Draft White Paper

Food Safety Project

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Food Safety Project

List of Abbreviations

AB1328 – Assembly Bill 1328

APPL – Agricultural and Priority Pollutants Laboratories, Inc.

ATSDR – Agency for Toxic Substance and Disease Registry

CALEPA – California Environmental Protection Agency

CASRN – Chemical Abstract Service Registry Number

CEBS – Chemical Effects in Biological Systems

CICAD – Concise International Chemicals Assessment Document

ECHA – European Chemicals Agency

ELAP – Environmental Laboratory Accreditation Program

EPA – Environmental Protection Agency

HBSL – Human Based Screening Levels

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 – Milligram per Liter

MRP – Monitoring and Reporting Program

NAWQA – National Water Quality Assessment

NIEHS – National Institutes of Environmental Health

NIH – National Institutes of Health

NOEL – No Observed Effect Level

NSRL – No Significant Risk Level

OEHHA – Office of Environmental Health Hazard Assessment

PPRTV – Provisional Peer-Reviewed Toxicity Values

REACH – Registration, evaluation, Authorization and Restriction of Chemicals

RfD – Reference Dose

SAP – Sampling and Analysis Plan

TOXNET – Toxicology Data Network

ug/L – Micrograms per Liter

umhos/cm – Micromhos per Centimeter

USGS – United States Geological Survey

WDRs – Waste Discharge Requirements

WHO – World Health Organization

Introduction

Purpose

This White Paper presents the results of a study completed by the staff of the California Regional Water Quality Control Board, Central Valley Region (Water Board) and its contractors, in consultation with a Panel of Experts (Panel). The Panel was assembled to seek input in the area of human health from the consumption of food crops irrigated with oil field produced water. Water Board staff solicited the assistance of experts in food safety to identify and address potential health impacts associated with the reuse of oil field produced water for irrigation of crops for human consumption.

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. Most of this land is irrigated using a complex system of canals to deliver water across the Central Valley. In the southern part of the Central Valley, the San Joaquin Valley, much of this land relies on imported surface water as local surface waters and groundwater are not a sustainable supply. Also, drought conditions in California have significantly impacted surface water sources during 1928-34, 1987-92, and 2012-16, according to the United States Geological Survey (USGS) website[1]. These circumstances have led some farmers in the southern San Joaquin Valley to look to unconventional or other sources of water for irrigation. One of these sources is oil field "produced water," or water that is extracted during oil and gas production. In parts of Kern County, produced water is typically blended with other waters to supplement the irrigation of approximately 95,000 acres of farmland.

The southern San Joaquin Valley is also a major oil producing area. Approximately 150 million barrels (42 gallons per barrel of oil) are produced in California every year. In most California oil fields, for every barrel of oil produced, 10-15 barrels of water are also produced. Produced water tends to be highly saline and is typically recycled back into the production system, discharged into underground injection wells, or discharged to percolation 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 fresh water. In these oil fields, the produced water is of sufficient quality (typically less than 1,000 mg/l total dissolved solids and less than 1.0 mg/l boron) that it can meet water quality objectives for agricultural and industrial uses without treatment beyond the removal of oil. This is discussed in more detail in the Quality of Produced Water section of this White Paper.

[1] USGS. 2018. California Drought. [https://ca.water.usgs.gov/california-drought/california-drought-comparisons.html]. Accessed 07/24/2019.

As of 2019, produced water from five petroleum companies is sent to five entities representing irrigators (collectively referred to as “Permit Holders”). The Water Board regulates Permit Holders under waste discharge requirements (WDRs), which establish specific effluent and groundwater limits and monitoring frequencies to monitor and protect the quality of waters of the State. The produced water supplements imported surface water and pumped groundwater supplies to meet irrigation demands. Produced water is treated to remove sediments, hydrocarbons, and other constituents. Typically, the irrigators receive the produced water in reservoirs where it is blended with surface and/or groundwater before it is used for irrigation. Some of the produced water, typically after blending, is sent to groundwater recharge basins. Discharge to the recharge basins occurs primarily during periods of low irrigation demand.

Since the most recent drought in California, the Water Board has met with new parties that have expressed interest in recycling produced water for irrigation. In 2019, the Water Board adopted two new WDRs for the reuse of produced water for irrigation, which are included in the 95,000 acres of farmland irrigated with produced water. One project was new and proposed to reuse produced water as the sole source of irrigation water. The second project proposed the expansion of an existing project, in which the operating parties sought to increase the volume of produced water reused for irrigation and construct a new reservoir for additional storage capacity. As of July 2019, staff with the Water Board have not received additional proposals for new or expanding projects related to the reuse of produced water for irrigation.

Waste Discharge Requirements (WDRs)

Recycling of water is encouraged by State policy as a means to supplement California’s limited water supply, if the water is suitable for the intended use. The *Water Quality Control Plan for the Tulare Lake Basin, Third Edition, revised May 2018* (Basin Plan) states that “blending of wastewater with surface or groundwater to promote beneficial reuse of wastewater may be allowed where the Regional 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 Board.

The reuse of produced water for irrigation is regulated under WDRs, which conditionally permit the practice and stipulate maximum groundwater and effluent limits for the facility. Included in the WDRs is a Monitoring and Reporting Program (MRP), which requires Permit Holders 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 constituents associated with oil field activities, including: salts, metals, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), radionuclides, and additives. Water samples required under the MRP are sent to a third-party laboratory certified under the California State Water Resources Control Board’s (State Board’s) Environmental Laboratory Accreditation Program (ELAP). Analytical results of produced water are available for review at the Water Board, Water Board's online databases (CIWQS and GeoTracker), and on the Water Board's Food Safety Web Page.

Treatment of Produced Water

In Kern County, the percent oil in production fluid varies depending on the oil field. For Permit Holders that reuse produced water for irrigation, production fluid consists of approximately 90 – 95% produced water. The separation / treatment process for Permit Holders that reuse produced water for irrigation consists of two phases. The first phase is the primary separation of the production fluid, which removes the majority of the oil from produced water. In Kern County, this phase normally consists of wash tanks that are designed to separate fluids based on their specific gravity. Some operators elect to heat the wash tanks for increased oil removal efficiency. Oil from the initial phase is pumped to stock tanks (temporarily stored prior to being transported to refineries) and produced water is pumped to the secondary phase.

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

1. WEMCOs – Remove residual oil and solids using a mechanically induced dissolved air flotation system.
2. Filters – Remove residual oil and solids by passing produced water through a filtering media.
3. Ponds – Provide additional retention time that enables residual oil to coagulate and rise to the fluid surface. Skimming operations remove the oil from the fluid surface.

Residual oil captured using a WEMCO or pond is either transferred to an oil stock tank or re-injected into the initial 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 Permit Holder are described in the WDRs that regulate the facility. The WDRs are available on the [Water Board's website](https://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/) (https://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/).

Oil Field Additives

Oil field "additives" are commonly used by oil producers for petroleum exploration, production, and treatment. Additives are used for a variety of purposes and vary depending on an individual oil operator's general operating procedures. In Kern County, additives can be used for the following:

1. Sealing the borehole to reduce the volume of fluid lost in the reservoir;

2. Reducing the swelling of clay in the borehole;
3. Reducing or preventing the corrosion of pipes, equipment, and tanks;
4. Removing oil and solids from produced water; and
5. Removing oil coating for water softeners.

The types and volumes of additives that are used depend on a variety of factors, including the geology and the petroleum facility. Through the use of additives, new chemicals may be introduced to the system that are not naturally occurring in produced water. Identification of chemicals that are not naturally occurring pose challenges as their presence depends heavily on the concentration and volume of the additive used during petroleum operations and how it breaks down in the environment. Recognized by Water Board staff as a potential concern, staff determined that the MRPs for Permit Holders that reuse produced water for irrigation should be updated to capture information regarding additives used during petroleum operations.

In 2015, Water Board staff started to generate draft Revised MRPs for Permit Holders that reuse produced water for irrigation. The Revised MRPs were issued under the authority of the Executive Officer and required Permit Holders to submit Safety Data Sheets for all additives used during petroleum exploration, production, and treatment. Safety Data Sheets identified the general chemical make-up (excluding trade secret information) of additives used by Permit Holders. During the development of the initial Revised MRPs, the Water Board did not have the authority to require chemical manufacturers to submit trade secret information, due to the limitations of section 13267 of the California Water Code (Water Code). Section 13267 of the Water Code authorized the Water Board to investigate persons who has discharged, discharges, or is suspected of discharging waste that could affect the quality of waters of the state, not entities or manufacturers that are not directly associated with the discharge.

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 all chemicals in produced water. AB 1328 amends the Water Code by adding section 13267.5. This section of the Water Code gives the State Board or a Regional Board the ability to require information on chemical additives, even information that is protected by trade secret claims. Water Code section 13267.5 also gives the Water Board the authority to acquire additive information directly from manufacturers.

From December 2017 to September 2018, Water Board staff issued more than 50 Orders pursuant to Water Code sections 13267 and 13267.5 (Orders) to users, distributors, manufacturers, and suppliers of additives. The Orders required the submittal of information on additives, their ingredients, and associated chemical abstract service registry numbers (CASRNs).

Information submitted to the Water Board in response to the Orders were compiled by staff. Due to issues regarding trade secret claims, responses to these Orders are not available for review by the public or the Panel. To publish the chemical data and not violate trade secret claims, Water Board staff generated a list of chemicals that were identified in the responses to the Orders, referred to as the Oil Field Chemical List. The Oil Field Chemicals List identifies chemical names and CASRNs for all chemicals that may be in produced water due to the use of additives.

The Oil Field Chemical List consists of 347 chemicals and is cited in the Referenced Material section of this White Paper.

Quality of Produced Water

The quality of produced water is highly variable and can change between oil fields depending on a variety of factors. In Kern County, there are approximately 76 oil fields that each have unique produced water quality. Due to the geology and migration of oil in Kern County, produced water from oil fields along the east side of the San Joaquin Valley is 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 beneficially reused for irrigation.

To effectively show the difference in produced water quality in Kern County, Water Board staff compiled water quality data for 2018 and summarized the results in Table 1. Table 1 includes three data columns that identify the following: (1) the average value of produced water, prior to blending, pumped to water management companies for irrigation; (2) average value of produced water discharged to a land disposal facility in the McKittrick Oil Field, located along the west side of Kern County; and (3) drinking water standards listed as a comparison for the first two data columns. Drinking water standards in Table 1 that have an asterisk are secondary standards, which are designated as non-health threatening and are based on aesthetic, cosmetic, and technical effects.

Table 1: Produced Water Quality for Oil Fields in Kern County

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

As shown in Table 1, produced water reused for irrigation is of better quality than produced water from the McKittrick Oil Field. In Table 1, water quality data compared between the east and west side varies by 3 to 89 times, depending on the constituent. This comparison highlights the significant change in water quality across Kern County. Table 1 also shows that produced water reused for irrigation is below the primary standards for drinking water and near or below secondary drinking water standards.

Irrigators

Produced water from oil companies is pumped to water management companies (also referred to as "irrigators"), which is typically discharged to reservoirs and blended with surface water and/or groundwater. As of 2019, there are three water districts and two privately owned companies that receive produced water that is subsequently reused for the irrigation of crops for human consumption. The following is a brief overview of each:

1. **Cawelo Water District (Cawelo)** - Cawelo's water supply sources include the Kern River, State Water Project, groundwater, and produced water from the Kern River and Kern Front Oil Fields. After treatment, produced water is received in Cawelo's reservoirs and blended with traditional sources. Most of the crops grown in Cawelo are permanent crops (e.g., citrus, nuts, and grapes), but occasionally row crops are grown (e.g., carrots, potatoes, and garlic).
2. **Kern-Tulare Water District (Kern-Tulare)** - Kern-Tulare's water supply sources include the Kern River, Central Valley Project, groundwater, and produced water from the Jasmin Oil Field. Most of the crops grown in Kern-Tulare are permanent crops (e.g., citrus).
    a. Note: Kern-Tulare's service territory spans Kern and Tulare Counties. Due to the use of isolated distribution networks, produced water is only available in the distribution network operating in Kern County.
3. **Jasmin Ranchos Mutual Water Company (Jasmin Water Company)** – The Jasmin Water Company is not a Water District and has access to groundwater, produced water, and irrigation water from Kern-Tulare. Most of the crops grown in the Jasmin Water Company service area are permanent crops (e.g., citrus).
4. **North Kern Water Storage District (North Kern)** - North Kern's water supply sources include the Kern River, groundwater, and produced water from the Kern Front Oil Field. Most of the crops in North Kern are permanent crops (e.g., citrus and nuts), but row crops are grown in some years (e.g., tomatoes, beans, garlic, carrots, and others).
5. **Sherwood Hills, LLC (Sherwood)** – Sherwood is not a water district and only has access to groundwater and produced water. Produced water from the Poso Creek Oil Field is pumped to Sherwood's Reservoirs, where it is not required to be blended with produced water prior to being used for irrigation. Produced water may be used to irrigate citrus, nuts, silage, oilseed, and/or grain crops.

Food Safety Expert Panel

Produced water has been used to irrigate crops in Kern County for over 30 years. With increased scrutiny of oil field activities and resources recently made available, Water Board staff determined that a review of reusing produced water for irrigation would be appropriate.

In 2015, Water Board staff began a project to evaluate the use of produced water to irrigate crops (Food Safety Project). However, since Water Board staff are not experts in food safety, outside experts and representatives of State agencies responsible for food safety were enlisted to advise the Water Board and ensure the Food Safety Project would be thorough and scientifically defensible. When choosing Panel members, the primary goal 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 wildlife. The Panel was a group of volunteers, and no financial compensation was provided to any of the members by the Water Board.

The Water Board convened the Panel to seek the expertise of individuals outside of the Water Board's purview, including representatives from state and federal agencies with regulatory roles in public health and food safety, non-government organizations, and industry. Water Board staff also contracted with a Science Advisor (Dr. William Stringfellow of Lawrence Berkeley National Laboratories).

The Water Board worked with the Panel to investigate whether the practice of reusing produced water for irrigation of crops for human consumption posed a threat to human health. With insight from the Panel, several studies on the practice were conducted. The studies included an assessment of additives used in the oil fields that supply produced water reused for irrigation, a literature review, and crop sampling. The studies followed a series of crop studies administered by Cawelo (discussed in more detail in the Historical Crop Study section of this White Paper).

Through a memorandum of understanding (MOU) between the Permit Holders and the Water Board, the studies were funded by the Permit Holders but performed by a neutral third-party consultant selected by the Permit Holders and approved by the Water Board. Results of the studies are available to the public and were presented at public meetings with the Panel. The MOU is discussed in more detail in the MOU section of this White Paper.

<u>Food Safety Expert Panel Project Charter</u>

In May 2017, the Panel finalized the Project Charter (Charter). The Charter establishes the project's purpose, scope, and the responsibilities for participants of the Food Safety Project. The charter defines the primary technical focus of the Panel as addressing food safety at the point of harvest. This section of the White Paper provides an overview of the Charter.

The Charter is cited in the Referenced Material section of this White Paper.

Project Participants

The Charter identifies parties that participated in the Food Safety Project. Panel members were selected based on their expertise in toxicology, risk assessment, agriculture, public health, and wildlife. Table 2 identifies the members of the Panel.

Table 2: Panel Members

Name	Title	Organization
Dr. Stephen Beam	Branch Chief	CA Dept. of Food and Agriculture
Dr. Andrew Gordus	Staff Toxicologist	CA Dept. of Fish and Wildlife
Dr. Gabriele Ludwig	Director, Sustainability & Environmental Affairs	Almond Board of California
Dr. David Mazzera	Branch Chief	CA Dept. of Public Health
Dr. Kenneth Kloc	Staff Toxicologist	CA Office of Environmental Health Hazard Assessment
Dr. Bruce Macler	Regional Toxicologist	US EPA Region 9
Dr. Seth Shonkoff	Executive Director	PSE Healthy Energy
Dr. Barbara Petersen	Principal Scientist	Exponent
Mr. Mark Jones	Staff Toxicologist	US Army Corps of Engineers

Roles and Responsibilities of the Food Safety Expert Panel (Panel)

The Charter states that the Panel will:

1. Review and provide recommendations on technical issues relevant to assessing food safety of crops irrigated with produced water.
2. Provide perspectives and feedback to the Water Board, including scientific justification and rationale.
3. Develop resources or text, or provide other assistance to Water Board staff and facilitators as appropriate. Consistently participate in Panel and public meetings.
4. Help identify, review, verify, and critique data, assumptions, analysis and methods used by the Water Board and others in support of food safety assessment.
5. Evaluate short- and long-term conditions related to food safety issues.
6. Seek consensus on proposals and/or recommendations.

Roles and Responsibilities of the Water Board

The Charter states that the Water Board will:

1. Consider feedback from the Panel in an open and receptive fashion, providing explanation and rationale for Board decisions to act or not act upon Panel input.

2. Communicate information about the Panel and Water Board process with the public.
3. Provide technical and administrative staff support to the Panel, including development of materials, maintenance of a website, publication of meeting notes, and similar.
4. Develop text and work products (as necessary).
5. Provide and update a project timeline and schedule to help manage deadlines.
6. Communicate to the Panel likely comments, actions, and recommendations from the Water Board on food safety related activities.

Roles and Responsibilities of the Science Advisor

The Charter states that the Science Advisor (Dr. William Stringfellow) will:

1. Extend internal Water Board expertise for food safety related issues.
2. Work as a liaison between Water Board staff and the Panel.
3. Advise and oversee future sampling activities and provide scientific review.

Food Safety Project Operating Guidelines

The Charter states that the Panel shall utilize standing operating guidelines to ensure efficient and respectful discussions. Panel members have agreed to:

1. Listen and openly discuss issues with others who hold diverse views.
2. View disagreements as problems to be solved rather than battles to be won.
3. Not engage in stereotyping and personal attacks on other Members, support staff, or participating members of the public.
4. Not ascribe motives or intentions of other Members, support staff, or participating members of the public.
5. Respect the integrity and values of other Members, support staff, or participating members of the public.
6. Keep commitments once made.
7. Honor meeting times.
8. Appreciate humor but not engage in humor at the expense of others.

Results of the studies, and progress of the Food Safety Project, were presented to the Panel during private and public meetings. During public meetings, members of the public were provided an opportunity to comment on the Food Safety Project. The meeting videos and summaries are available on the Food Safety webpage.

Food Safety Project Outcome

The Charter states that it is anticipated that Water Board staff would produce a White Paper that would represent the documents that have been generated throughout the Food Safety Project. As a result, this White Paper summarizes the studies conducted as part of the Food Safety Project, which included a hazard assessment, a literature review, and a study conducted on crops grown with produced water. The studies are discussed below and the reports are cited in the Referenced Material section of this White Paper. Also, included in this White Paper are the recommendations of the Panel. Panel members shared insights on potential next steps, possible triggers for additional crop sampling, revisions to Monitoring and Reporting programs, and parameters for produced water use.

Memorandum of Understanding (MOU)

The Memorandum of Understanding (MOU) was generated to develop the general roles, relationships, and responsibilities of parties and stakeholders involved in the Food Safety Project. Also, the MOU specified the process by which the Permit Holders funded the project and how the Water Board oversaw, managed, and reviewed academic and/or scientific studies conducted by GSI. The MOU is outlined as follows:

1. Identification of Parties to the MOU and Studies Covered by the MOU,
2. Statement of Facts,
3. Development of Scope 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.

The MOU was entered into among the Water Board and the Permit Holders in June 2017. The MOU is cited in the Referenced Material section of this White Paper.

The primary objective of the MOU was to develop a Scope of Work to complete the Food Safety Project. After several public and working meetings with the Panel, the Water Board and Permit Holders agreed on a final Scope of Work. The final Scope of Work consisted of three tasks for moving forward with the Food Safety Project. Each of the tasks included the following: objective, suggested approach, deliverables, and budget. This section of the White Paper will provide an overview and results for each of the tasks.

Task 1 – List of Chemicals of Interest

The objective of Task 1 was to identify and conduct a preliminary hazard assessment of potential chemicals in produced water. This list was limited to chemicals that are either naturally occurring in produced water or that are introduced to the system through additives used during petroleum exploration, production, or treatment. Chemicals that satisfied one of the criteria were included in a new chemical list prepared by GSI. The GSI list of chemicals is separate from the Water Board's Oil Field Chemical List, which only identifies chemicals that were identified in petroleum additives.

The next phase of Task 1 was to complete a preliminary hazard assessment of GSI's list of chemicals. The preliminary hazard assessment consisted of an initial toxicological review by GSI, which resulted in the assignment of chemicals to one of five categories based on readily available toxicological data. Chemicals that were designated as toxic or had comparative toxicological data were included in the Chemicals of Interest list. The Chemicals of Interest list would undergo a more comprehensive toxicological evaluation in Task 2.

The following sections provide an overview and discussion of the work completed by GSI for Task 1. The Scope of Work for Task 1 and the Task 1 Report are cited in the Referenced Material section of this White Paper.

List of Chemicals to Be Evaluated

The initial objective of Task 1 was to identify chemicals that may be present in produced water. Chemicals that are being examined are either (1) from additives that are used for petroleum exploration, production, or treatment or (2) are naturally occurring in produced water. As described in more detail in the Oil Field Additives section of this White Paper, the Water Board published a list of chemicals that make-up the additives used by Permit Holders reusing produced water for irrigation. The Oil Field Chemical List is comprised of 347 chemicals that were added to GSI's list of chemicals for the preliminary hazard assessment.

The second part of the GSI list are chemicals that are naturally occurring in produced water. To identify chemicals that are naturally occurring in produced water, GSI reviewed: peer reviewed journals, government documents, and other published materials. GSI noted that the research materials indicated the chemical make-up of produced water is highly variable and is subject to change depending on the geology, age of the formation, and techniques for extraction. At the conclusion of GSI's research, 45 organic and 45 inorganic chemicals were identified as having the potential to be naturally occurring in produced water. The complete list of naturally occurring chemicals is available in Appendix A of the Task 1 Report.

GSI combined the two chemical lists to generate a new list of chemicals that have the potential to be present in produced water reused for irrigation. Due to overlapping chemicals on both lists, the complete list of chemicals consisted of 400 chemicals. The next step was for GSI to conduct a preliminary hazard assessment to identify chemicals that would be designated as Chemicals of Interest.

Overview of the Preliminary Hazard Assessment

Oil field additives and naturally occurring chemicals may cause toxic effects if exposure levels are sufficiently high. To minimize the chances overlooking a particularly toxic chemical, toxicity was the primary consideration in the selection of the Chemicals of Interest for further evaluation. Environmental persistence in water was also considered because of the influence this factor can have on the potential for these constituents to be delivered with irrigation waters to agricultural sites. For example, an additive being used in an oil field may be considered carcinogenic but biodegrades before it reaches an irrigated field. Due to its biodegradability in water, this chemical would not be considered a priority for further evaluation as there is little likelihood that it would be available to be taken up into the edible crop.

The Food Safety Project is an evaluation of the potential impacts to human health associated with the consumption of crops irrigated with produced water. The oral route of exposure is the most important in the assessment of risks contributed to the ingestion of crops. Due to this, chronic toxicity values for oral exposures were considered for the preliminary hazard assessment. GSI focused the scope of the research to government published data, but due to limited toxicological data had to expand the search to other sources. The following were considered in the preliminary hazard assessment:

- EPA Integrated Risk Information System (IRIS) Reference Dose (RfD),
- EPA IRIS Oral Slope Factor for Cancer,
- EPA Provisional Peer-Reviewed Toxicity Values (PPRTV) Oral RfD,
- EPA Human Health Benchmarks for Pesticides (HHBP),
- PPRTV Oral Slope Factor,
- Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Level (MRL) Oral Chronic Exposure,
- California Office of Environmental Health Hazard Assessment (OEHHA) Oral Slope Factor,
- OEHHA Child Specific RfD,
- OEHHA Cancer No Significant Risk Level (NSRL) Oral Exposure,
- OEHHA Reproductive/Developmental Maximum Allowable Daily Dose (MADL) Oral Exposure,
- United States Geological Survey (USGS) Noncancer Human Based Screening Levels (HBSL),
- USGS Cancer HBSL,
- Human Health Toxicity Values in Superfund Risk Assessments Health Effects Assessment Summary Table (HEAST) Oral Slope Factor,
- HEAST Chronic Oral RfD,
- HEAST Oral Exposure NOAEL, and

- Other Toxicity Values Derived to Protect Health.

With regard to *Other Toxicity Values Derived to Protect Public Health*, GSI conducted searches on Google, Google Scholar, and other health and toxicologic databases that include: PubMed, National Institutes of Environmental Health (NIEHS), Chemical Effects in Biological Systems (CEBS), National Institutes of Health (NIH), Toxicology Data Network (TOXNET), NIH PubChem, World Health Organization (WHO) Concise International Chemicals Assessment Document (CICAD), International Programme on Chemical Safety from Intergovernmental Organizations (IPS-INCHEM), and the database of the registration dossiers through the European Chemical Agency's (ECHA) Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) Program. These databases were used by GSI to obtain pertinent toxicological data.

The GSI list of chemicals consists of 399 chemicals that have the potential to be in produced water. To accurately assess each chemical for the preliminary hazard assessment, GSI developed the following methodology that utilizes the sources identified above:

1. Identify published chronic toxicity values for the chemicals on the list, where available;
2. From the list of chemicals remaining after Step 1, a sub-list was generated that represents produced water chemicals that are constituents of food, food additives, considered non-toxic, have therapeutic oral use with low toxicity, inert compounds, and compounds that break down into one of the previously identified chemicals in this step;
3. From the remaining chemicals, after Steps 1 and 2, research the available peer reviewed literature, government / industry reports, and relevant databases to identify data that characterizes the toxic potential of the remaining chemicals as it relates to chronic oral exposures;
4. From the research activities under Step 3, identify the sub-list of chemicals for which there are no relevant data characterizing toxic potential related to chronic oral exposures;
5. From the remaining chemicals, after Steps 1, 2, 3, and 4, create three sub-lists that represent: chemicals with unclear / unquantifiable chronic toxicity, chemicals with no apparent chronic toxicity, and chemicals with quantifiable chronic toxicity;
6. For chemicals without published toxicity values, GSI developed ad hoc surrogate toxicity values based on the scientific literature, where applicable.

For many of the chemicals, GSI was able to identify toxicological data that was used for the preliminary hazard assessment. For other chemicals, limited or no information was available regarding a chemical's toxicity. For chemicals with limited information, GSI was able to develop surrogate comparative values (Step 6) depending on the type of information available. This enabled GSI to develop toxicity values for a subset of chemicals that have limited information. This approach is generally considered an acceptable practice, as long as the use of a surrogate can be justified with sufficient information.

Results of the Preliminary Hazard Assessment

Using the methodology and toxicological values outlined in the Overview of the Preliminary Hazard Assessment section in this White Paper, GSI evaluated and categorized 400 chemicals that have the potential to be in produced water. Chemicals were assigned to one of five categories developed by GSI. The categories were used to group chemicals together based on the toxicological data available in the databases described in the previous section. The following is a summary of the categories and the findings by GSI.

Category 1 – Chemicals That Are Essentially Non-Toxic

Seventy-one chemicals were identified as essentially non-toxic and did not appear to have toxicological data that yielded potential issues regarding chronic oral toxicity. This assessment of the 71 chemicals was based on the following:

1. Known constituents of the human diet in that they are normally and naturally found in unadulterated food for humans;
2. Common food additives or supplements, this includes chemicals that have therapeutic use through ingestion that are known to be non-toxic;
3. Other chemicals considered to be non-toxic (i.e., those where human exposures have not shown adverse effects);
4. Inert chemicals; and
5. Upon combination with water, the chemical will react and become one of the previously mentioned groups.

This list of chemicals is shown in Table 3 of the Task 1 Report.

Category 2 – Chemicals with Insufficient Data to Identify Toxicity

Sixty chemicals did not have adequate data available to make an assessment regarding the toxicity. GSI searched relevant databases for alternate names and reviewed read-across assessments for compounds that may have been representative of the original chemical. Chemicals in this category are not considered to have toxicity data available.

This list of chemicals is shown in Table 4 of the Task 1 Report.

Category 3 – Chemicals without Chronic Oral Toxicity

Sixty-nine chemicals were researched and did not have chronic oral toxicity data. Chemicals were assigned in this category as a result of one or both of the following:

1. Research indicated that a chemical did not have chronic toxicity values due to no identified health risks associated with repeated dosages via oral exposure; or
2. Research from animal toxicological studies demonstrated a No Observed Effect Level (NOEL) for carcinogenic, reproductive/developmental, and system effects and the NOEL was at least 500 mg/kg/day.

GSI used a NOEL of 500 mg/kg/day based on published data regarding the average consumption rate of fruits and vegetables and the use of the following uncertainty factors for conversion (as needed): (1) animal to human, (2) susceptible populations, and (3) the potential need to account for extrapolation of sub-chronic studies to chronic effects. The complete summary for the use of 500 mg/kg/day is available in the Chemicals Without Chronic Oral Toxicity section in the Task 1 Report. Chemicals in this category were presumed to be non-toxic for chronic oral toxicity based on the available data and assumptions defined by GSI.

This list of chemicals is available in Table 5 of the Task 1 Report.

Category 4 – Chemicals with Incomplete Chronic Oral Toxicity

Fifteen chemicals were assigned to this category. Results of the research for these twelve chemicals indicated one of the following:

1. Insufficient data on chronic oral toxicity to make a determination regarding the potential toxicity of the chemical for humans;
2. Conflicting results regarding the toxicity of a specific chemical; or
3. Unable to identify a CASRN.

Due to incomplete toxicological data regarding the twelve constituents, GSI was not able to identify their potential toxicity with regard to the irrigation of crops for human consumption.

The list of chemicals is available in Table 6 of the Task 1 Report.

Category 5 – Chemicals with Quantified Chronic Oral Toxicity Values

A total of 181 chemicals were identified by GSI as having quantifiable chronic oral toxicity data. Of the 181 chemicals, GSI identified published toxicity values for 107 of the chemicals. For 23 of the chemicals, GSI was able to identify toxicity values using a read-across approach by utilizing some of the data collected from the 107 chemicals with published toxicity data. These 130 chemicals are listed in Table 8 of the Task 1 Report. Table 8 of the Task 1 Report lists the chemicals in order by toxicity. In addition, Table 8 includes the toxicity value, source of the toxicity value, biodegradation classification, and identifies whether the chemical is naturally occurring or originates from additives.

For 51 chemicals, GSI developed ad hoc surrogate comparative values. The 51 chemicals are reported separately from the 130 chemicals identified in Table 8 of the Task 1 Report, due to the assessment completed by GSI. The 51 chemicals are listed in Table 9 of the Task 1 Report. As discussed in the Overview of the Preliminary Hazard Assessment section of this White Paper, the development of ad hoc surrogate values is a generally accepted approach upon adequately demonstrating that the data used is appropriate. All toxicity values and uncertainty factors are defined in the text and Table 9 of the Task 1 Report.

GSI reviewed the 181 chemicals and assigned biodegradation classifications based on a memorandum prepared by the Science Advisor to the Water Board, Dr. William Stringfellow. The biodegradation classifications consisted of “readily,” “inherently,” and “poorly” biodegradable. The biodegradation classification is based on the percent degradation of a specific constituent within 28 days. Biodegradation was identified, in the memorandum, as the primary step in screening based on the fate and transport of a chemical. Due to the memorandum prepared by the Science Advisor, GSI assigned biodegradation classifications to the 181 chemicals. The memorandum by the Science Advisor is in Appendix C of the Task 1 Report.

List of Chemicals of Interest

GSI conducted a preliminary hazard assessment of 399 chemicals. The 399 chemicals were assigned to one of five categories. Categories 1 – 4 state that the chemicals are either non-toxic or that there is insufficient data to evaluate the toxicity of the chemical. Category 5 consists of 179 chemicals that had toxicity data and/or comparative data readily available. The chemicals assigned to Category 5 are the chemicals that were considered for the Chemicals of Interest list.

The 179 chemicals were evaluated based on toxicity and biodegradation in water. Chemicals that had a toxicity comparison value of 0.5 mg/kg/day or less were considered to be of low concern for toxic effects at concentrations expected (or observed) in irrigated crops and were not designated as a chemical of interest. In addition, chemicals that were readily or inherently biodegradable were also removed from consideration of the Chemicals of Interest list. At the conclusion of GSI’s preliminary hazard assessment, 66 chemicals were identified as potentially toxic and poorly biodegradable. The 66 chemicals are listed in Table 3 below and Table 10 of the Task 1 Report.

Table 3 – Chemicals of Interest List

CASRN	Chemical	CASRN	Chemical
53-70-3	Dibenzo(a,h)anthracene	108-90-7	Chlorobenzene
50-32-8	Benzo(a)pyrene	120-12-7	Anthracene
119-65-3	Isoquinoline	129-00-0	Pyrene
111-44-4	Bis (2-chloroethyl) ether	64742-95-6	Solvent naphtha, petroleum, light arom.

CASRN	Chemical	CASRN	Chemical
7440-38-2	Arsenic	29868-05-1	Alkanolamine phosphate
205-99-2	Benzo(b)fluoranthene	206-44-0	Fluoranthene
193-39-5	Indenopyrene	16984-48-8	Fluoride
56-55-3	Benzo(a)anthracene	7664-39-3	Hydrofluoric acid
218-01-9	Chrysene	83-32-9	Acenaphthene
123-91-1	1,4 Dioxane	14797-65-0	Nitrite
7440-43-9	Cadmium	7440-62-2	Vanadium
7439-97-6	Mercury	7439-96-5	Manganese
7440-48-4	Cobalt	7446-09-5	Sulfur dioxide
7439-92-1	Lead	7440-42-8	Boron
7440-36-0	Antimony	12179-04-3	Sodium tetraborate pentahydrate
1309-64-4	Antimony trioxide	7440-39-3	Barium
7439-93-2	Lithium	7727-43-7	Barite
1310-65-2	Lithium hydroxide	7440-31-5	Tin
13453-71-9	Lithium chlorate	7440-66-6	Zinc
13840-33-0	Lithium hypochlorite	7646-85-7	Zinc chloride
554-13-2	Lithium carbonate	60-24-2	2-mercaptoethanol
7440-41-7	Beryllium	25265-78-5	Benzene, tetrapropylene-
7447-41-8	Lithium chloride	64742-53-6	Distillates, hydrotreated light naphthenic
7440-61-1	Uranium	126-97-6	Ethanolamine thioglycolate
7440-47-3	Chromium	115-19-5	2-methyl-3-Butyn-2-ol
7439-98-7	Molybdenum	68308-87-2	Cottonseed, flour
7782-49-2	Selenium	26027-38-3	Ethoxylated 4- nonphenol
7440-22-4	Silver	127087-87-0	Nonylphenol polyethylene glycol ether
7440-50-8	Copper	No CASRN	Nonylphenol ethoxylates
7553-56-2	Iodine	68412-54-4	Oxyalkylated alkylphenol
7758-99-8	Copper sulfate pentahydrate	2809-21-4	Hydroxyethylidenediphosphonic acid
7440-02-0	Nickel	68439-70-3	Alkyl amine
7786-81-4	Nickel sulfate	61790-41-8	Quaternary ammonium compound

The 66 chemicals identified in Table 3 were designated as the Chemicals of Interest and were further evaluated in Task 2.

Task 2 – Literature Review

The objective of Task 2 is to conduct a rigorous and thorough review of the available literature on produced water to irrigate crops and the potential occurrence of constituents from the Chemicals of Interest list. In addition to a literature review, Task 2 identified potential sources of Chemicals of Interest in the environment other than produced water, including natural sources. Sources for the literature review include government reports, peer reviewed scientific literature, and peer reviewed technical documents.

The Scope of Work for Task 2 is cited in the Referenced Material section of this White Paper.

Overview of the Literature Review

The literature review is a comprehensive review of the Chemicals of Interest list identified in Task 1. This provided a detailed summary of the state of knowledge for the chemicals potentially present in produced water used for irrigation. In addition, the results discuss the strengths and limitations of the existing knowledge.

The literature review will be guided by the approach of a Cochrane style review. The Cochrane style review includes the following steps: 1) Define a question and objective methods 2) Search for relevant data 3) Extract the relevant data 4) Assess the quality of the data, and 5) Analyze and combine the data.

Results of the Literature Review

In Progress

Overview of Alternate Sources of Chemicals of Interest

The final objective of Task 2 was to identify potential sources of constituents from the Chemicals of Interest list in the environment other than produced water, including natural sources. GSI examined an extensive array of potential sources, including herbicides, pesticides, fungicides, and chemicals used during the drilling of agricultural and domestic wells. In addition, GSI also conducted a review of the occurrence of these constituents in foodstuff in the context of normal and low-risk levels for food, and the transport and fate of the constituents in the environment in the context of beneficial reuse in agriculture.

Although this was not a comprehensive risk assessment, this section does provide risk context for the potential hazards identified in Task 1.

Results of Alternate Sources of Chemicals of Interest

In Progress

Task 3 – Crop Sampling and Analysis

The objective of Task 3 was to collect and analyze food crop samples from both test and control fields[2]. Analytical results were reviewed by the Panel, Water Board staff, GSI, and the Science Advisor to the Water Board. GSI prepared a technical report that summarized the results regarding the presence of Chemicals of Interest identified in the crop samples.

The Scope of Work for Task 3 is cited in the Referenced Material section of this White Paper.

Historical Crop Study

In 2016, Cawelo hired consulting firm Enviro-Tox Services, Inc., to conduct three independent evaluations of Cawelo's crops and irrigation water (Cawelo's Crop Study). The purpose of Cawelo's Crop Study was to evaluate whether petroleum related constituents are present in Cawelo's irrigation water and accumulating in the crops. Citrus, almonds, grapes, carrots, and pistachios grown in Cawelo were analyzed for volatile organic compounds and polycyclic aromatic hydrocarbons. The results of Cawelo's Crop Study stated that the constituents detected in crops grown with Cawelo's irrigation water were also found in crops grown with traditional irrigation water. Based on the analytical results, Cawelo's Crop Study concluded that consuming crops irrigated with Cawelo's water is safe.

Cawelo's Crop Study reports are cited in the Referenced Material section of this White Paper.

Overview of Crop Sampling

As part of the Food Safety Project, Water Board staff oversaw the sampling of crops grown with produced water (test samples), as well as crops grown with traditional sources (control samples). The purpose of the crop sampling study was to determine if there is a difference in the concentration of petroleum related constituents in test samples when compared to control samples. The samples were analyzed for a variety of constituents including volatile organic compounds, polycyclic aromatic compounds, metals, and general minerals. From 2017 through 2019, Water Board staff oversaw the collection of the following crop types for analysis:

- Citrus (e.g., lemons, oranges, and mandarins);
- Nuts (e.g., pistachios and almonds);
- Carrots;

[2] Test fields are cropland irrigated with produced water (blended with other supplies, or not). Control fields are croplands growing similar crops as the test fields in the same general geographic area, but which are not and have not been irrigated with produced water.

- Garlic;
- Grapes;
- Potatoes;
- Tomatoes;
- Apples; and
- Cherries.

Samples were collected by a third-party sampling consultant in accordance with a Sampling and Analysis Plan (SAP), which was prepared prior to the sampling events for each crop type. The SAP was reviewed by the Science Advisor, Permit Holders, and Water Board staff. The SAP contained specific procedures for collecting, handling, and analyzing each crop type. The procedures identified in the SAP were discussed with the Panel during working and public meetings to identify potential issues or alternate methods for collecting crop samples. Ultimately, the Panel, Science Advisor, and Water Board staff concurred with the sampling procedures described in the SAP for each crop type.

Generalized procedures for collecting samples stated that crops needed to be collected at least 100 feet into the field to minimize potential contamination from sources other than irrigation water. Also, crop samples were not to be damaged and needed to resemble what a consumer would encounter in an average store. In addition, samples were immediately placed in sample containers and stored in an ice chest for transportation. Crop samples remained in the possession of Water Board staff and were not relinquished until the ice chest was either mailed or delivered to the laboratory.

Crop samples from 2017 through May 2019 were mailed, by FedEx, to Weck Laboratories (Weck) in City of Industry, California. Starting July 2019, crop samples were submitted to Agricultural and Priority Pollutants Laboratories Inc., (APPL) in Clovis, California. Due to time delays receiving complete laboratory reports, the Water Board, Science Advisor, GSI, Panel, and Permit Holders agreed that changing laboratories from Weck to APPL was appropriate.

Crop Sample Results

In Progress

Discussion

Possible Contaminant Sources

Data Gaps

Recommendations from the Food Safety Expert Panel

Recommended Next Steps

Potential Triggers for Future Crop Sampling

Recommended Criteria

Recommended Changes

Conclusions

Referenced Material

1. Food Safety Expert Panel Project Charter. (May 2017) https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/information/offsep_charter.pdf.
2. Recordings and Meeting Summaries for Panel Meetings
    i. 28 October 2016
    ii. 21 April 2017
    iii. 28 June 2017
    iv. 7 November 2017
    v. 24 January 2018
    vi. 25 April 2018
    vii. 25 July 2018
    viii. 24 January 2019
    ix. 9 May 2019 https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety.
3. Memorandum of Understanding Between the Central Valley Regional Water Quality Control Board and the Permit Holders Governing the Solicitation, Management and Review of Academic, Technical and/or Scientific Studies Related to the Irrigation of Food Crops with Oil Field Produced Water. (June 2017) https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/2017_0627_offs_mou.pdf.
4. Attachment 1 of the MOU - Scope of Work for Tasks 1 and 2. (7 June 2018).
5. Oil Field Chemical Additive List. (June 2019) https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/data/2018_0628_additive_info.pdf.
6. Attachment 2 of the MOU – Scope of Work for Task 3. (7 June 2018)
7. Studies on behalf of Cawelo Water District:
    i. Irrigation Water Quality Evaluation (7 April 2016)
    ii. Citrus Crop Sampling & Analysis Report (11 October 2016)
    iii. Root Crop Sampling and Analysis Results (2 November 2016)

    https://www.cawelowd.org/recycled-produced-water/.