

Draft Food Safety Project White Paper

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



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This White Paper also summarizes the work completed by GSI Environmental, Inc., (GSI) under 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.

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Food Safety Project White Paper (White Paper)

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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

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 – 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 – Trichloroethylene
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

The 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 oil and gas fields to agricultural lands. However, the public has raised questions regarding the safety of reusing produced water as a source of irrigation. Crops grown with produced water and are regulated under waste discharge requirements (WDRs) adopted by California Regional Water Quality Control Board, Central Valley Region, (Central Valley Water Board). Staff of 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 for human consumption.

The Panel provided technical guidance and recommendations on the Food Safety Project components. 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 via roots and other pathways, 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 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.
- 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) 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 selected for further evaluation and designated as “Chemicals of Interest.”

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 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 by Task 2 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 and analyzed and compared to crops grown that have not been irrigated with 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.

Some of the Chemicals of Interest were found in crops irrigated with produced water; however, in most cases the concentration of these chemicals in crops irrigated with produced water did not exceed the concentration found in comparable control crops. Chemicals of Interest that were found at a higher concentration in crops irrigated with produced water 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 a function of the concentration of these elements in soils and soil chemical 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 results 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, a technical third-party contractor, 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 technical contractor, Central Valley Water Board staff oversaw the Food Safety Project 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 Environmental, Inc., (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. Due to drought conditions in California, surface water sources in California have been significantly impacted during the droughts of 1928-34, 1987-92, and 2012-16, according to the United States Geological Survey (USGS) website (USGS 2018). These conditions have resulted in significant concerns that available water supplies are not

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 by 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 entities (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 being reused 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 is regulated by the Central Valley Water Board to be irrigated with produced water. A map of the farmland authorized for the reuse of produced water for irrigation is available in Figure 1 of this White Paper.

2.4 Oil Field Additives

Oil field additives consist of chemicals, compounds, and other materials, some inert, 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 general operating procedure. In the Central Valley, oil field additives can be used for the following:

1. Sealing the borehole to reduce the volume of fluid lost in a formation;
2. Reducing the swelling of clay in the borehole;
3. Reducing or preventing the corrosion of pipes, casing, equipment, and tanks;
4. Controlling microbial activities in the subsurface environment;
5. Removing oil and solids from produced water; and
6. Removing oil coating for water softeners.

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. Chemicals and constituents considered for the preliminary hazard assessment needed to be naturally occurring in produced water; introduced to the system through oil field additives used during oil exploration, production, or treatment; or otherwise identified as potentially present in produced water based on the available literature. Chemicals or constituents that satisfied at least one of these criteria were included in a new list prepared by GSI. This new GSI list is separate from the *Central Valley Water Board Oil Field Additive List* (Oil Field Additive List), which only identifies chemicals and constituents that are in oil field additives used during oil exploration, production, or treatment. The comprehensive list generated by GSI identifies 399 chemicals and constituents that underwent a preliminary hazard assessment to identify the subset of chemicals and constituents to be identified as Chemicals of Interest and undergo a more extensive literature review under Task 2.

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 Data 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 the 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 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. Table 1 consists of two repeating data columns that list the Chemical Abstract Service Registry Number (CASRN) and chemical or constituent name. 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:
 - 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:
 - 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:
 - 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:
 - 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:
 - 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 designated the radionuclides as Chemicals of Interest. The 143 chemicals and 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.

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 several environmental media, including air, soil, surface water, and food. The literature review of ambient levels in the environment yielded varying levels of 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, and lastly the United States.

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

This section examines the quality of produced water and irrigation water, blended with produced water, prior to reuse for irrigation. The goal of this section is to compare crop sample results, water quality results, and Chemicals of Interest to identify any potential 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 is available on Table 5 in the *Final Task 2 Report*.

4.3 Plant Uptake

This section summarizes GSI's findings on the available literature related to the uptake of organic and inorganic chemicals by food crops. GSI notes that plant uptake of inorganic chemicals occurs at the roots while organic chemicals can occur at the roots and/or leaves. The method of 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 roots. While there is some evidence that organic chemicals have been detected in crops, 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.

4.4 Fate and Transport

Since root uptake appears to be the dominant route by which plants can accumulate chemicals in irrigation water, GSI examined the potential for chemicals to reach 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.

Another important aspect of chemical fate and transport is the potential for a chemical to degrade or transform into another chemical in the environment. The degradation and transformation potential of the Chemicals of Interest is discussed in Section 4.5 of this White Paper. Also, this section does not examine whether a chemical that has reached the root zone of a crop will undergo plant uptake and be present in the edible portion of the crop. Information related to plant uptake is discussed in more detail in Section 4.3 of this White Paper.

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 data available, 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 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 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 of the well, in the irrigation distribution system, or in the soil. This section evaluates the potential degradation and transformation of the Chemicals of Interest.

GSI found limited data regarding the degradation and transformation products related to chemicals expected to be present in produced water. Most studies focused on hydraulic fracturing, which produces downhole conditions that differ from those associated with conventional oil extraction methods. Specifically, GSI notes that the temperature and pressure associated with hydraulic fracturing would generate an ideal environment for degradation and transformation products that would not likely occur in a conventional oil well. The use of hydraulic fracturing studies in Task 2 was a result of the relevance of this material to better understand the chemicals that may overlap between produced water and hydraulic fracturing. Some of the chemicals included in the preliminary hazard assessment for Task 1 were the same as chemicals identified in the hydraulic fracturing literature addressing downhole chemical degradation and transformation products. This overlap of available literature focused on biocides and surfactants. 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 concentrations observed in the produced water and crop samples, endocrine disrupting chemicals are not likely to be present at levels that would impact human health or crop safety.

GSI's research of *in vivo* and *in vitro* toxicity testing methods identified potential hazards associated with the direct contact of produced water and chemicals associated with hydraulic fracturing. These findings are difficult to extrapolate to crops irrigated with produced water, as some of the fate and transport processes discussed above are likely to affect the chemicals in produced water and alter the composition of the chemical mixture reaching the root zone. The concentration of at least some 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.

Although crop testing may not have covered all degradation and transformation products, the testing of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) included chemicals that were not on the Chemicals of Interest list. 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.

Thus, for at least some of the organic Chemicals of Interest whose possible transformation products were detected in crop samples, the concentrations do not appear to have been elevated.

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. This section summarizes GSI's evaluation of the radionuclides that have the potential to be in produced water reused for irrigation.

Uranium-238 (uranium) and radium were identified as naturally occurring in produced water. While researching radium, GSI identified that the most common forms of radium (33 known forms) found in produced water are radium-226 and radium-228. In addition to identifying radium-226 and -228, GSI identified that radium appears to be a decay product 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 for 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 produce 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 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 (location where produced water is being reused for irrigation) has a lower risk of containing high levels of radionuclides due to the low salinity.

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. 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.

GSI's evaluation of radionuclides examined radium-226, radium-228, uranium, thorium, krypton, and xenon. Based on consideration of their fate and transport in 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 chemicals are also used in agrochemicals and are found as natural components of soil. For general uses, 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 method 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 successful 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 this practice of reusing untreated (with regard to water quality) produced water for irrigation. This is mostly due to the quality of the produced water in the region.

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. These case studies show that produced water quality in these areas is most commonly three to six times higher for electrical conductivity than produced water reused for irrigation in the Central Valley. Case studies that have successfully grown crops using produced water include the following: 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 in these areas 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 SOW 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 fate and transport characteristics 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 a great deal is known about the fate and transport, plant uptake, and comparison of produced water quality to ambient levels, there is currently no known method to successfully 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 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. Crop types included: 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 that were 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 the laboratory for analysis.

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 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 chemicals.

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;
- Evaluation of normal distribution curves using a graphical analysis (Q-Q Plot) and statistical analysis (Shapiro-Wilks test);
- Box and whisker plot;
- 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 completed by GSI were done 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 the same.

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 data, for select Chemicals of Interest, were available with regard to plant uptake and physiology which could be expanded on to determine specific chemicals or constituents that pose a threat to crop safety or human health.
- **Potential Long-Term Impacts to Soil and Plants** – The potential accumulation of Chemicals of Interest in the soil has not been fully evaluated in this Food Safety Project and, therefore, has the potential to adversely impact the soil and / or plants due to the recurring reuse of produced water for irrigation.
- **Chemicals with No Toxicity Data or Analytical Method** – Chemicals or constituents that do not have toxicity data or an approved analytical method 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 complete assessment of all transformation and daughter products was not able to be completed under this Food Safety Project due to the scale of work needed to accomplish this task. Therefore, there is the 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 in this section 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 call attention to the limitations of the study results and highlight potential areas of interest for future studies.

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

- (1) necessary technology or analytical methods are not currently available,
- (2) necessary scope and funding far exceeds that of the Food Safety Project, or
- (3) necessary scientific information is not available at this time.

The work and findings of the Food Safety Project are based on the scientific information available at 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 the Central Valley Water Board and 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 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 A – C 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 (Task 1) designated 143 of the 399 chemicals and constituents 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 level 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 Chemical of Interest that were measured in crops were all within the normal range of concentrations for food.
- The current monitoring required for produced water used for irrigation by the Central Valley Water Board is 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 insuring 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.
- Tasks 1 through 3 did not yield any evidence that the reuse of produced water for irrigation poses an immediate 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 Food Safety Panel to develop recommendations for the Central Valley Water Board concerning how to move forward with regulating new and expanding projects that propose the reuse of produced water for irrigation (Section 8).

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 does 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 this 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. 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 chemical 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 non-targeted 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

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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
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

CASRN	Name	CASRN	Name
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	Iodine
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
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 arom.
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 naphtha	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
68123-18-2	Phenol, 4,4'-(1-methylethylidene) bis-, polymer with 2-(chloromethyl)oxirane, 2-methyloxirane and oxirane	1309-64-4	Antimony trioxide

CASRN	Name	CASRN	Name
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
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

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
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)

Analytical Method	Analyte	Analytical Method	Analyte
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
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		

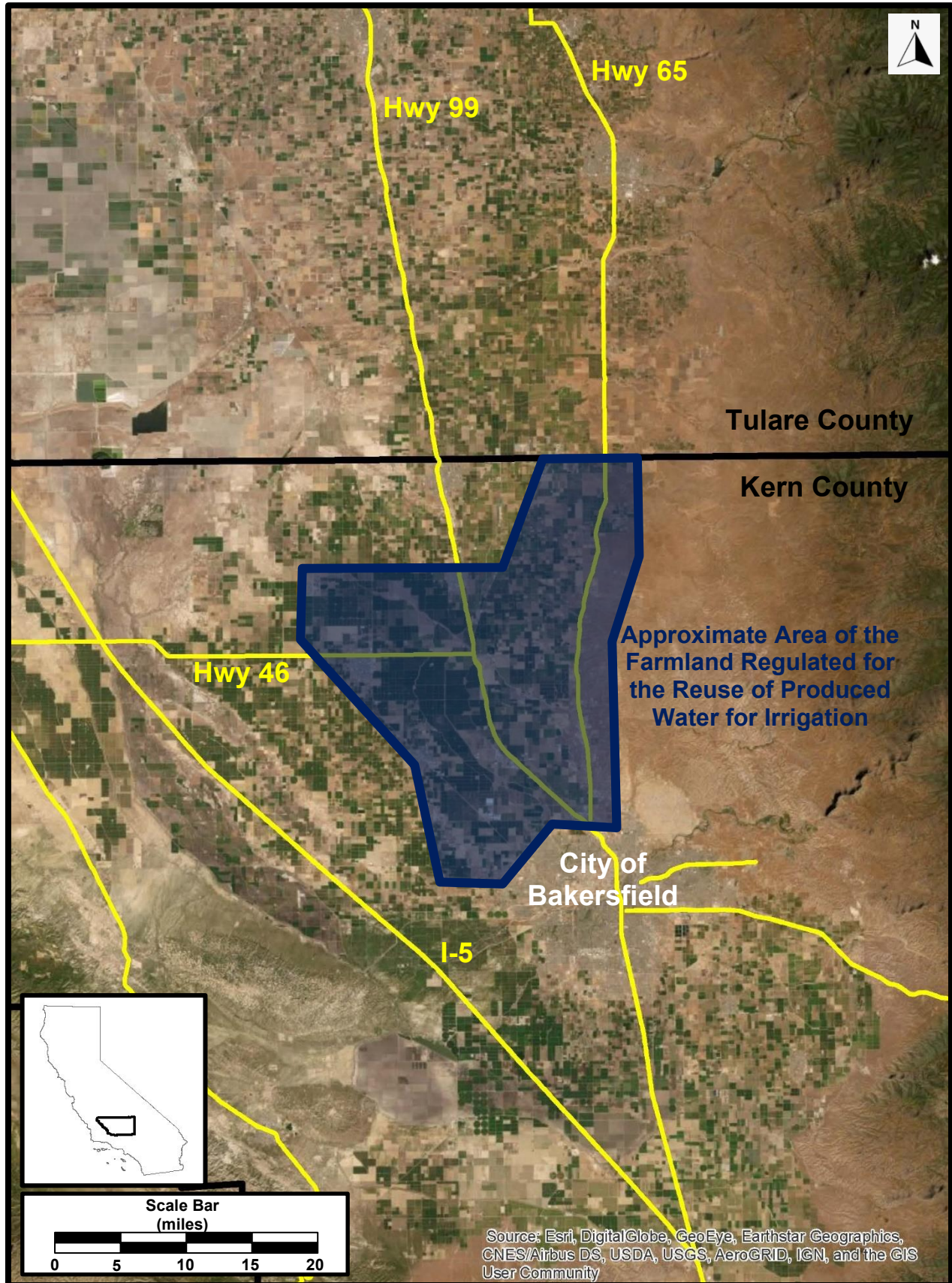
Table 3: Detected Analytes in Crop Samples

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

11.0 List of Figures

Figure 1: Vicinity Map

Figure 1: Vicinity Map



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

Appendix C – Final Task 1 Report

Appendix D – Final Task 2 Report

Appendix E – Final Task 3 Report

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

MEMORANDUM

Date: 28 January 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 the audience with additional information that is not included in the Food Safety Project White Paper (White Paper). 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. Treatment of Produced Water
6. Oil Field Additives
7. Quality of Produced Water
8. Food Safety Expert Panel
9. Memorandum of Understanding
10. Science Advisor
11. Technical Consultant
12. Food Safety Charter
13. Sampling Protocols Under Task 3
14. Analysis of Crops Under Task 3

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, consists of oil and water. The water fraction is called produced 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 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 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 have not used produced water from wells that have been hydraulically fractured. 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 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:

1. Dissolved Air Flotation – Removes residual oil and solids using a mechanically induced dissolved air flotation system. Commonly referred to as WEMCOs by oil operators.
2. Filters – Removes residual oil and solids by passing produced water through a filtering media.

3. 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.

The complete separation / treatment system configurations for each of the Dischargers are described in the WDRs that regulate each discharge. [The WDRs are available on the Central Valley Water Board's website](https://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/) (https://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/).

6.0 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: volatilize 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 in 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 (CASRN).

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/)

(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.

7.0 Quality of Produced Water

The quality of produced water is highly variable and can change 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 and 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 show 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, that is pumped to irrigators for irrigation; (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

Parameters	Units	Produced Water Reused for Irrigation	Produced Water from the McKittrick Oil Field	Drinking Water Standards
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.

* = Secondary Drinking Water Standard

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.

8.0 Food Safety Expert Panel

Following increased scrutiny of oil field activities and resources made available by budget augmentations, 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 organizations of employment.

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	Principal Scientist	Exponent, Inc.
Bruce Macler, PhD	Regional Toxicologist	US EPA Region 9 (Retired on 31 July 2020)
David Mazzer, PhD	Chief, Division of Food, Drug, & Cannabis Safety	CA Dept. of Public Health
Gabriele Ludwig, PhD	Director, Sustainability & 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	PSE Healthy Energy
Stephen Beam, PhD	Branch Chief	CA Dept. of Food and Agriculture

9.0 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 describes the following as it relates to the Food Safety Project:

1. Identification of Parties to the MOU and Studies Covered by the MOU,
2. Statement of Facts,
3. Development of Scopes of Work,
4. Roles and Responsibilities of the Parties to the MOU,
5. Schedule and Performance of Work, and
6. General Terms of the MOU.

10.0 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 Lawrence Berkeley National Laboratory was selected as the Science Advisor to the Central Valley Water Board. With over 35 years of experience in wastewater treatment and management and one of the lead scientists on the Senate Bill 4 scientific study evaluating hydraulic fracturing in California, Central Valley Water Board staff and the Panel agreed this was an appropriate appointment.

11.0 Technical Consultant

Through the MOU between the Dischargers under WDRs and Central Valley Water Board staff, 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 of the Food Safety Project that was completed by GSI. 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.

12.0 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/) (https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/).

13.0 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 to be 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 collect the tomato samples in compliance with the SAP.
- Cawelo personnel collected potatoes at a Smart and Final in Bakersfield to send 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.

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 from the local grocery store). 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 custodies were maintained for each sampling event and are available in the laboratory reports.

14.0 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 receiving complete laboratory reports, Central Valley Water Board staff (with consensus 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 temperature-controlled 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 were 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.

Appendix B – Data Gaps Related to the Food Safety Project

MEMORANDUM

Date: 28 January 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 the audience with additional information related to data gaps of the Food Safety Project. Data gaps discussed in this memorandum are items that have been brought up 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 obscure chemicals, that may be present in produced water and crops, have not been approved by state or federal agencies for regulatory use;
- Limited information currently available in both public and private sectors;
- Scope and funding needed to fully evaluate the issue far exceeds that of the Food Safety Project; or
- Data with the Central Valley Water Board staff was 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 is needed to fully understand plant uptake and associated plant physiology concerning specific chemicals found in produced water. 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 conducted³ 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.

Appendix C – Final Task 1 Report

Appendix D – Final Task 2 Report

Appendix E – Final Task 3 Report