritize and potentially remove chemicals from the Chemicals of Interest list based on the maximum amounts of chemicals that may be present in produced water.

Lack of knowledge concerning the mass of chemicals derived from oil field additives is considered, by the Panel, to be a data gap. Under trade secret claims, the volume and mass of chemicals in oil field additives can be submitted to the Central Valley Water Board, but not disseminated to the Panel or public for review. The Panel has stated that the mass of a chemical is needed to better determine whether a chemical poses a potential threat to crop safety or human health. Utilizing mass data of a chemical, the concentration in produced water could be estimated using a mass balance approach. With the mass data, Chemicals of Interest could be eliminated or re-prioritized based on the potential mass or concentration of the chemical in produced water.

#### **Chemical Uptake in Plants**

The chemical uptake of plants is needed to determine specific chemicals that pose a threat to crop safety or have the potential to migrate to the edible portion of the crop.

Additional information regarding plant uptake and associated plant physiology concerning specific chemicals found in produced water may be useful. Information related to plant uptake and physiology will identify chemicals that can or cannot be taken up by plants. Chemicals that do not have the potential to reach the edible portion of the crop could be eliminated from the Chemicals of Interest list. A better understanding of plant uptake could also determine if there are specific chemicals that may need additional research to ensure that there are no impacts to crop safety or public health.

#### **Potential Long-Term Impacts to Soil and Plants**

The accumulation of chemicals from the use of produced water for irrigation may have the potential to adversely impact the soil and plants.

The reuse of produced water for irrigation has the potential to cause accumulation of chemicals in crops and soil. Although crop sampling conducted under Task 3 did not yield significant differences between control and treated crop samples that could be attributed to the use of produced water, there is an unknown potential that chemicals from produced water and other environmental sources may be accumulating in the soil.

#### **Chemicals with No Toxicity Data or Analytical Method**

Chemicals that do not have toxicity data or an analytical method of measurement may pose a threat to crop safety and human health due to potential unknowns associated with the chemical.

Chemicals that do not have an approved analytical method or adequate safety characterization pose a challenge for identifying potential threats to human health and crop safety. Under Task 2, chemicals that do not have an approved analytical method for analysis were identified. Task 2 also identified chemicals that were not fully characterized for safety. In some cases, chemicals did not have either toxicity data or an approved analytical method. Without an approved analytical method for food or water, it is not feasible to determine if these chemicals are present in produced water or crops.

#### **Transformation Products of Chemicals**

Chemicals have the potential to transform in the environment, resulting in transformation or daughter products that may not have been included in the list of chemicals evaluated under Task 1.

The transformation and breakdown of chemicals in produced water has the potential to result in new chemicals that may not have undergone a preliminary hazard assessment under Task 1. Due to numerous potential sources of additional chemicals from the environment, the identification of transformation products is not feasible and aggregate methods for measurement of transformation products may be needed. This was not completed under Task 1 or Task 2 due to the scale of work needed to conduct a review of the transformation and daughter products associated with 399 chemicals identified under Task 1.

8 September 2021

### Appendix C – Response to Public Comments

### MEMORANDUM

Date: 8 September 2021

Prepared By: CA Regional Water Quality Control Board

(Central Valley Region) Staff

### RESPONSE TO WRITTEN PUBLIC COMMENTS REGARDING THE FOOD SAFETY PROJECT WHITE PAPER (WHITE PAPER)

On 29 January 2021, the Regional Water Quality Control Board, Central Valley Region, (Central Valley Water Board) posted a draft of the Food Safety Project White Paper (White Paper) on the <u>Food Safety webpage</u> for public review. In addition, Central Valley Water Board staff presented an information item about the Food Safety Project and the draft White Paper during a public meeting of the Central Valley Water Board on 18 February 2021. Included in the presentation and in the public notice for comments, Central Valley Water Board staff stated that comments related to the draft White Paper would be accepted by the Central Valley Water Board though 5 March 2021.

The following submitted written comments to the Central Valley Water Board related to the draft White Paper:

- Alan and Meg Giberson
- Catherine Fowler
- Environmental Defense Fund (EDF)
- Environmental Working Group (EWG)
- Justin Bass
- Kenneth T. Gibson
- Laura Rosenberger Haider
- Norma Williamson
- Todd T. Cardiff

Based on the written comments, Central Valley Water Board staff made some changes to the draft White Paper. Staff also made minor edits to improve clarity. Specific changes are discussed below.

#### ALAN AND MEG GIBERSON COMMENTS

**COMMENT No. 1 –** The study depended heavily on the literature review but would have benefited from more research in the field. For instance, chemicals of concern were "identified as potentially present in produced water based on the available literature." Actual field research should have been done to inform the "compiled and posted" water quality data.

**RESPONSE** – The report was modified and Section 3.0 was clarified to acknowledge that water quality monitoring data were considered in the development of the Task 1 list of chemicals, not just literature values.

Field research conducted as part of the Food Safety Study included collection of crop samples, as described in the Task 3 report. In addition, water quality monitoring data were (and are) collected as part of the regulatory oversight program for produced water reuse. These water quality data are collected by regularly sampling both produced water and blended produced water used for irrigation and provides direct measurement of chemicals in produced water used for irrigation. Although this data collection is not research, per se, it is important "real-world" data that informed decision making by the Food safety Panel. The field data collected as part of the water quality monitoring program are described in the Task 2 report and were considered by GSI and informed the comprehensive list of potential chemicals of interest in Task 1.

**COMMENT No. 2 –** Organics in the water were not adequately considered. Despite evidence that organics have been detected in crops, the study notes that insufficient information available precludes a general conclusion: "direct measurements of chemicals in the edible portion of the crops is limited. Due to the limited literature available for plant uptake of organic chemicals, insufficient information is available to reach a general conclusion regarding the potential impact of organic chemicals on crops for human consumption."

**RESPONSE** – Section 4.3 was rewritten to clarify that there are few scientific studies that have directly examined the uptake of organic chemicals by plants that produce food crops for humans and, therefore, GSI did not draw definitive conclusions about plant uptake of organic chemicals by crop plants. It is noted that much more is known about the fate of organic chemicals in water and soils and that the crops grown with produced water were directly examined in Task 3. The relative importance of these areas of science in understanding the potential impacts of produced water reuse on crops has been clarified in Section 4.3 and 4.4 of the White Paper.

Under Task 2 of the Food Safety Project, the literature review examined plant uptake, fate and transport, degradation or transformation products, and toxicity. Provided below is a brief overview of the findings of the literature review related to organics:

- Plant Uptake: Limited data available related to organics prevented GSI from reaching a general conclusion related to the potential fate of organic chemicals in crops grown for human consumption.
- Fate and Transport: GSI determined that the organic Chemicals of Interest had at least one of four traits that would make it less likely to be available for

plant uptake. These traits include their solubility, biodegradability, volatility, and sorption to organic matter.

- Degradation or Transformation Products: GSI determined that based on the
  array of testing for volatile organic compounds and polycyclic aromatic
  hydrocarbons, this would have included constituents that were not identified
  as Chemicals of Interest and/or had the potential to be degradation or
  transformation products. GSI notes that some of the detections observed in
  the sample results for produced water and crops may have been degradation
  or transformation products, but the source of those chemicals was not
  related to produced water since treated crop samples did not have
  significantly higher concentrations than control crop samples.
- Toxicity: GSI concluded that organic Chemicals of Interest in produced water reused for irrigation were either at or below the MCL, making it unlikely to pose a threat to crop safety or human health.

Lastly, GSI also compared the findings from the literature review to the crop sample results collected under Task 3. In this comparison, GSI found that both treated (irrigated with blended/ produced water) and control (not irrigated with produced water) sample types had similar concentrations of organic chemicals as compared with crops grown elsewhere. As expected, based on the literature review conducted under Task 2, these concentrations are low and not considered higher than expected for crops grown in the US. According to the Task Reports, organics were evaluated to the best of GSI's ability using the best available science.

**COMMENT No. 3 –** The literature review found that inorganic chemicals generally concentrate in the roots, stems, and/or leaves, rather than the edible portion of the plant. However, roots, stems, and leaves of crops are often consumed by individuals. Individuals that consume more than the "center of the edible portion of the root crop" are not protected by this anodyne conclusion.

**RESPONSE** – Crop samples collected under Task 3 of the Food Safety Project were analyzed using the "edible portion" of the crop. The edible portion of the crop for the Food Safety Project is defined as the part of the crop that is typically consumed by individuals in the US. Although the literature review suggests that some constituents may accumulate in the skin, roots, or leaves, the analysis of crops under Task 3 included these parts if the majority of individuals in the US would typically consume them. As an example, carrots and potatoes were analyzed with the skin/peel and citrus was analyzed without the peel. By only analyzing what would be considered the edible portion, the sampling study eliminated finding constituents from factors other than produced water irrigation (e.g., finding vehicle exhaust related volatile organic constituents). The analytical results of the crops were within the normal range for food consumed

in the US. This method of analysis was also reviewed and approved by the Panel, Science Advisor, and GSI.

For more information related to this comment, see Section 15 in Appendix A of the White Paper. No changes were made in response to this comment.

**COMMENT No. 4 –** Arsenic in produced water was not thoroughly reviewed. On page 21 of the draft White Paper, an independent study is cited that shows there was too much arsenic in the water, but nonetheless dismissed the problem as also being in local water sources without adequate further study.

**RESPONSE** – Arsenic is naturally occurring in the Central Valley and is often observed in local surface and groundwater. Under Task 3, GSI found that the levels of arsenic observed in produced water are similar to those found in local surface water and groundwater. Approximately 50% of the arsenic sample results of blended produced water are higher than the drinking water standard of 0.01 mg/L (maximum detected concentration is 0.065 mg/L). Drinking water standards are used in the Food Safety Project for comparative purposes only as there are not standards used for irrigation water. Despite the levels of arsenic observed in produced water, only one crop sample had a detectable result for arsenic (carrots with a non-quantifiable (or J-Flag) result). Although arsenic is in produced water, GSI determined under Tasks 2 and 3 that it does not appear to be at a threshold that poses a threat to crop safety or human health.

For more information related to this comment, see the Tasks 2 and 3 Reports. No changes were made in response to this comment.

**COMMENT No. 5 –** The impacts associated with the long-term use of produced water for irrigation were not sufficiently evaluated. Although the draft White Paper states that there does not appear to be an immediate threat to human health or crop safety, California consumers deserve research that looks beyond just an immediate threat.

**RESPONSE** – The unknowns concerning the potential long-term impacts associated with the reuse of produced water for irrigation is identified as a data gap in the draft White Paper. Although this practice of reusing produced water for irrigation has occurred in Kern County for over 30 years, the Panel and GSI identified potential long-term impacts as a data gap. In addition, the Panel recommends that the Central Valley Water Board conduct a soil study to develop a better understanding of the long-term impacts on soils from the reuse of produced water for irrigation. Central Valley Water Board staff and the Board are aware of this data gap and are working to close the data gaps and complete the Panel's recommendations.

In Section 7 of the draft White Paper, the following has been changed:

 Tasks 1 through 3 did not yield any evidence that the reuse of produced water for irrigation poses an elevated immediate threat to human health or crop safety.

**COMMENT No. 6 –** The draft White Paper appears to suffer from some scientific procedural defects, such as not posting its source code. A "Monte Carlo" analysis was used (meaning a computer analysis was used), but the paper should have explained how the algorithm worked or how results were calculated.

**RESPONSE –** Study methodology are described in-depth in Task Reports prepared by GSI, which is appended to the White Paper. The intent of the White Paper is to provide a general overview of the Food Safety Project. This overview was generated so that the general public would be able to read and comprehend the work and findings of the Food Safety Project. For more specific information on the analyses and methodology, the Task Reports are referenced in the text of the White Paper and included as appendices.

No changes were made in response to this comment.

#### **CATHERINE FOWLER COMMENTS**

**COMMENT No. 1 –** Under claims of trade secret, the oil and gas industry are not required to report or be held responsible for production substances which may impact the public and environmental health and safety. If trade secrets are not known, how can they be tested?

**RESPONSE** – Since the "amount" information (i.e., mass or volume) was not available for chemicals identified as oil field additives, GSI assumed that the complete list of constituents was present in produced water. This is a conservative approach that assumed each constituent was present, even though some constituents may not be in produced water due to the use of only small amounts of an additive in an oil field. This approach was reviewed and approved by the Panel, Science Advisor, and GSI.

The legal issue related to trade secret information pertains to the disclosure of the amount of each chemical that makes-up an oil field additive. As part of the Food Safety Project, the Central Valley Water Board issued orders under sections 13267 and 13267.5 of the California Water Code requiring oil companies and chemical manufacturers to provide a complete list of the chemicals that have the potential to be in produced water from the use of oil field additives. In order to be transparent in the specific constituents and avoid legal issues related to trade secret information, Central Valley Water Board staff did not require the volume or percent make-up of the chemicals for each oil field additive. The information obtained under these orders are similar to the ingredient list found on food labels in the US, which provides the information of what is in the product without providing the exact volume or recipe. Obtaining

information in this manner not only protected trade secret information, but it allowed Central Valley Water Board staff to share the chemical list with the Panel, Science Advisor, GSI, and general public.

For more information related to this comment, see Section 7 in Appendix A of the White Paper. No changes were made in response to this comment.

**COMMENT No. 2 –** According to the USEPA, the oil extraction process actually concentrates "naturally" occurring radionuclides, or more precisely Technically Enhances Naturally Occurring Radioactive Material (TENORM). What data has been evaluated to assure the public that radionuclides are not accumulating in the distribution systems delivering produced water for irrigation.

**RESPONSE** – Radioactive substances (including radium-226, radium-228, alpha radiation, and beta radiation) are monitored in produced water and blended produced water as part of the requirements for produced water reuse. GSI reviewed produced water quality data (summarized in Task 2 Table 7) and completed a comprehensive literature review of radioactive materials potentially found in produced water. Using produced water quality data from facilities that are implementing this practice, GSI found that there are no systemic exceedances of MCLs for drinking water (Table 7) and that produced waters in this region are very low in radioactivity (i.e., TENORM) compared to produced waters from other regions. Of the 33 produced water sample results from the Central Valley Water Board, only two different samples exceeded the drinking water MCL for one of the following: gross alpha radiation and radium 226+228. Under the literature review, GSI concluded that radionuclides were most likely to bind to particles or soil minerals, making them immobile and unavailable for plant uptake. In addition, the soil transfer factors for radionuclides are very low suggesting that radionuclides, if available, are not likely to be taken up by the plant.

Although GSI did not evaluate the potential for radionuclides to accumulate in the water distribution system, GSI did conclude that radionuclides do not appear to be a health risk in irrigated crops. This conclusion was generated based on the fact that radionuclides have limited ability for plant uptake and that the concentrations observed in produced water reused for irrigation are typically low.

For more information related to this comment, see the Task 2 Report. No changes were made in response to this comment.

**COMMENT No. 3 –** The draft White Paper references the Duke Study (Kondash et al, 2020), but does not mention that the study also found that soils irrigated with produced water showed higher salts and boron relative to soil irrigated with groundwater. Numerous studies have shown that irrigation with saline water often results in cycles of salt accumulation and can transport through the soil resulting in contamination of the groundwater. The practice of reusing produced water for irrigation should not be considered safe until it is proven to be so.

**RESPONSE** – The investigation of long-term impacts to soil was not within the scope of the Food Safety Project. A better understanding of long-term impacts on soil was identified as a data gap. See response to Comment No. 5 under Alan and Meg Giberson.

No changes were made in response to this comment.

**COMMENT No. 4 –** Additional information and research is needed related to the potential uptake of chemicals by plants. The assertion in the draft White Paper that chemicals do not have the potential to reach the edible portion of the plant is wishful, convenient, and irresponsible. GSI's assertion that plants compartmentalize chemicals in certain cellular structures is without scientific merit. No chemicals should be removed from the Chemicals of Interest list until there has been an in-depth sampling of all crops irrigated with produced water and they are certified free of contaminants.

**RESPONSE** – The need to better understand the uptake of chemicals by plants was identified as a data gap. However, much more is known about the fate of chemicals in soil and water. The relative importance of these areas of science in understanding the potential impacts of produced water reuse on crops has been clarified in Section 4.3 and 4.4 of the White Paper. See response to comment 2 by Alan and Meg Giberson (above).

Under Task 2 of the Food Safety Project, GSI completed a comprehensive literature review of the Chemicals of Interest that examined plant uptake, fate and transport, degradation or transformation products, and toxicity. Although some chemicals had limited data in some areas, GSI was able to find data in other areas that provided evidence that there does not appear to be elevated threats to human health or crop safety due to reuse of produced water for irrigation.

Also, under Task 3 of the Food Safety Project, GSI compared crop sample results from treated and control sites. This comparison looked at 113 chemicals across 13 crop types collected from 2017 through 2019. From this comparison, GSI concluded that:

- Levels of constituents detected in crops irrigated with produced water are within ranges expected for food supplies in the US;
- While there are some specific crop/chemical combinations for which chemical concentrations are different, the overall chemical profiles in crops are the same for crops irrigated with blended produced water and crops irrigated with conventional sources; and
- The chemical profiles are very similar for several groups of crops, which may help to establish baseline conditions and guide future studies with similar objectives.

The findings identified above, in the Task Reports, and in the draft White Paper have been reviewed by the Panel and Science Advisor. In addition, the methodology for the project was reviewed and approved by the Panel and Science Advisor and according to GSI, the work for Tasks 1 through 3 were completed using the best available science.

**COMMENT No. 5 –** The Panel's recommendations state that the Central Valley Water Board should conduct additional studies to close data gaps. Studies needed to close the data gaps would be labor intensive and expensive and should be the financial responsibility of the petroleum industry, not the Central Valley Water Board.

**RESPONSE** – The users of produced water have been engaged in independently researching the use of produced water to irrigate food crops. Before the Central Valley Water Board convened the Panel for the Food Safety Project, Cawelo Water District contracted with a third-party to develop a study similar to the crop study conducted under Task 3. The results of this study are published in a report available on Cawelo Water District's website. Members of the public expressed concern about these studies, and a general skepticism that they were conducted objectively. In response to this concern and to ensure that the on-going work was conducted objectively, work under the Food Safety Project was conducted under a Memorandum of Understanding (MOU), which stated that the dischargers and users of the produced water would fund the studies, but could give no technical oversight or input on study designs. In order to maintain this separation for future studies referenced in the Panel's recommendations, the Central Valley Water Board, or other public agencies, would likely try to maintain a similar principle of separation to ensure the public can trust the work and findings.

No changes were made in response to this comment.

**COMMENT No. 6 –** In the Task 2 Report, GSI states that a study reviewed over 474 produced water samples from the US, Australia, South Africa, and Qatar and determined that only 8.4% of samples met agricultural irrigation water quality guidelines for electrical conductivity and sodium adsorption ratio. Under this context, 91.6% of the samples did not meet agricultural standards. The quality of produced water is highly variable and high saline water can, according to the USEPA, affect the outcome of water quality analyses and high salt effects toxicity.

**RESPONSE** – The produced water being reused for irrigation in the southern Central Valley is considered untypical of produced water in terms of quality, especially in regard to salt. For example, in Kern County, electrical conductivity of produced water on the west side is often 20,000 umhos/cm or higher, while produced water reused for irrigation is on average 751 umhos/cm. This difference in produced water quality also reflects the difference in produced water quality across the world. Typical produced water is highly saline and requires treatment prior to any reuse, even reuse for industrial purposes. Due to the

quality of the produced water reused for irrigation in Kern County, significant effects on analytical results caused by salts is unlikely. In addition, the crop sample results met quality assurance and quality control standards.

For more information related to this comment, see Section 8 in Appendix A of the White Paper. No changes were made in response to this comment.

**COMMENT No. 7 – I** am concerned about the Panel's recommendation to discontinue crop sampling. Additional crop sampling and data collection would produce more competent and valid results that could be used to prove or disprove that the reuse of produced water for irrigation does not pose a threat to crop safety or human health.

**RESPONSE** – The recommendation that crop sampling should be discontinued was developed and approved by the Panel. During the Panel's deliberation process to develop their recommendations, the Panel agreed that crop sampling is less productive/informative than soil and water sampling and controlled plant-uptake studies. The Panel came to this decision after reviewing crop sampling analytical results and considering the complexities of these results. The Panel recommended that crop sampling cease and provided additional recommendations for future studies.

For more information related to this comment, see Section 8 of the White Paper. No changes were made in response to this comment.

**COMMENT No. 8 –** The draft White Paper states that 26 "sampling events" for 13 crop types were conducted as part of the Food Safety Project. I would like to know what a "sampling event" is and where, when, and by whom these events were conducted.

**RESPONSE** – The definition of a sampling event has been added to Section 5.1 of the White Paper. A sampling event is a single day in which a third-party consultant went into the field and collected at least one crop sample. During the sampling events, Central Valley Water Board staff witnessed the sampling and retained control of the samples before delivering or mailing the samples to the laboratory (exceptions include two sampling events where Cawelo Water District staff took the samples and one sample event where Central Valley Water Board staff were not present for one control potato sample collected at a grocery store). Sampling events occurred from 2017 through 2019.

For more information related to this comment, see Section 13 in Appendix A of the White Paper.

**COMMENT No. 9 –** The draft White Paper states that crop samples received by the laboratory were cleaned and homogenized for analysis. The practice of homogenizing crop samples contradicts the laboratory practices used by the California Department of Food and Agriculture (CDFA) for evaluating pesticide residue. For pesticide residue, the samples are swabbed and homogenization of crop samples is avoided.

**RESPONSE** – The goal of the Food Safety Project is to determine potential impacts to human health from the consumption of crops that have been irrigated with produced water. One of the major goals of the Food Safety Project was to explore the potential for oil field produced water constituents to accumulate in the portion of a crop consumed by the general public. During Food Safety meetings, the Panel, Science Advisor, and GSI agreed that the best practice for analysis would be for the laboratory to clean the crop and homogenize the edible portion of the crop for analysis. The intent of cleaning the samples is to remove any external contaminants (e.g., pesticides, smog, dirt, etc.) that do not originate from produced water and that could distort analytical results of the edible portion of the crop. As discussed during Food Safety meetings, these external contaminants are not correlated to the reuse of produced water for irrigation and would likely have been observed in both control and treated samples depending on farming practices.

For more information related to this comment, see Sections 14 and 15 in Appendix A of White Paper. No changes were made in response to this comment.

**COMMENT No. 10 –** Control sites should have been selected from organic farms, not just sites that have not been irrigated with produced water. The use of organic farms for control samples should have been used as a base since these would be certified free of agricultural applications.

**RESPONSE** – The goal of the Food Safety Project is to determine the potential impact to human health from the consumption of crops that have been irrigated with produced water. During public and working Food Safety meetings, the Panel, Science Advisor, and GSI agreed control sample locations should be similar, as much as possible, to treated locations. The use of land that implements similar farming practices as control sample locations was preferred to provide a balanced scientific study with limited variabilities between control and treated sites. To accomplish this goal, farmers that have land both in and out of produced water irrigation service territories were used since farming practices would likely be similar and the major variable between sites is the reuse of produced water for irrigation.

For more information related to this comment, see Section 14 in Appendix A of the White Paper. No changes were made in response to this comment.

**COMMENT No. 11 –** In Cawelo Water District's February 2014 Agricultural Management Plan, it states that "water shall be delivered by the District for agricultural use only. Water supplied by the District is not potable or fit for domestic use and may not be suitable for stock watering or mixing with pesticides. [Cawelo Water District] makes no warranty or representation whatsoever as to it quality or fitness for use or purpose of the water it delivers." This statement appears to suggest that Cawelo Water District is protecting itself and members of the public should all be very concerned.

**RESPONSE** – This comment does not pertain to the draft White Paper. No changes were made in response to this comment.

## **ENVIRONMENTAL DEFENSE FUND (EDF) COMMENTS**

**COMMENT No. 1 –** Environmental Defense Fund (EDF) has a standing research and policy focus on issues related to produced water and has developed a database of produced water chemicals that total over 1,300 constituents. Of these, less than 24% have approved analytical methods and less than 15% have comprehensive toxicological data. This data gap presents a significant challenge in regulating this waste and also completing comprehensive studies related to potential impacts.

**RESPONSE** –The Panel, GSI, and White Paper identified a need for more information on chemicals as a data gap. Specifically, information on certain chemicals with no available toxicity data in scientific literature or an approved analytical method was identified as a data gap. The information needed to fill this data gap is not available at this time. Central Valley Water Board staff will work to close data gaps as information becomes available. Despite this data gap, GSI determined that there does not appear to be a threat to crop safety or human health from the reuse of produced water for irrigation in Kern County. This finding is consistent with GSI's determination from the crop sample results under Task 3 that there does not appear to be a significant difference between control and treated crop samples.

Under Task 1 of the Food Safety Project, GSI generated a list of 399 chemicals that had the potential to be in produced water reused for irrigation in Kern County. A chemical was added to this list if it met one of the following categories: identified by the chemical manufacturers to be a component of an oil field additive used during petroleum exploration, production, or treatment; and/or likely to be naturally occurring in produced water based on available literature. Under Tasks 1 and 2, GSI completed a preliminary hazard assessment and comprehensive literature review of the 399 chemicals. Based on this review, 143 of the 399 chemicals were designated by GSI as Chemicals of Interest for further evaluation.

For more information related to this comment, see the Tasks 1 and 2 Reports or Sections 3 and 4 of the White Paper. No changes were made in response to this comment.

**COMMENT No. 2 –** The draft White Paper identifies many challenges to this project, which include data gaps and recommendations by the Panel for future studies. The EDF strongly recommends that the Central Valley Water Board seriously consider these challenges when considering whether and how to move forward with this practice. The EDF supports the comments by the Environmental Working Group and their conclusion that this practice should not expand until additional questions raised by the Panel are satisfactorily answered.

**RESPONSE –** The Panel, GSI, and Science Advisor identified several data gaps summarized in the draft White Paper. Despite these data gaps, the Panel recommends that applications proposing new projects or expanding projects should be based on Central Valley Water Board staff's experience with existing produced water reuse projects and the information and recommendations developed in the Task Reports and in the White Paper. This recommendation in part, comes after the Panel reviewed the Central Valley Water Board's permitting process, which requires dischargers of produced water to make a demonstration showing that the proposed produced water reuse will be protective of surrounding water quality. The Central Valley Water Board will continue to work to close data gaps and complete the recommendations from the Panel while stringently reviewing new applications related to the reuse of produced water for irrigation.

For more information related to this comment, see Sections 6, 7, or 8 of the White Paper. No changes were made in response to this comment.

## **ENVIRONMENTAL WORKING GROUP (EWG) COMMENTS**

**COMMENT No. 1 –** Upon review of the data gaps and the majority of the Panel's recommendations requesting additional studies, a good case can be made for the rescission of the waste discharge requirements (WDRs) that currently regulate the practice of reusing produced water for irrigation. The draft White Paper raises many unanswered questions that should be addressed to protect the health of those growing and eating the food as well as to protect the long-term usability of the land. The Board should not approve new or expanding projects related to the reuse of produced water for irrigation until the data gaps and recommendations have been satisfied.

**RESPONSE** – See the response to Comment No. 2 from the Environmental Defense Fund. No changes were made in response to this comment.

**COMMENT No. 2 –** The use of produced water for irrigation poses questions related to the blending ratios that are used by water districts. Currently, produced water is blended with higher quality water not impacted by hydrocarbons. In the event of a drought, is the volume of freshwater blended with produced water reduced? If there was a long-term drought, would this practice be a good resources-use policy even as farmer's supplies from other sources are cutback?

**RESPONSE** – The reuse of produced water for irrigation has occurred in Kern County for over 30 years. During that time, there have been several droughts that have limited the supply of surface water to water districts. Prior to receiving produced water for irrigation, drought conditions would likely result in the water district prorating the water supply. In response, farmers would likely pump more groundwater to offset the water supply lost during these drought conditions. Using produced water for irrigation, drought conditions are likely to be less

impacted since produced water would be available to either offset the surface water lost or help prevent additional groundwater from being pumped.

Since water districts have designated service territories and track the crops grown by each farmer, water management practices are able to be maintained to ensure that the distribution systems are not overwhelmed. In addition, water districts such as Cawelo Water District and North Kern Water Storage District have groundwater recharge basins to discharge excess blended produced water that is not needed. Due to the increasing demand of water in these areas, the use of produced water for irrigation has been considered a valuable resource by water districts.

Section 5 of Appendix A was added to the White Paper in response to this comment.

**COMMENT No. 3 –** As long as chemical manufacturers continue to hide information under claims of trade secret, the public is not able to see the full picture of what their food is being irrigated with. How can the public be reassured that everything is functioning safely when a significant portion of the chemicals being used are being hidden both in terms of identity and mass? Full transparency must take place to assure the public that their food supplies are safe.

**RESPONSE** – In the absence of information concerning the mass of materials used, a conservative approach that assumed each constituent was present was used in this study. See the response to Comment No. 1 from Catherine Fowler for further discussion. No changes were made in response to this comment.

**COMMENT No. 4 –** Chemicals in produced water reused for irrigation have the potential to accumulate in the soil. Could this soil dust become air-borne and be inhaled by farm workers or nearby residents? The Panel's recommendation that the potential accumulation of chemicals in the soil has not been fully evaluated under the Food Safety Project, which could adversely impact the soil and/or plants due to recurring reuse of produced water for irrigation. EWG believes that potential impacts to farm workers health should be considered a data gap included in the White Paper.

**RESPONSE** – The goal of the Food Safety Project is to determine the potential impacts to human health from the consumption of crops irrigated with produced water. The potential for farm workers to breathe in dust that may contain chemicals accumulated in soil was outside the purview of the Food Safety Project.

No changes were made in response to this comment.

#### **JUSTIN BASS COMMENT**

**COMMENT No. 1 –** We need to stop using our good water for oil drilling and instead give the good water directly to the farmers to grow our food.

**RESPONSE** – Management of water uses is not within the purview of the Food Safety Project or under the authority of the Central Valley Water Board. No changes were made in response to this comment.

#### **KENNETH T. GIBSON COMMENT**

**COMMENT No. 1 –** The cheapest and safest way to manage produced water would be distillation. This could be done on a variety of scales and the condensed water could be checked for pollutants. The continuation of the practice of reusing untreated produced water for irrigation will result in me avoiding Central Valley produce and meat.

**RESPONSE** – Produced water reused for irrigation meets the water quality standards set in the *Water Quality Control Plan for the Tulare Lake Basin, Third Edition, Revised May 2018* (Tulare Lake Basin Plan) and is of similar quality to conventional surface and groundwater in the area. Treatment of the produced water varies between dischargers but can include a number of methods including gravity separation, flotation, and filtration. Due to the quality of the produced water reused for irrigation, there is no evidence that additional treatment is needed. In addition, based on the findings of the Food Safety Project and the Panel's recommendations, the Central Valley Water Board has not received any evidence that the reuse of produced water for irrigation in Kern County will have elevated negative impacts on human health or crop safety.

No changes were made in response to this comment.

#### LAURA ROSENBERGER HAIDER COMMENTS

**COMMENT No. 1 –** The study related to produced water reused for irrigation should be continued and additional chemicals analyzed.

**RESPONSE –** See response to Comment No. 1 by Kenneth T. Gibson.

No changes were made in response to this comment.

**COMMENT No. 2 –** Since last year, pollution standards have been more relaxed and new oil wells and fracking activities have been permitted in Kern County. Where is this fracking wastewater discharged to?

**RESPONSE** – The Central Valley Water Board does not have any evidence that oil wells that are used to generate produced water for irrigation undergo hydraulic fracturing ("fracking"). New WDRs adopted by the Central Valley Water Board that regulate the reuse of produced water for irrigation in Kern County prohibit the

reuse of produced water from wells that have been hydraulically fractured as defined by California Code of Regulations, title 14, section 1761.

No changes were made in response to this comment.

#### NORMA WILLIAMSON COMMENT

**COMMENT No. 1 –** Historical studies by "experts" that have examined the side effects of tobacco, DDT spraying, glyphosate pesticides, asbestos, etc., have too often been motivated by profit. Produced water is comprised of carcinogens that include: radium, arsenic, benzene, polonium-210, and more. It would be better to research and implement regenerative agricultural practices which support soil health, carbon sequestration, and reduce the need of the limited water supply.

**RESPONSE** – The implementation of regenerative agricultural practices that support soil health, carbon sequestration, and reduce the need of the limited water supply is outside the scope of the Food Safety Project. No changes were made in response to this comment.

### **TODD T. CARDIFF COMMENTS**

**COMMENT No. 1 –** Is there a label or process to identify produce that has been irrigated with produced water? Also, are foods labeled as "organic" permitted to be irrigated with produced water.

**RESPONSE** – The Central Valley Water Board is not aware of a label or process for consumers to identify crops that have been irrigated with produced water. The WDRs that authorize the reuse of produce water for irrigation establish a variety of requirements for compliance, including boundary lines that prohibit the discharge and reuse of produced water outside of designated areas.

The Central Valley Water Board does not keep a record of organic farms within the boundaries authorized to reuse produced water for irrigation. Also, the Central Valley Water Board does not have the authority to prohibit or limit the type of irrigation water used by organic farmers.

No changes were made in response to this comment.

**COMMENT No. 2 –** Is methanol naturally occurring in citrus and is there an increased uptake of methanol from produced water reused for irrigation?

**RESPONSE** – Under Tasks 1 and 3 of the Food Safety Project, GSI conducted a hazard assessment and reviewed crop sample results, including results for methanol. From the Task 1 hazard assessment, GSI determined methanol is naturally occurring and readily biodegradable. Therefore, GSI determined that the probability of methanol being available in soils for plant uptake from irrigation water is unlikely and methanol was not included in the Chemicals of Interest list.

Since methanol was detected in crops as part of Task 3, it was further investigated. GSI found that methanol is often a product of the ripening process and has the potential to occur naturally in crops. Numerous studies, identified by GSI, found that methanol has the potential to increase over time as fruit ripens, with one study citing that the concentration of methanol nearly doubled over three hours. Therefore, methanol found in crops is highly unlikely to originate from irrigation water.

For more information related to this comment, see the Tasks 1 and 3 Reports. No changes were made in response to this comment.

**COMMENT No. 3 –** What is the blending ratio of produced water with non-produced water and is it feasible for crops to be irrigated with 100% produced water? In scenarios where 100% produced water is used, what is the Central Valley Water Board going to do to ensure that the concentration of chemicals do not exceed the concentration used in this study?

**RESPONSE** – At this time, one facility regulated under WDRs is authorized to use 100% produced water for irrigation. The reason for this is that the produced water is exceptionally low in mineral salts and is of similar quality to local surface water. Remaining operators blend the produced water with surface and groundwater, although the blending ratio can fluctuate throughout the year as the availability of surface water changes. To ensure that the concentrations of chemicals in produced water reused for irrigation going forward are below or similar to those used in the Task Reports, GSI reviewed water quality results of both produced water and blended produced water as part of the Food Safety Project. The produced water quality results used by GSI are analytical results that were compiled by Central Valley Water Board staff. Using this conservative approach, produced water reused for irrigation in Kern County is not expected to exceed the concentrations as examined in the Food Safety Project since it has already been assessed for the potential reuse of 100% produced water for irrigation.

For more information related to this comment, see the Task 3 Report. No changes were made in response to this comment.

**COMMENT No. 4 –** How is the variability of produced water being accounted for?

**RESPONSE** – Understanding the variability of produced water quality has been identified as a data gap and gaining a better understanding of variability is a recommendation of the Panel, as described in the White Paper. Recent WDRs adopted by the Central Valley Water Board require continuous water quality monitoring for electrical conductivity. This measurement is designed to identify any major changes in constituent concentrations and close knowledge gaps concerning the variability of produced water quality. To address the Panel's recommendations, Central Valley Water Board staff will be moving forward to

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include this requirement in WDRs that authorize the reuse of produced water for irrigation.

No changes were made in response to this comment.

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Appendix D - Final Task 1 Report

The Final Task 1 Report is available on the <u>Food Safety Project webpage</u> under Reports & Documents

(https://www.waterboards.ca.gov/centralvalley/water\_issues/oil\_fields/food\_safety/)

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Appendix E – Final Task 2 Report

The Final Task 2 Report is available on the <u>Food Safety Project webpage</u> under Reports & Documents

(https://www.waterboards.ca.gov/centralvalley/water\_issues/oil\_fields/food\_safety/)

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Appendix F - Final Task 3 Report

The Final Task 3 Report is available on the <u>Food Safety Project webpage</u> under Reports & Documents

(https://www.waterboards.ca.gov/centralvalley/water\_issues/oil\_fields/food\_safety/)