Preliminary Hazard Assessment of Chemical Additives Used in Oil Fields that Reuse Produced Water for Irrigation

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Outline

- Background & Objectives
- Dataset
- Methods
- Results
- Summary and Future Recommendations

Produced Water

- During oil & gas production water is produced with hydrocarbons
- Amount varies by many factors
  - Gas vs. oil fields, reservoir geology, age of reservior
  - Production methods
    - Water flooding, etc.
- Reuse of produced water for irrigation, livestock, and groundwater recharge
- Interest in regional reuse practices & nationwide
  - Wyoming, Texas

Water Quality Challenges to Beneficial Reuse of Produced Water

- Naturally occurring inorganic compounds
  - TDS, boron, arsenic, sulfate, calcium, etc.
- Naturally occurring organic compounds
  - Total oil & grease, BTEX, etc.
- Anthropogenic inorganic compounds
  - Phosphates, boron, copper, etc.
- Anthropogenic organic compounds
  - Surfactants, biocides, etc.

Objective

- Survey chemical use on oil fields where produced water is used for agriculture in California
  - “Anthropogenic organic & inorganic chemicals”
- Conduct a preliminary HAZARD ANALYSIS of chemicals used on oil fields
  - Hazard analysis is a first steps in a RISK ASSESSMENT, which is a more complete analysis of chemical constituents, their concentrations, and environmental and human exposure pathways
- Identify data gaps
- Identify specific chemicals for further investigation

Dataset Summary

- Data collected under authority of California Water Code section 13267 by CVRWQCB
  - Chemical additive data from seven operators that provide produced water for reuse in California
    - Chevron, Valley Water Management Company, California Resources Production Corporations, Bellaire Oil Company, Hathaway, Modus, and Little Creek Properties/Daybreak Oil and Gas
  - Period of Jan 2014 – June 2016
  - Operations spanned five oil fields
    - Deer Creek, Mount Poso, Jasmine, Kern Front, and Kern River oil fields
  - Chemical identification data with limited volume and mass data

Methods

- Characterized chemicals for physical, chemical, biological, and toxicological properties
  - Approach used in several prior studies
    - Camarillo, et al., 2016, *J. Environ. Management* 183: 164
    - Stringfellow et al., 2016, *Environ. Pollution* (in press)
    - Stringfellow et al., 2014, *J. Hazardous Materials* 275: 37
- Utilized various publically available databases including:
  - ChemIDplus, TOXNET, SciFinder, InChem, IUCLID, ECOTOX, NITE-CHRIP, ACToR
- Filled in experimental data gaps with computational models from U.S. EPA Estimation Programs Interface Suite (EPISuite)

Methods

- Chemical toxicity was rated according to United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals
  - Lower numbers indicate higher toxicity
  - Designation of “1” is the most toxic
- Biodegradability was categorized according to OECD criteria for biodegradability
- Bioconcentration factor was calculated using U.S. EPA EPISuite Software and categorized according to U.S. EPA criteria for bioaccumulation

Dataset

Total Chemicals	Chemicals without CASRN	Chemicals with CASRN
173	66 (38%)	107 (62%)

- Chemicals without Chemical Abstract Services Registry Numbers (CASRN) could not be definitively identified and no further chemical analysis could be done on these chemicals
- The following analyses focus on the remaining 107 chemicals with valid CASRNs

Results – Acute Toxicity

	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

- A total of 14 chemicals with CASRNs had no available mammalian or ecotoxicity data
- 5 chemical additives are categorized as “category 1 and 2” in the Globally Harmonized System (GHS) for mammalian toxicity
- 39 chemical additives are categorized as “category 1 and 2” in the Globally Harmonized System (GHS) for ecotoxicity

Results - Biodegradation

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

Additional Analysis

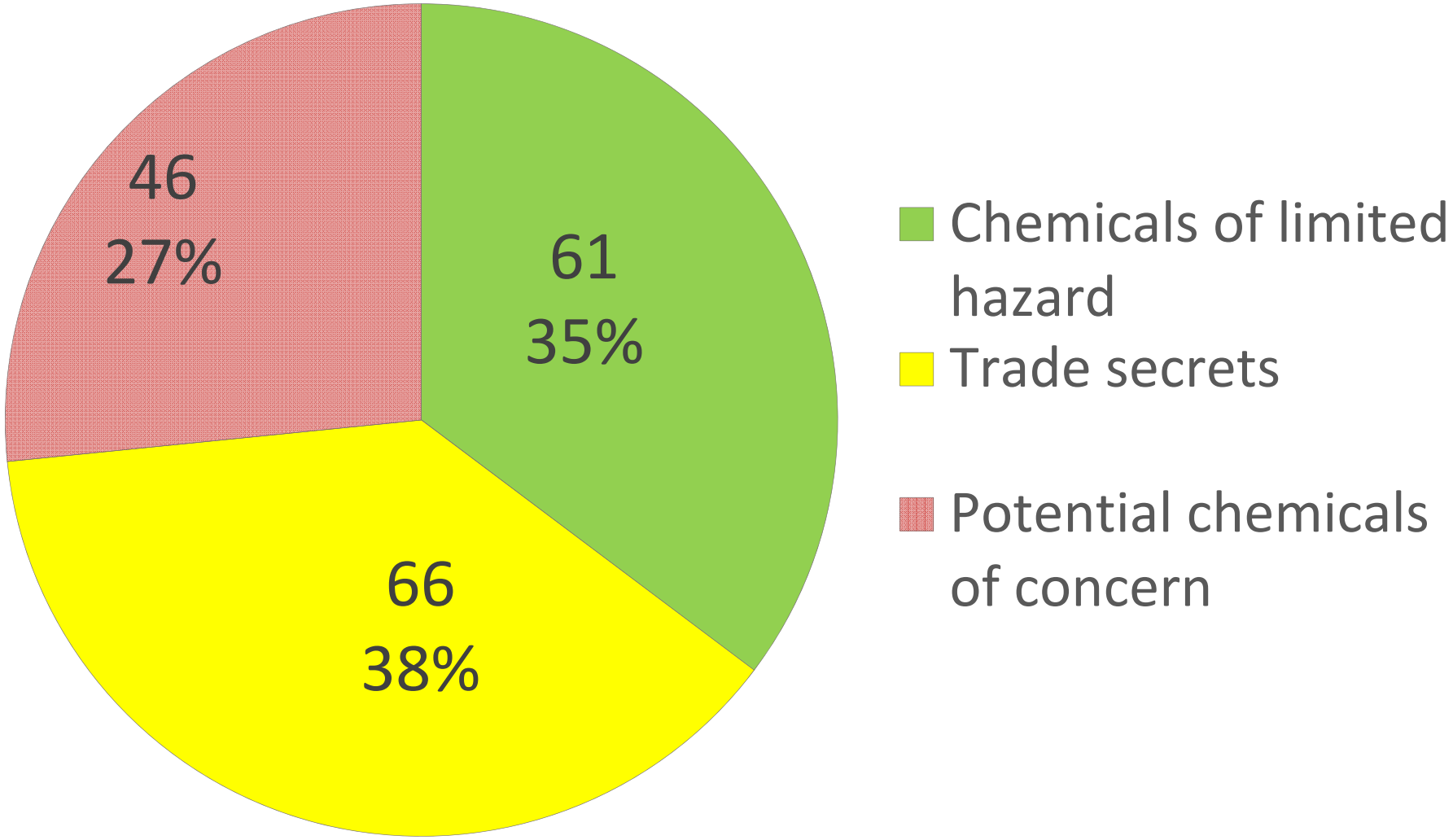
- Bioconcentration factor data available for 86 chemicals, of which only 1 was considered **bioaccumulative**
- 8 chemical additives are on the **California Proposition 65 List**
- 8 chemical additives are on the list of **U.S. EPA National Primary Drinking Water Standard and Health Advisory chemicals**
- 10 chemical additives are classified by the **International Agency for Research on Cancer** as carcinogenic or possibly carcinogenic in humans
- 11 chemical additives are considered hazardous air pollutants according to the **Clean Air Act**

Potential Chemicals of Concern

- Chemicals must have met one of the following criteria:
  - GHS Category 1 ecotoxicity
  - GHS Category 2 mammalian toxicity
  - California Prop 65 chemical
  - IARC Group 1 (carcinogenic) or 2b (possibly carcinogenic)
  - Non-biodegradable
  - Bioaccumulative (bioconcentration factor >1000)
  - U.S. EPA National Primary Drinking Water Standards or Health Advisory Chemical
  - No available toxicity data
    - Chemicals without toxicity data that were not expected to be toxic (e.g. food additives, minerals, inert gasses) were omitted

Preliminary Hazard Summary

173 total chemical additives were disclosed



Potential Chemicals of Concern

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
Chlorinating compound	2893-78-9	GHS1 ECO
Heavy aromatic naphtha	64742-94-5	GHS1 ECO
Iodine	7553-56-2	GHS1 ECO

Potential Chemicals of Concern

Name	CASRN	Why compound appears on table
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

Potential Chemicals of Concern

Name	CASRN	Why compound appears on table
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

*Hydrofluoric acid was added to the table due to proven inhalation toxicity, which was not included in the preliminary report

Study Limitations

- Potential chemicals of concern were not prioritized due to the lack of mass data
  - Potential risks and impacts are dependent on chemical mass & concentrations
  - Current disclosed data contains volume without corresponding density data
  - Mass data is vital for hazard and risk analysis
- Cannot analyze “trade secret” chemicals (38% of all chemicals reported) without disclosure of CASRNs
- Chronic toxicity data was not analyzed
  - Chronic toxicity data is more representative of potential exposure; however, it is less available than acute toxicity data
- Endocrine disrupting compounds (EDCs) were not evaluated
- Chemical mixtures & degradation products were not assessed

Recommended Next Steps

- Collect chemical additive mass and frequency of use data for hazard analysis (data gap)
  - Needed to identify any problem compounds & set priorities for testing, treatment, etc.
- Identify chemicals reported without CASRN & conduct hazard analysis (data gap)
- Conduct systematic scientific investigation examining the beneficial reuse of produced water in the agricultural sector
  - Examine both “natural & anthropogenic” chemicals
  - Combine literature review, analysis of practices in other states, and novel scientific studies (field & laboratory)

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Full technical report can be found at:
http://www.psehealthyenergy.org/site/view/1306

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