Hazard Assessment of Chemical Additives Used in Oil Fields that Reuse Produced Water for Agricultural Irrigation, Livestock Watering, and Groundwater Recharge in The San Joaquin Valley of California: Preliminary Results

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INTRODUCTION

Oil field produced water has been used to irrigate food crops in the Cawelo Water District since the mid-1990s. The practice has recently been expanded to the North Kern Water Storage District and produced water is being examined widely as a potential source of water for agriculture, livestock watering, drinking water and other uses. One important knowledge gap with respect to assessing potential human health and environmental hazards associated with reuse of oil field produced water for irrigation is an understanding of the types and amounts of chemical additives used during oil and gas development.

Disclosure of chemical use during oil and gas development is considered an important component for understanding the potential risks associated with hydraulic fracturing and other well stimulation activities and disclosure is an important component of creating effective regulation of hazardous chemicals. For instance, regulations developed under California Senate Bill 4 require the reporting and public disclosure of chemical additives used for hydraulic fracturing and other well stimulation activities common to oil and gas development. These disclosure requirements, however, do not apply to other common or routine oil and gas field activities such as drilling, well maintenance, routine acidizing, and well completions (State of California 2013). Hazardous chemicals are used throughout the entire oil and gas development process, not just during well stimulations (Economides et al. 2013; Fink 2015; Hudgins 1992; Hudgins 1994; Kelland 2014). Recent research shows that many of the same chemicals used in hydraulic fracturing and well stimulation are also used for other purposes in oil and gas development (Shonkoff et al. 2016; Shonkoff et al., under review).

The Central Valley Regional Water Quality Control Board (CVRWQCB) is investigating the use of produced water for agriculture and one of the issues being examined by the CVRWQCB and other stakeholders is how the use of chemicals for oil and gas production, including chemicals used in produced water management, may impact the quality and safety of produced water used for agriculture, including livestock watering, and recharging regional aquifers (CVRWQCB 2012).

To understand chemical use in fields that provide produced water for agricultural irrigation, livestock watering, and recharging aquifers, under the authority of the California Water Code section 13267, the CVRWQCB ordered seven California oil and gas operators (Chevron USA, Inc.; Valley Water Management Company; California Resources Production Corporation; Bellaire Oil Company; Hathaway, LLC; Little Creek Properties/Daybreak Oil and Gas, Inc.; and Modus, Inc.) to provide information regarding chemical use in the oil and gas fields that provide produced water for crop irrigation and livestock watering in the Cawelo Water District and the North Kern Water Storage District in the San Joaquin Valley pursuant to section 13267 of the California Water Code. The resulting chemical disclosures included information from oil and gas development operations in the Deer Creek, Mount Poso, Jasmin, Kern Front, and Kern River oil fields from the period of January 2014 to June 2016. This information included the types and amounts of chemical additives used in oil and gas development operations as well as the volume of produced water provided for irrigation.

Here we report the preliminary findings of our analysis of the chemical data disclosed in response to the 13267 orders from the CVRWQCB. In this preliminary analysis, we provide the list of chemicals reported in the context of their acute mammalian and ecological toxicities, biodegradability, bioaccumulation potential, carcinogenicity, and whether chemicals are included on specific chemical priority lists. The purpose of this analysis is to identify potential chemicals of concern as a first step prior to more complete human health and environmental hazard and risk analyses. Actual hazards associated with a chemical are dependent on numerous factors, including the mass of chemical used, the physical properties of the chemical, and many other variables that are not explored in this report of preliminary findings. Assessing the risks associated with chemical use (e.g., the probability that a chemical or group of chemicals will cause harm) requires an understanding of the frequency, mass, and context of chemical use, including potential exposure pathways, and is beyond the scope of this short technical report of preliminary findings.

The findings of this report belong to the co-authors and do not necessarily represent the opinions of the Food Safety Expert Panel convened by the Central Valley Regional Water Quality Control Board in California, or any other party.

METHODS

Data collected under the authority of the California Water Code section 13267 by the CVRWQCB from Chevron USA, Inc.; Valley Water Management Company; California Resources Production Corporation; Bellaire Oil Company; Hathaway, LLC; Little Creek Properties/Daybreak Oil and Gas, Inc.; and Modus, Inc. was downloaded from the Oil Fields – Food Safety website[1] for analysis. The disclosures included operations in the Deer Creek, Mount Poso, Jasmin, Kern Front, and Kern River oil fields from the period of January 2014 to June 2016.

[1] http://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/index.shtml

Chemical entries were edited to standardize chemical names and to validate the assigned Chemical Abstracts Services Registry Number (CASRN). Changes to names of proprietary chemicals that could not be identified by CASRN were limited to correcting obvious spelling errors, changing capitalization, and altering punctuation. For chemical constituents identified with unique CASRN, physical, chemical, and toxicological data were collected from material safety data sheets (MSDS) and various online chemical databases including: U.S. National Library of Medicine TOXNET, Japan's National Institute of Technology and Evaluation Chemical Risk Information Platform, U.S. EPA's ECOTOX, U.S. EPA's Aggregated Computational Toxicology Resource (ACToR), European Chemical Agency's International Uniform Chemical Information Database (IUCLID), American Chemical Society's SciFinder, and International Agency for Research on Cancer (IARC) Monographs. Computational estimates from U.S. EPA EPISuite software were used to fill in data gaps when available.

In addition to chemical, physical, and toxicological properties, the disclosed chemicals were compared to various state, federal, and international lists of chemicals of concern. These lists included the California Proposition 65 Chemicals Known to the State of California to Cause Cancer or Reproductive Toxicity List, European Union REACH Substances of Very High Concern (SVHC) Candidate and Authorization Lists, U.S. EPA National Primary Drinking Water Standards (NPDWS) and Advisory Chemicals, U.S. EPA Contaminate Candidate List 4 (CCL4), California EPA Toxic Air Contaminant List (TAC), U.S. EPA Clean Air Act Hazardous Air Pollutant List, and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) Substances that Pose Little or No Risk (PLONOR) to the environment, Substances of Possible Concern, and Priority Action Chemicals lists.

Rat, mouse, and rabbit acute oral toxicity data were collected to represent mammalian toxicity; and data for water flea (*Daphnia magna*), fathead minnow (*Pimephales promelas*), rainbow trout (*Oncorhynchus mykiss*), and green algae were collected to represent ecotoxicity. All green algae toxicity data were computational estimates from U.S EPA's EPISuite software. Toxicity ratings were assigned according to the United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals (United Nations 2015) for acute toxicity and acute ecotoxicity hazards. In the GHS system, lower numbers indicate higher toxicity, with a designation of "1" indicating the most toxic category.

Biodegradability data were categorized according to OECD criteria for biodegradability (OECD 1992). Bioconcentration-factor (BCF) data were calculated using U.S. EPA EPISuite software and categorized according to U.S. EPA criteria for bioaccumulation (Federal Register 1999).

RESULTS & DISCUSSION

A total of 173 chemical constituents were identified by unique name or CASRN. Of these 173 chemicals, 66 (38%) were classified as "trade secret" or did not have an associated valid CASRN and could not be positively identified. The remaining 107 chemicals (62%) were identified by CASRN, a definitive identifier, and could therefore be further evaluated for physical, chemical, and toxicological properties.

An evaluation of acute toxicity data (Table 1) shows that only five chemicals were classified GHS category 2 for oral mammalian toxicity and no chemicals were GHS category 1, the most toxic category. In contrast, a total of 39 chemicals (36%) were classified as GHS category 1 or 2 for ecotoxicity, indicating that the chemicals may pose a significant hazard to aquatic environments. Fourteen chemicals (13%) had no available ecotoxicity or mammalian toxicity data and could not be ranked or evaluated (Table 2). Chemicals without published toxicity data should be evaluated further.

Table 1. Summary of the numbers of chemicals with available toxicity data and a CASRN in each GHS toxicity category

	Acute Oral Mammalian Toxicity GHS (rat, mouse, and rabbit)	Acute Ecotoxicity GHS (*Daphnia magna*, fathead minnow, rainbow trout, and green algae [computational])
GHS 1	0	18
GHS 2	5	21
GHS 3	11	15
GHS 4	22	-
GHS 5	19	-
> GHS 5*	22	34
No data	28	19
Total	107	107

*Greater than GHS 3 for ecotoxicity values

Of the 107 chemicals with CASRN, eight appeared on California's Prop 65 list, eight were on the U.S. EPA NPDWS and Health Advisory Chemical list, three were on the U.S. EPA CCL4, twenty-two were on the California EPA Toxic Air Contaminant list, and eleven are considered hazardous air pollutants according to the Clean Air Act (Table 3). A total of ten chemicals were classified by the International Agency for Research on Cancer (IARC) as either carcinogenic or possibly carcinogenic in humans (Table 4). Inclusion on these lists suggests that these chemicals are recognized as being hazardous and subject to regulatory control under at least some circumstances.

Table 2. Chemicals with a CASRN for which no ecotoxicity or mammalian toxicity data was found.

Chemical Name	CASRN
Aluminum chloride hydroxide	12042-91-0
Gypsum	13397-24-5
Lignite	1415-93-6
Xenon radionuclide	14932-42-4
Silica, crystalline, tridymite	15468-32-3
Aluminum stearate	300-92-5
Lithium chlorate	36355-96-1
Polyamine	64114-46-1
Coke, petroleum, calcined	64743-05-1
Cottonseed hulls	68308-87-2
Fatty acid oxyalkylate	70142-34-6
Krypton	7439-90-9
Hydroxyethyl cellulose	9004-62-0
Cellophane	9005-81-6

Table 3. Chemicals with a CASRN that are on National and State Priority Lists

Chemical Name	CASRN	California Prop 65	EPA NPDWS and Health Advisory Chemical	EPA CCL4	CA EPA Toxic Air Contaminant List*	Clean Air Act Hazardous Pollutant
Ethylbenzene	100-41-4	X	X		2a	X
Ethylene glycol	107-21-1	X	X	X	2a	X
Toluene	108-88-3	X	X		2a	X
Antimony trioxide	1309-64-4	X			2a	
Lithium carbonate	554-13-2	X				
Methanol	67-56-1	X		X	2a	X
Naphthalene	91-20-3	X	X		2a	X
Cumene	98-82-8	X	X		4a	X
1,3,5 Trimethylbenzene	108-67-8		X			
Xylene	1330-20-7		X		2a	X
1,2,4 Trimethylbenzene	95-63-6		X		4b	
Acrolein	107-02-8			X	2a	X
Glutaraldehyde	111-30-8				2b	
2-Butoxyethanol	111-76-2				2a	
Hydroquinone	123-31-9				4a	X
Sodium hydroxide	1310-73-2				2b	
Isopropanol	67-63-0				2b	
Amorphous silica	7631-86-9				3	
Hydrochloric acid	7647-01-0				2a	X
Phosphoric acid	7664-38-2				2b	
Hydrofluoric acid	7664-39-3				2a	X
Sulfuric acid	7664-93-9				2b	
Ammonium sulfate	7783-20-2				4b	
Peroxyacetic acid	79-21-0				4b	

*CA EPA Toxic Air Contaminant List Categories:

2a: Substances identified as Toxic Air Contaminants, known to be emitted in California, with one or more health values under development by the Office of Environmental Health Hazard Assessment (OEHHA) for review by the Scientific Review Panel.
2b: Substances NOT identified as Toxic Air Contaminants, known to be emitted in California, with one or more health values under development by the OEHHA for review by the Scientific Review Panel.
3: Substances known to be emitted in California and are NOMINATED for development of health values or additional health values
4a: Substance identified as Toxic Air Contaminants, known to be emitted in California and are TO BE EVALUATED for entry into Category III.
4b: Substance NOT identified as Toxic Air Contaminants, known to be emitted in California and are TO BE EVALUATED for entry into Category III.

Table 4. Chemicals with a CASRN categorized as carcinogenic or possibly carcinogenic by the IARC

Chemical Name	CASRN	IARC Group	IARC Meaning
Crystalline silica (quartz)	14808-60-7	1	Carcinogenic to humans
Xenon radionuclide	14932-42-4	1	Carcinogenic to humans
Silica, crystalline, tridymite	15468-32-3	1	Carcinogenic to humans
Ethanol	64-17-5	1	Carcinogenic to humans
Sulfuric acid	7664-93-9	1	Carcinogenic to humans
Nickel sulfate	7786-81-4	1	Carcinogenic to humans
Ethylbenzene	100-41-4	2B	Possibly carcinogenic to humans
Antimony trioxide	1309-64-4	2B	Possibly carcinogenic to humans
Naphthalene	91-20-3	2B	Possibly carcinogenic to humans
Cumene	98-82-8	2B	Possibly carcinogenic to humans

Twenty-five chemicals (23%) were found on the OSPAR Commission List of Substances that Pose Little or No Risk (PLONOR) to the environment (Table 5). OSPAR is a treaty governing oil and gas development in the North Sea (OSPAR 2016) and chemicals on the PLONAR list are allowed for use during off-shore development and may be discharged with produced water at low concentrations to marine environments with no expected negative impacts. These chemicals are primarily inert minerals, salts, and readily biodegradable substances. However, it is important to note that the OSPAR list was developed for discharge into saline, marine environments and may not be directly applicable to irrigation, livestock watering, groundwater recharge, and other reuse practices that may have different human and environmental consequences. For instance, methanol and ethylene glycol are on the OSPAR list, but also are found on National and State Priority lists (Table 3).

Table 5. Chemicals on the OSPAR List of Substances that Pose Little or No Risk (PLONOR) to the Environment

Chemical Name	CASRN	Chemical Name	CASRN
Ammonium bisulfate	10192-30-0	Methanol	67-56-1
Ethylene glycol	107-21-1	Isopropanol	67-63-0
Xanthan gum	11138-66-2	Potassium chloride	7447-40-7
Ammonium chloride	12125-02-9	Amorphous silica	7631-86-9
Sodium acetate	127-09-3	Sodium chloride	7647-14-5
Bentonite	1302-78-9	Citric acid	77-92-9
Sodium bicarbonate	144-55-8	Sodium sulfate	7757-82-6
Crystalline silica (quartz)	14808-60-7	Disodium dihydrogen diphosphate	7758-16-9
Calcium carbonate	471-34-1	Graphite	7782-42-5
Sodium carbonate	497-19-8	Carboxymethyl cellulose sodium salt	9004-32-4
Urea	57-13-6	Cellulose	9004-34-6
Ethanol	64-17-5	Hydroxyethyl cellulose	9004-62-0
Acetic acid	64-19-7		

The OSPAR Commission and other European agencies also have lists of banned chemicals or chemicals of concern (ChemSafetyPro 2016). No chemicals reported under the 13267 order appeared on the OSPAR List of Substances of Possible Concern, the OSPAR List of Chemicals for Priority Action, or the European Chemicals Agency Candidate List of Substances of Very High Concern for Authorization.

Biodegradability is a major determinant for environmental persistence of chemical compounds, and it is known that that chemicals susceptible to rapid biodegradation are less likely to cause long term environmental impacts if released into the environment. The biodegradability of organic chemicals can be measured and compared using standardized tests (e.g. 40 CFR 796.3100 - Aerobic aquatic biodegradation). Of the 107 chemicals with CASRN, 40 were classified as inorganic and were not evaluated using standard organic chemical biodegradation protocols. The majority of the organic chemicals for which data could be found were biodegradable, but twelve chemicals were determined to be resistant to biodegradation (not readily biodegradable) and three were found to be not biodegradable in the standard aerobic test (Table 6). Of the compounds found to be non-biodegradable in standardized tests, scientific literature suggests that the trimethylbenzene isomers should biodegrade eventually in the environment (e.g. Häner *et al*. 1997). In addition, bioconcentration-factor data, a standard measure for bioaccumulation potential, was available for 86 chemicals, of which only one fell in the bioaccumulative range. The remaining 85 chemicals were classified as non-bioaccumulative (Table 7). These results suggest that most additives that could be characterized are unlikely to persist or accumulate in the environment if released, but some compounds should be further evaluated for persistence and bioaccumulation in the environment. Standardized measurements should be made on chemicals that are not yet characterized. We were unable to evaluate the biodegradation and bioaccumulative properties of those chemicals that lacked a disclosed CASRN.

Table 6. Summary of available biodegradability data

Category	Count
Readily Biodegradable	34
Inherently Biodegradable	4
Biodegradable	2
Not readily biodegradable	12
Non-biodegradable	3
Inorganic	40
No Data	12

A separate list of chemicals approved by Chevron and California Resources Corporation (CRC) for use their oil and gas operations that provide produced water for irrigation was provided by the Central Valley Regional Water Quality Control Board in California. This list contained a total of 108 chemicals, 72 of which were identified by unique CASRN. When these two lists were cross referenced, only 52 chemicals with CASRN appeared on both lists.

Table 7. Bioconcentration-factor categorization

Category	Criteria (BCF)	Count
Non bioaccumulative	<1000	85
Bioaccumulative	1000-5000	1*
Very bioaccumulative	≥5000	0

*The one chemical is Siloxanes and Silicones (63148-62-9)

Table 8 is a list of potential chemicals of concern identified through this initial screening process. This list contains the chemicals with GHS 1 ecotoxicity, GHS 2 mammalian toxicity, California Proposition 65, IARC Groups 1 and 2b, NPDWS, non-biodegradable, and bioaccumulative chemicals identified in our analysis. Since the focus of this analysis is on water, we excluded CA EPA TAC and Clean Air Act Chemicals unless they met one of the other criteria for inclusion. Hydrofluoric acid was also included on the potential chemicals of concern list as it is classified as a GHS 1 hazard based on mammalian inhalation toxicity. Inhalation toxicity analysis was otherwise left of out of this preliminary chemical screen, but has been included as a criteria in previous studies (Stringfellow *et al.* 2015). Finally, chemicals with no toxicity data available that were minerals (lignite, gypsum) or not expected to be toxic (hydroxyethyl cellulose, krypton, cottonseed hulls) were not included in Table 8. Chemicals that did not have a unique CASRN or are marked as trade secrets are also of potential concern given the lack of information available for a hazard assessment.

Table 8. Oil and gas field chemical additives with CASRN identified by preliminary analysis as potential chemicals of concern. The last column on the right indicates why they appear on this table.

Name	CASRN	Why compound appears on table*
Ethylbenzene	100-41-4	Prop 65, NPDWS, IARC 2B, CA TAC, CAA
Ethylene glycol	107-21-1	Prop 65, NPDWS, CCL4, CA TAC, CAA
Toluene	108-88-3	Prop 65, NPDWS, CA TAC, CAA
Antimony trioxide	1309-64-4	Prop 65, IARC 2B, CA TAC
Lithium carbonate	554-13-2	Prop 65
Methanol	67-56-1	Prop 65, CCL4, CA TAC, CAA
Naphthalene	91-20-3	Prop 65, GHS1 ECO, IARC 2B, NPDWS, CA TAC, CAA
Cumene	98-82-8	Prop 65, IARC 2B, NPDWS, CA TAC, CAA
Xylene	1330-20-7	NPDWS, CA TAC, CAA
1,3,5 Trimethylbenzene	108-67-8	Non-biodegradable[§], NPDWS
Isoquinoline	119-65-3	Non-biodegradable[§]
1,2,3 Trimethylbenzene	526-73-8	Non-biodegradable[§], NPDWS
Siloxanes and silicones	63148-62-9	Bioaccumulative, GHS1 ECO
Glutaraldehyde	111-30-8	GHS1 ECO, CA TAC
Hydroquinone	123-31-9	GHS1 ECO, CA TAC, CAA
Lithium hypochlorite	13840-33-0	GHS1 ECO
Sodium dichloroisocyanurate	2893-78-9	GHS1 ECO
Heavy aromatic naphtha	64742-94-5	GHS1 ECO
Iodine	7553-56-2	GHS1 ECO
Zinc chloride	7646-85-7	GHS1 ECO
Hydrochloric acid	7647-01-0	GHS1 ECO, CA TAC, CAA
Sodium hypochlorite	7681-52-9	GHS1 ECO
Copper sulfate pentahydrate	7758-99-8	GHS1 ECO
Hydrotreated light distillate	64742-47-8	GHS1 ECO
Stearic acid	57-11-4	GHS1 ECO
Kerosene	8008-20-6	GHS1 ECO
Dinonylphenyl polyoxyethylene	9014-93-1	GHS1 ECO
Acrolein	107-02-8	GHS2 MAM, GHS1 ECO, CCL4, CA TAC, CAA
Propargyl alcohol	107-19-7	GHS2 MAM
Cyclohexylamine	108-91-8	GHS2 MAM
Ethyl acetate	141-78-6	GHS2 MAM
Stoddard solvents	8052-41-3	GHS2 MAM, GHS1 ECO
Crystalline silica (quartz)	14808-60-7	IARC 1
Xenon radionuclide	14932-42-4	IARC 1, No toxicity data
Silica, crystalline, tridymite	15468-32-3	IARC 1, No toxicity data
Ethanol	64-17-5	IARC 1
Sulfuric acid	7664-93-9	IARC 1, CA TAC
Nickel sulfate	7786-81-4	IARC 1
Hydrofluoric acid	7664-39-3	CA TAC, CAA
Aluminum chloride hydroxide	12042-91-0	No toxicity data
Aluminum stearate	300-92-5	No toxicity data
Lithium chlorate	36355-96-1	No toxicity data
Polyamine	64114-46-1	No toxicity data
Coke, petroleum, calcined	64743-05-1	No toxicity data
Fatty acid oxyalkylate	70142-34-6	No toxicity data
Cellophane	9005-81-6	No toxicity data

*GHS1 ECO = GHS Category 1 for Acute Ecotoxicity

GHS2 MAM = GHS Category 2 for Acute Mammalian Oral Toxicity
IARC 1 = International Agency for Research on Cancer Group 1 (Carcinogenic to humans)
IARC 2B = International Agency for Research on Cancer Group 2B (Possibly carcinogenic to humans)
NPDWS = U.S. EPA National Primary Drinking Water Standards and Health Advisory Chemical
CCL4 = U.S. EPA Contaminant Candidate List 4
Prop 65 = California Proposition 65
CA TAC = CA EPA Toxic Air Contaminant
CAA = Clean Air Act Hazardous Pollutant
§Found non-biodegradable in standard aerobic test.

SUMMARY

In this preliminary assessment, we evaluated the list of chemicals reported as used in oil fields from which produced water is deployed for irrigation, for watering livestock, and for recharging groundwater in the San Joaquin Valley of California. We found a total of 173 different chemical additives were used in these oil and gas fields, of which more than one-third (38%) were not able to be sufficiently identified for preliminary hazard evaluation, largely due to the withholding of information under proprietary claims. Over 100 chemicals (62% of the total list) were identified by CASRN for acute toxicological properties, biodegradability, and environmental persistence using publically available data and toxicological screening software. The CASRN identified oil and gas field additives were also cross-referenced with a variety of lists used to identify or regulate chemicals suspected or known to cause negative environmental or health impacts if released into the environment. Of the chemicals that had a CASRN, we found that 46 (43%) of them can be classified as potential chemicals of concern from human health and/or environmental perspectives and require a more thorough investigation (Table 8).

RECOMMENDED NEXT STEPS

Standardized measurements for toxicity and environmental persistence, including biodegradability, should be made on all chemicals that are not yet characterized. Our analysis suggests that most additives that could be characterized are unlikely to persist or accumulate in the environment if released, but some compounds need to be further evaluated for persistence and bioaccumulation. In addition to acute toxicity data, chronic toxicity data should be collected for all chemicals and analyzed to assess potential longer-term human health or environmental hazards associated with the use of oil field produced water for agricultural irrigation, livestock watering, and aquifer recharge. Screening chemical constituents for other attributes that may cause human health or environmental impacts, such as endocrine disrupting activity should also be considered.

Future analysis should evaluate the mass and frequency of chemical use, which is an important determinant of both hazard and risk (Shonkoff *et al.* 2015; Stringfellow, *et al.* 2015). The chemical disclosures evaluated in this study frequently provided chemical constituent concentrations and chemical usage data on a volumetric basis, however density values are also needed for mass calculations. We recommend that the *mass* of each chemical used be provided by the operators as part of disclosures, to avoid miscommunication and possible error in determining how much of each chemical additive is used in the oil and gas fields.

We did not evaluate chemicals that were not identified by CASRN and the use of proprietary chemicals should be further evaluated. It is difficult or impossible to estimate risks to consumers, farmworkers, or the environment, when identification of chemical additives remains in trade secret form and/or lacks toxicity and environmental profile information.

Hazardous chemical are only a risk if they are released into the environment in sufficient quantities to cause harm and have a pathway to reach sensitive receptors, such as animals or humans. Hazardous chemicals potentially found in produced water include both the oil field chemical additives, identified here, and naturally occurring contaminants such as metals and hydrocarbons that originate from the geological reservoir. In order to identify potential pathways for environmental release and exposure, it is recommended that a literature review be conducted to establish what is known about the fate and transport of these contaminants, especially in the context of agricultural ecosystems. It is recommended that a thorough literature review include chemical uptake by crops and livestock. The review should be interpreted specifically in the context of current produced water reuse practices in California.

Oil field produced water is being used to recharge aquifers to maintain regional groundwater supplies for agriculture, however regional aquifers can also be used for domestic water supply (including drinking water). Given the direct nature of this potential human exposure pathway, further investigation of the use of produced water for groundwater recharge is warranted. This investigation could include a scientific analysis of existing data combined with field studies as needed.

Many of the chemicals used on oil fields do not have standard analytical protocols for their detection in water, so current water quality monitoring programs are mainly focused on naturally occurring contaminants (e.g. hydrocarbons, metals). It is recommended that standard methods for the analysis of oil field chemicals be developed and validated for use in water quality monitoring. The development of monitoring tools would be a useful step for insuring adequate protections are in place. Methods for monitoring these chemicals in soils and crops may also be needed if an analysis of pathways suggest the potential for crop uptake.

Finally, naturally occurring chemical constituents and chemical additives when combined in various surface and subsurface oil and gas development and produced water processing activities may interact under envrionments of elevated temperatures and pressures to form new substances. An investigation beyond the individual chemical constituents to evaluate chemical hazard and risk attributable to these synergistic products may also be warranted.

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