

**Measurement of Produced Water Air Emissions from
Crude Oil and Natural Gas Operations**

Final Report

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California Air Resources Board

Field Work Completed By:
Dr. Charles Schmidt
Thomas R. Card, P.E.

California Air Resources Board
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Chapter 1 -- Executive Summary

California is a major producer of oil and gas resources, ranking 7th in the U.S. in crude oil production during 2018. These operations produce large volumes of a liquid by-product called “produced water,” which usually contains much higher concentrations of total dissolved solids (TDS) and volatile organic compounds (VOC) than are acceptable for most beneficial uses, such as drinking water or irrigation. Therefore, operators must establish produced water disposal methods. In California, one method of disposal is transport to a produced water pond facility where residual oil is removed and water is stored in unlined earthen pits, called ponds. The water is able to either evaporate into the air or percolate into the ground. These produced water pond facilities can be a source of air pollutants, including greenhouse gases, VOCs, and toxic air contaminants (TACs). This study aims to better understand and quantify these emissions.

The California Air Resources Board (CARB) entered into an agreement with Charles E. Schmidt on June 30, 2017 titled “**Measurement of Produced Water Air Emissions from Crude Oil and Natural Gas Operations**” to quantify emissions of VOCs, TACs, and methane from produced water in California. Analytical methods used to determine emissions include the United States Environmental Protection Agency (U.S. EPA) Flux Chamber Method combined with U.S. EPA Methods TO-14/15 and ASTM 1945 for gas composition analyses and U.S. EPA Methods 1664 and 8260b for liquid composition analyses. A total of 123 samples were collected during the study: 95 gas phase and 95 liquid phase sample pairs were collected from 25 facilities throughout California. In addition, 28 sample pairs were collected to meet QA/QC objectives.

The study was conducted in two phases. In Phase 1 (screening), the objective was to obtain many data points from produced water ponds statewide and to characterize how produced water emissions vary regionally. Produced water pond facilities in Phase 1 were selected based on proximity to population, geographical region (southern, central, and northern California), and by operator (small, medium, and large) to ensure samples are representative of facilities within the state.

In Phase 2 (characterization), the objective was to select the highest emitting facilities near populated areas based on the data collected in Phase 1 for further air and water testing. The selected pond facilities were tested multiple times throughout the year to account for potential seasonal variability and to characterize changes in air and water among ponds within a single facility.

A summary of the study is included in Table 1.1 detailing all trip dates, number of samples collected, and identification nomenclature of facilities tested.

Table 1.1: Summary of study activities. Nomenclature uses the Regional Water Quality Control Board (RWQCB) region name as a modifier.

DATES	TRIP #	PHASE	SAMPLES COLLECTED	ID OF FACILITIES TESTED
9/26/17 - 9/28/17	1	1	15	R5S7, R5S8, R5S9, R5S10, R5S11, R5S12, R5S13
10/10/17 – 10/12/17	2	1	15	R5S1, R5S1B, R5S2, R5S3, R5S4, R5S5, R5S6,
11/01/17	3	1	8	R3S4, R3S5, R3S6, R3S8, R3S9
1/18/18	4	1	5	N3, N5, N6, N8, N10,
4/10/18 – 4/11/18	5	2	20	R5S1, R5S1B, R5S3, R5S4,
7/31/18 – 8/02/18	6	2	21	R4S1*, R5S1, R5S1B, R5S3, R5S4
10/03/18	7	2	11	R5S1, R5S3, R5S4
		TOTAL	95**	

*Facility R4S1 was intended to be sampled during phase 1. However, due to scheduling constraints, it was sampled during phase 2.

**Sample count does not include QA/QC samples.

The data collected through testing of air samples in Phase 1 was used to calculate the potential to emit (PTE) at each facility. PTE was estimated by applying the measured air flux to the pond surface area at full capacity (i.e. every available pond at a facility is full to capacity with produced water). PTE was estimated for the total non-methane hydrocarbons (TNMHC), methane, and total benzene, toluene, ethylbenzene, and xylene (BTEX) compound groups, and was used to decide which facilities to revisit in Phase 2.

The PTE data show highly variable emissions of TNMHC, methane, and total BTEX compounds among facilities. Results show this variability is not necessarily solely a function of the full capacity surface area of a facility (Figure 1.1). Facilities in California’s Central Valley Region 5 (R5) generally show the highest PTE values for all compounds, but these facilities also have large surface areas at full capacity. PTEs from Santa Barbara County in California Region 3 (R3) are especially high considering the small surface area at full capacity. The PTE of methane from the northern California dry gas fields (N) was proportionally (compared to other compound groups) highest at these facilities, but low compared to methane PTE associated with wastewater from crude oil production. The same dry gas facilities tested also indicated very low total BTEX emissions compared to facilities in other regions.

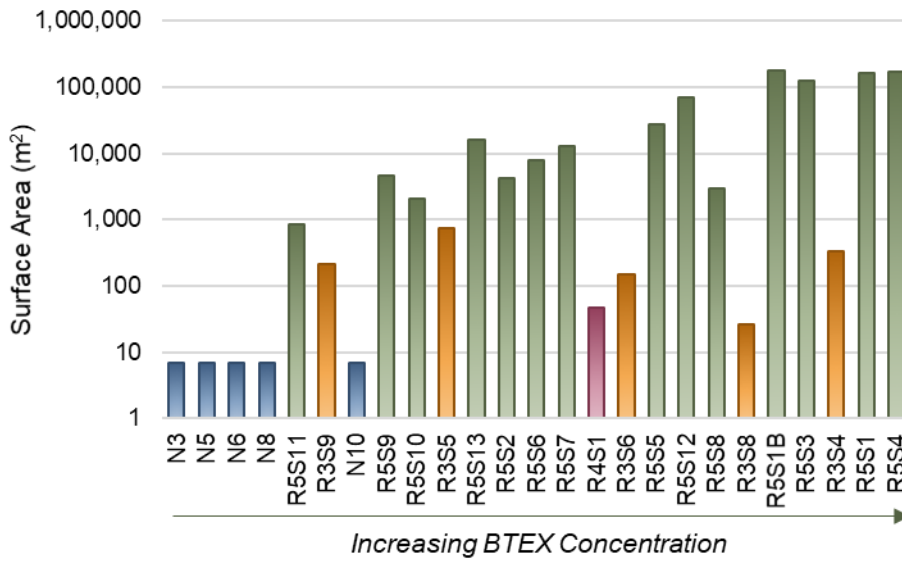


Figure 1.1: Ranked Phase 1 total BTEX flux versus surface area. Regions are differentiated by color.

PTE is a useful metric to understand potential emissions from these facilities on a screening level; however, for Phase 2 facilities, actual emissions were calculated (Figure 1.2). Several data points from a facility were needed to calculate an accurate emission estimate. During Phase 2, four facilities were revisited and sampled multiple times. While variability was high, facility R5S1 consistently had the highest actual emissions for total BTEX, TNMHC, and methane. Generally, facility R5S3 had the lowest actual emissions for all compound groups. While actual emissions estimates vary over time, a seasonal component to emissions variation is not evident. Variation is more likely linked to changes in upstream operations.

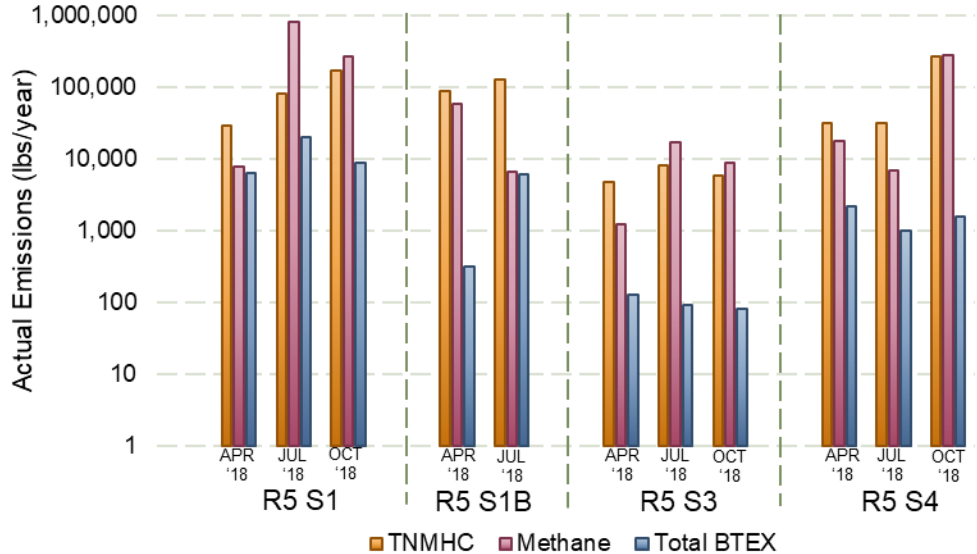


Figure 1.2: Actual emissions of Phase 2 facilities. An average of all samples from the sampling day was calculated and plotted. R5S1B was not sampled in the fall of 2018 due to limited number of samples remaining in the test plan.

Data was further utilized to assess whether the liquid concentrations could be used to predict BTEX emissions. A regression analysis was performed, showing a high correlation between liquid and air concentrations for benzene, ethylbenzene, and toluene, indicating that the concentration of these compounds in the produced water may be used to estimate flux at a facility. The model generated could be further refined by better quantifying the effects of temperature, TDS concentration, and suspended oil on partitioning behavior.

Total BTEX emissions estimated in this study were then compared to the California Toxics Inventory for the San Joaquin Valley (SJV) air basin, showing that emissions from the facilities measured as part Phase 2 of this study represent 1-2% of the SJV air basin inventory (Figure 1.3). At this time, emissions from produced water pond facilities are not included in the toxics inventory, and results from this study suggest that these facilities could be significant sources of emissions and their inclusion in the inventory should be considered. A similar analysis was completed for methane emissions; however, results indicated that methane emissions from produced water ponds may be insignificant compared to other major sources of methane in the SJV Air Basin and the state.

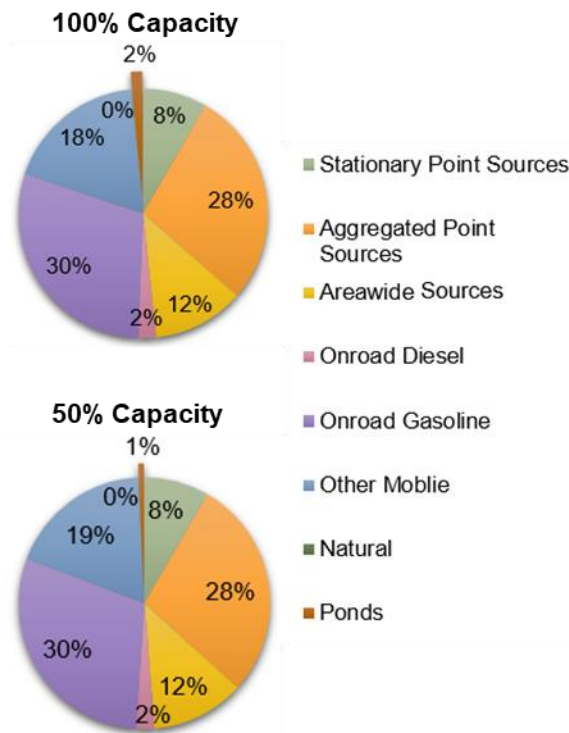


Figure 1.3: San Joaquin Valley Air Basin total BTEX emissions sources compiled from the 2010 California Toxics Inventory and estimated average total BTEX from Phase 2. The natural category indicates emissions from native tar pits and seeps present in the air basin, accounting for 0.03% of total BTEX emissions.

This study resulted in a large data set that advances the understanding of VOC, TAC, and methane emissions from produced water pond facilities in California. These facilities are sources of emissions; however, it is still not fully understood how these emissions vary over time. Further study is required to understand temporal changes in emissions at facilities in the state.

Chapter 2 – Study Background and Introduction

2.1 Introduction

California is a major producer of oil and gas resources, ranking 7th in the U.S. in crude oil production during 2018 (Figure 2.1). During crude oil production, water is brought to the surface as a byproduct. This water is referred to as “produced water.” Produced water is generated at high volumes, and in California’s most productive region, the San Joaquin Valley, for every barrel of crude oil produced, 15 barrels of water are co-produced¹. Since produced water comes from oil bearing formations, it can be high in TDS and VOCs, making it unsuitable for beneficial uses without substantial treatment. In California, historically and currently, the most common disposal methods for produced water have been subsurface injection followed by produced water pond facilities (Figure 2.2). Subsurface injection involves the pumping of produced water into U.S. EPA Class II injection wells for recycling in oil field operations, such as water flooding, or for disposal, where water is pumped into a designated saline aquifer². In a produced water pond facility, produced water is piped and/or trucked to a lined or unlined manmade surface impoundment where the produced water remains in a pond and is allowed to evaporate into the air and/or percolate into the ground over time³.

¹ Department of Conservation, Division of Oil, Gas, and Geothermal Resources, 2017 Report of Oil and Gas Production Statistics, September 2018, Accessed 04/23/2019.

² Department of Conservation, Division of Oil, Gas, and Geothermal Resources, Injection Wells – Frequently Asked Questions, Accessed 06/06/2019.

https://www.conservation.ca.gov/dog/general_information/Pages/class_injection_wells.aspx

³ California State Water Resources Boards, Water Quality in Areas of Oil and Gas Production – Produced Water Ponds, Accessed 06/06/2019.

https://www.waterboards.ca.gov/water_issues/programs/groundwater/sb4/oil_field_produced/produced_water_ponds/

2018 U.S. Crude Oil Production

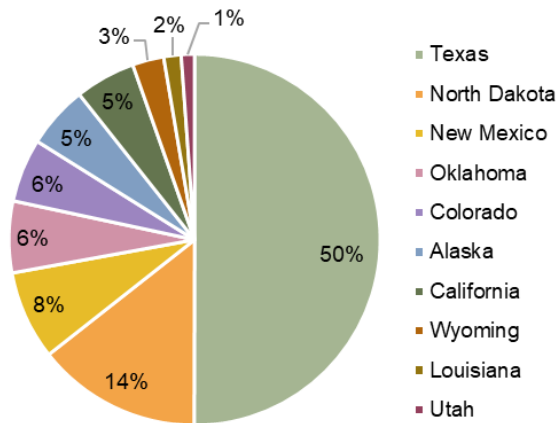


Figure 2.1: Ranking of the top 10 states in terms of crude oil production in 2018. California ranks 7th, producing over 169 million barrels of crude oil.⁴

Produced Water Disposition in CA

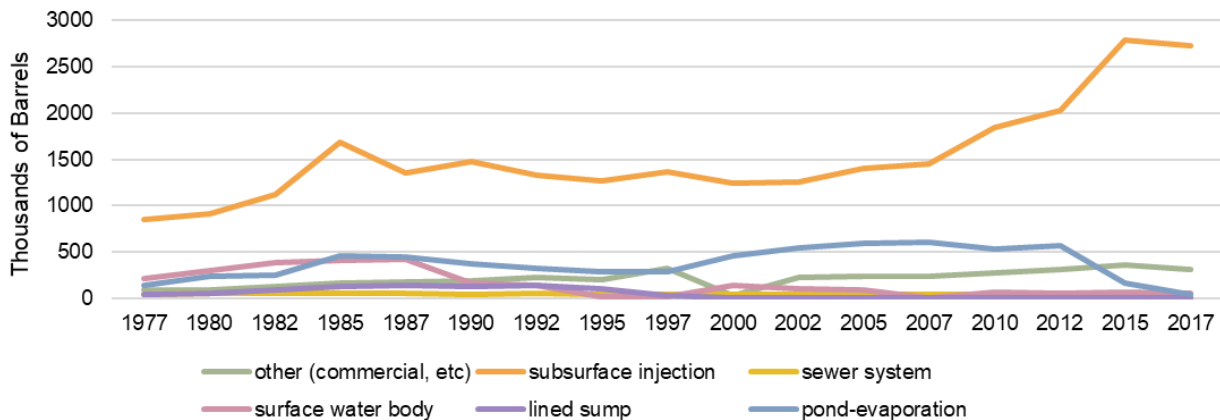


Figure 2.2: Produced water disposal method over time reported to the California Division of Oil, Gas, and Geothermal Resources (DOGGR), renamed CalGEM in January 2020⁵.

Produced water pond facilities are located near oil and gas fields in order to reduce disposal costs by shortening the distance the produced water must be piped and/or trucked for disposal. The energy costs associated with pumping for subsurface injection can be high, making disposal via produced water pond facilities more economic.

⁴ United States Energy Information Administration, Crude Oil Production, Release date 03/29/2019. Accessed 09/24/2019. https://www.eia.gov/dnav/pet/pet_crd_crpdn_adc_mbb1_a.htm

⁵ Department of Conservation, Division of Oil, Gas, and Geothermal Resources, Well Production and Injection Summary Reports, accessed 09/24/2018. ftp://ftp.consrv.ca.gov/pub/oil/online_data/production_injection_data/Pre-2018_Data_Format/

Most active produced water pond facilities are located in the Central Valley, however there are also facilities on the Central Coast and Los Angeles regions of California (Figure 2.3). The ponds at these facilities can be lined or unlined. Lined ponds have a concrete or rubber tarp-like lining to inhibit percolation; however in California, 76% of active facilities contain unlined ponds⁶. When produced water is received at these facilities, oil is separated from the water in a cleaning pond, then the water is moved through channels or pass-through ponds to shallow, earthen evaporation/percolation ponds where the produced water remains until it either evaporates or percolates (Figure 2.4). The free crude oil that rises to the surface in the cleaning ponds is collected and refined. By law, the cleaning ponds contain a cage for wildlife protection. All types of ponds in these facilities are open to the atmosphere, presenting the opportunity for air emissions of greenhouse gases, VOCs, and TACs, including BTEX compounds.

Water produced through the production of natural gas (unassociated with oil production or dry gas) is collected and stored in tanks. Tanks used to store produced water from natural gas fields are not sealed nor do they have vapor recovery, allowing for fugitive emissions to vent to the atmosphere. Water is then trucked off-site to treatment facilities.

In the case of facility R4S1 of this study, the facility is a subsurface injection facility receiving produced water via truck, processing the liquid to remove oil and solids and storing the produced water in a series of tanks prior to injecting below ground.

⁶ California State Water Quality Control Board, Produced Water Ponds Status Report: January 31, 2019, accessed 04/23/2019.

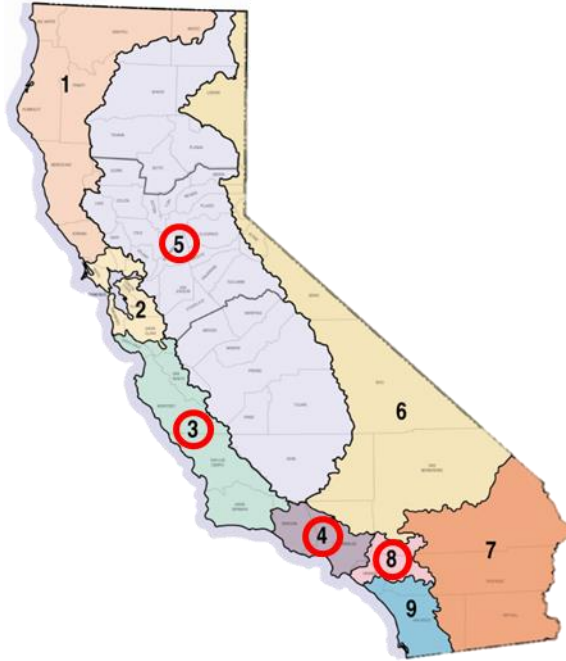


Figure 2.3: California State Water Quality Control Board (SWRCB) map showing the geographic boundaries of the nine RWQCB jurisdictions. Region numbers circled in red indicate which regions contain produced water pond facilities.

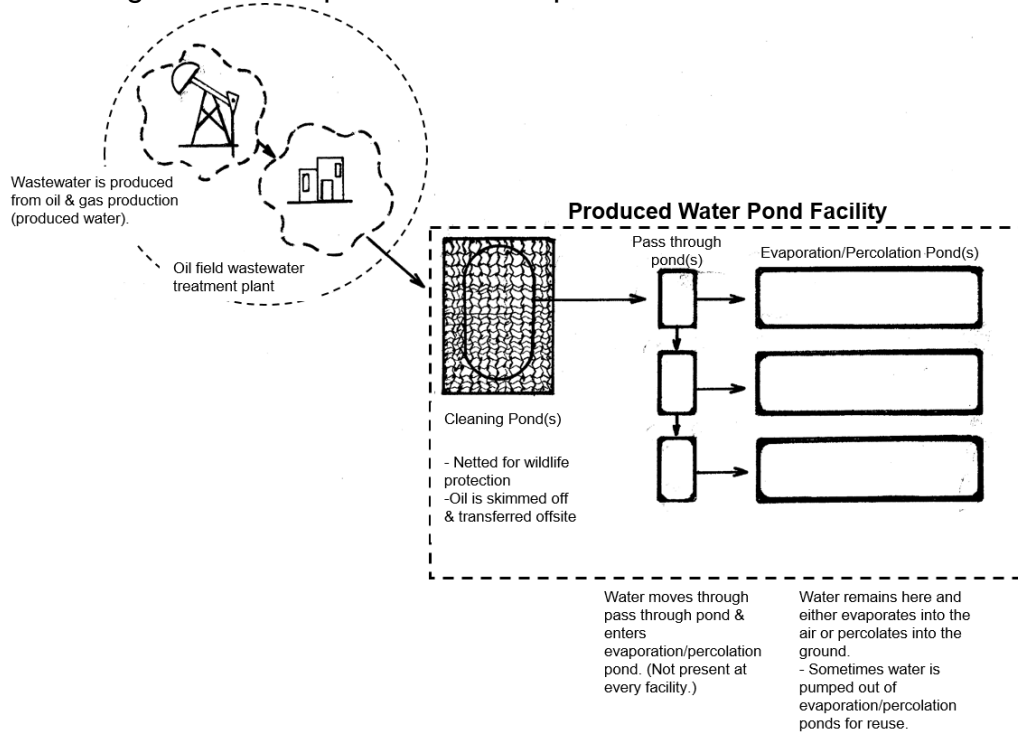


Figure 2.4: Generalized process schematic showing a typical California produced water pond facility.

The produced water discharged to produced water pond facilities is regulated by the California RWQCB. These facilities are permitted when it is determined by the local RWQCB that the discharge will not adversely impact the current or future beneficial use of water⁶. Permitting the water in the produced water pond facilities allows for the quantification of toxic contaminants that may be present in the water; currently there is little data that defines how air quality may be impacted by these facilities.

2.2 Previous Work

In October 2014, CARB funded a limited screening-level study at two facilities (R5S1 and R5S1B in this study) to gather information about the extent of emissions from produced water⁷. Seven flux chamber measurements were taken between the two facilities along with testing of the co-located produced water samples. The goal of the 2014 study was to quantify TNMHC, methane, CO₂, and TAC⁸ emissions from produced water. The PTE was calculated for each facility based on the flux measurements made in the field (Table 2.1). BTEX emissions were especially high, exceeding the Federal major source criteria of 10 tons/year⁹ for these produced water pond facilities alone. Therefore, CARB determined that these facilities needed further study.

Table 2.1: Emission Results from CARB Study in October 2014.

Facility ID	Methane (lbs/year)	BTEX (lbs/year)	TNMHC (lbs/year)	CO ₂ (lbs/year)
R5S1	452,600	148,190	255,500	8,541,000
R5S1B	65,700	21,900	2,562,300	2,722,900

2.3 Study Goals

Since CARB's 2014 study revealed that emissions from produced water pond facilities could cause degradation of air quality, the goal of the current study is to expand on the findings from 2014 and provide further analysis on the impacts produced water pond facilities have on air emissions. A secondary goal is to determine whether air emissions can be estimated from chemical constituents found in produced water.

⁷ California Air Resources Board, Source Testing of Fugitive and Vented Emissions from Hydraulic Fracturing Operations and Wastewater Ponds Used in Crude Oil and Natural Gas Operations in California, Sage Environmental Consulting, June 2016
<https://ww2.arb.ca.gov/sites/default/files/2018-06/wastewater%20ponds%20jun%202016.pdf>

⁸ California Air Resources Board, Toxic Air Contaminant Identification List,
<https://www.arb.ca.gov/toxics/id/taclist.htm>

⁹ San Joaquin Valley Air Pollution Control District, 2018 Annual Air Toxics Report,
https://www.valleyair.org/busind/pto/Tox_Resources/2018-Annual-Report.pdf

2.4 Study Overview

The study was conducted in two phases;

In Phase 1 (screening), the objective was to obtain many data points from produced water ponds statewide and to characterize how produced water emissions vary regionally. Produced water pond facilities in Phase 1 were selected based on proximity to population, geographical region (southern, central, and northern California), and by operator (small, medium, and large) to ensure samples are representative of facilities within the state.

In Phase 2 (characterization), the objective was to select the highest emitting facilities near populated areas based on the data collected in Phase 1 for further air and water testing. The selected pond facilities were tested multiple times throughout the year to account for potential seasonal variability and to characterize changes in air and water among ponds within a single facility.

Chapter 3 – Methods

3.1 Facility Selection and Nomenclature

Facilities for this study were selected in cooperation with RWQCB staff for the designated region of interest. CARB staff compiled a list of produced water ponds in California from the SWRCB Produced Water Ponds Report¹⁰ and used the SWRCB GeoTracker¹¹ tool to visualize the location of facilities in relation to population and select an even geographical distribution of pond facilities in California. The list of potential facilities to test was discussed with RWQCB staff to confirm the existence and accessibility of the facilities and to obtain contact information for facility operators. Facilities were uniquely identified with an ID number consisting of the RWQCB region and a sequential facility number. In the case of ponds R5S1 and R5S1B, the pond facility is divided by a highway and the letter “B” was placed in the ID number to differentiate between the west and east side. R5S1B is the east side of the facility. Natural gas wells in Northern California use the letter “N” in place of the region number. Facilities are not identified by commonly used names or owners/operators. Complete facility data, including location and calculations can be found in Appendix C. In total, 25 facilities were sampled out of the 189 facilities listed in the SWRCB Produced Water Ponds Report from September 2017 through October 2018, resulting in the collection of 123 gas phase samples and liquid phase sample sets (60 sample sets from Phase 1 and 63 sample sets from Phase 2, including QA/QC samples).

After facilities were selected for field screening, CARB obtained permission from the facility manager to access the facility for sampling. Testing activities were observed by one or more owner/operator representatives, and sometimes representatives from the local RWQCB. During Phase 1, facility managers were given several weeks’ notice regarding the request for preferred test dates. However, in Phase 2 requests for testing were shortened to a week or less notice to ensure operations upstream of the facility would be representative of typical operations and prevent attempts to change upstream operations.

3.2 Field Methods

Field and equipment set up was identical to the set up used in the 2014 CARB study. The assessment included using the U.S. EPA flux chamber technology complete with all test equipment as specified in the Measurement of Gaseous Emission Rates from Land

¹⁰ California State Water Resources Control Board, Produced Water Pond Report July 30, 2016, https://www.waterboards.ca.gov/water_issues/programs/groundwater/sb4/docs/produced_pond_rpt_2016_jul.pdf

¹¹ California State Water Resources Control Board, GeoTracker, <https://geotracker.waterboards.ca.gov/>

Surfaces Using an Emission Isolation Flux Chamber, Users Guide¹², to measure the “flux” of study compounds from selected sources on these facilities. Flux is an engineering unit that describes the mass transfer of compounds from a known surface of a source over time.

Locations for flux chamber testing and liquid sample collection were selected based on the facility design and function of the ponds within the facility, the availability or access to locations for testing, and liquid screening data collected before testing. Prior to measuring air emissions, candidate ponds for testing were screened by taking a liquid dip sample and a probe was used to measure pH, temperature, and conductivity reported as salinity. The screening data helps determine differences among ponds, such as the aging of the produced water in the pond; e.g., high conductivity indicates water has undergone evaporation over a longer period than a low conductivity sample.

Once locations for flux chamber testing were identified, a suspension system (Figure 3.1A) was erected consisting of an extension ladder and saw horse which was used to suspend the flux chamber out onto and over test locations. The chamber with attached air introduction and sampling lines were lowered and interfaced to the test surface and the flux chamber measurement was performed following the protocol described in the work plan in Appendix B.

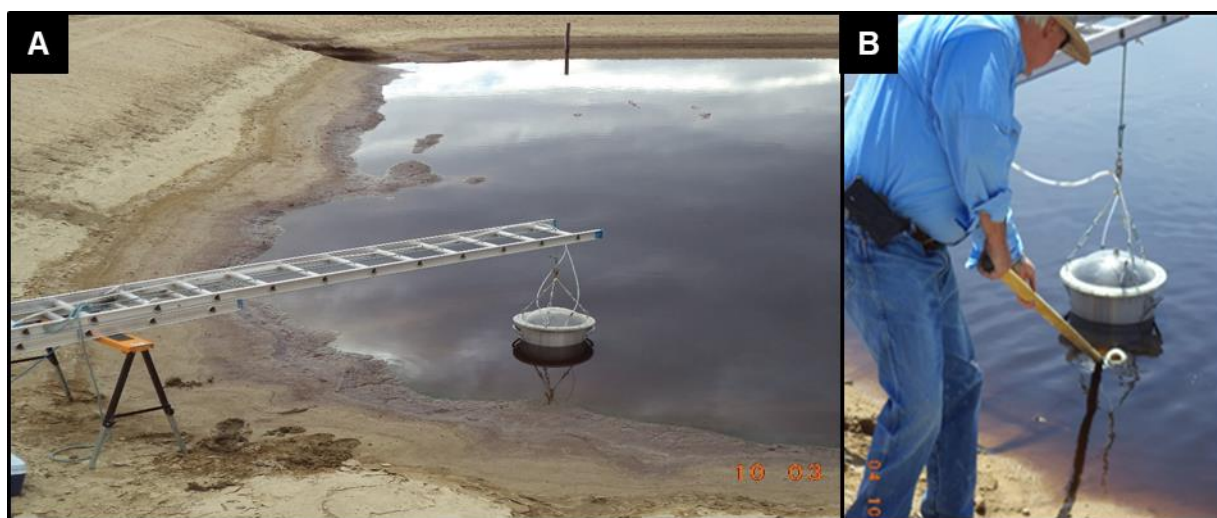


Figure 3.1: (A) Typical flux chamber sampling activity. U.S. EPA flux chamber is suspended from a boom arrangement and interfaced to the selected test location. (B) Liquid dip sampling, taken next to flux chamber.

¹² USEPA, "Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide." EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, EPA Contract No. 68-02-3889, Work Assignment No. 18, Radian Corporation, February 1986. NTIS # PB 86-223161, 1986.

Flux testing included using a fixed sweep air flow rate of 5.0 liters per minute and a 30 liter dynamic flux chamber as per the U.S. EPA Flux Chamber User's guidance document. Dynamic flux chambers use sweep air in the measurement so that an emission rate can be calculated once equilibrium is achieved, which occurs after five residence times in the flux chamber or after five exchange volumes have been added and cycled through the chamber and vented out the exhaust port in the chamber. During this process, all of the ambient air is removed from the chamber and the only gases in the chamber are the pure sweep air mixed with the fugitive compound emissions from the liquid surface in the chamber or enclosure. The contents of the chamber are mixed and at constant compound concentration at equilibrium conditions for 30 minutes, in accordance to the standard Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide¹².

Once equilibrium conditions were achieved in the flux chamber, gas phase sample collection was conducted by filling a 6-liter evacuated Summa polished stainless-steel canister. These canister samples were then shipped to the laboratory (Environmental Analytical Services, San Luis Obispo, CA) where an assessment was performed for VOCs and TACs using U.S. EPA Methods TO-14/TO-15, and fixed gases carbon dioxide and methane by ASTM Methods 1945 and 3416, respectively. After sample collection, the flux chamber system and suspension apparatus were removed from the test location and the flux chamber was cleaned with soap and water.

Liquid phase measurements were performed by collecting a water sample adjacent to the location where the flux chamber measurement was being performed (Figure 3.1B). These activities were coordinated so that a comparison could be made between the water chemistry as the hydrocarbon emission source and the flux measurement of air emissions. A standard dipper fixed to an extension pole was used to collect the water sample. The liquid samples were labeled, bagged and stored in an ice chest maintained at 4°C. The water samples were stored following protocols in method-specific containers and shipped to a laboratory for analysis (BC Labs, Bakersfield, CA). Liquid samples were analyzed for dissolved phase VOCs by U.S. EPA Method 8260b, and for oil and grease by U.S. EPA Method 1664 as described in Appendix B.

A summary of the flux measurements and samples collected for the program are shown below in Table 3.1. The summary shown provides information on the number of facilities tested, the number of samples collected from the Phase 1 and Phase 2 field tests, and the individual facilities tested as shown by their site ID number. The facility ID number is used throughout the report to identify individual facilities.

Table 3.1: Summary of Samples Collected Per Trip.

DATES	TRIP #	PHASE	SAMPLES COLLECTED	ID OF FACILITIES TESTED
9/26/17 - 9/28/17	1	1	15	R5S7, R5S8, R5S9, R5S10, R5S11, R5S12, R5S13
10/10/17 – 10/12/17	2	1	15	R5S1, R5S1B, R5S2, R5S3, R5S4, R5S5, R5S6,
11/01/17	3	1	8	R3S4, R3S5, R3S6, R3S8, R3S9
1/18/18	4	1	5	N3, N5, N6, N8, N10,
4/10/18 – 4/11/18	5	2	20	R5S1, R5S1B, R5S3, R5S4,
7/31/18 – 8/02/18	6	2	21	R4S1*, R5S1, R5S1B, R5S3, R5S4
10/03/18	7	2	11	R5S1, R5S3, R5S4
		TOTAL	95**	

*Facility R4S1 was intended to be sampled during phase 1. However, due to scheduling constraints, it was sampled during phase 2.

**Sample count does not include QA/QC samples.

The total area of each facility sampled during this study and the number of samples collected at each facility are shown in Table 3.2. These data are used to calculate the PTE at each facility. QA/QC samples were omitted from the sampled collected count.

Table 3.2: Area of Facility and Number of Samples Collected.

FACILITY ID	AREA (m ²)	NUMBER OF SAMPLES COLLECTED
N3 ⁺ *	7	1
N5 ⁺ *	7	1
N6 ⁺ *	7	1
N8 ⁺ *	7	1
N10 ⁺ *	7	1
R3S4	325	1
R3S5	743	2
R3S6	151	1
R3S8	26	2
R3S9	217	2
R4S1 ⁺	46	1
R5S1	162,942	16
R5S1B	174,475	11
R5S2	4,180	1
R5S3	125,803	19
R5S4	172,970	15
R5S5	27,443	2
R5S6	7,901	2
R5S7	12,998	3
R5S8	3,000	2
R5S9	4,559	2
R5S10	2,097	1
R5S11	831	2
R5S12	70,553	3
R5S13	15,741	2
Total		95

Sample count does not include QA/QC (duplicate and trip blank) samples

*Sample was collected from a sample port in a separator

*Sample was collected from a facility that stored produced water in tanks, not ponds.

3.3 Report Organization

Since a substantial amount of data was collected, only summary data and data analysis are presented in text. However, all data can be found in Appendices A, B, and C, which are organized as follows:

Appendix A – Summary of Analytical Data.

This appendix contains summary data tables. These include:

- Gas phase data – flux rates
- Gas phase data – concentrations
- Liquid phase data – concentrations

These tables are organized by sample date and sample number.

Appendix B – Data Validation Technical Memoranda

This appendix includes data validation information including:

- Quantitative QA/QC performance
- Field Notes
- Chain of Custody Forms
- Laboratory Reports

Appendix C – Detailed Facility Data and Individual Facility Emissions Estimates

This appendix includes facility data, sample location maps, and the emissions calculations for each facility.

3.4 Analytical Methods

The complete list of all analytes tested and test results can be found in Appendix A. A brief description of the analytical methods is given here.

Method TO-14

Method TO-14¹³ is a gas chromatography (GC) method that uses a flame ionization detector (FID) which is a carbon counter method or a carbon molecule counter. Compounds are identified by the retention time or elution time from the GC separation

¹³ US EPA, "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air." TO-14, EPA-600/4-84-041, 1984.

column and the species identified are summed and used for a TNMHC assessment. The advantage of this assessment method is that a single value can be attained that represents the total hydrocarbon mass loading in the sample. This value of hydrocarbon mass can be expressed as total C1 hydrocarbon or as a C6 hydrocarbon, depending on the data use. This number is useful in assessing hydrocarbon emission levels. Gas samples are collected and stored in stainless steel canisters, shipped to the laboratory, and sample gas is delivered to the GC/FID by pressurizing the canister. Method detection limits for most compounds were below 1 part per billion, volume (ppbv). The analytes sampled for in Method TO-14 are shown in Table 3.3.

Table 3.3: Gas Phase Analytes – U.S. EPA TO-14.

CAS No	Compound	CAS No	Compound
71-43-2	Benzene	100-41-4	Ethylbenzene
108-88-3	Toluene	179601-23-1	m,p-xylene
95-47-6	o-xylene	5989-27-5	d-Limonene
142-82-5	n-Heptane	526-73-8	1,2,3-Trimethylbenzene
111-65-9	n-Octane	95-63-6	1,2,4-Trimethylbenzene
110-54-3	n-Hexane	106-97-8	n-Butane
108-87-2	Methylcyclohexane	584-94-1	2,3-Dimethylhexane
592-27-8	2-Methylheptane	105-05-5	1,4-Diethylbenzene
108-08-7	2,4-Dimethylpentane	110-82-7	Cyclohexane
111-84-2	n-Nonane	112-40-3	Dodecane
540-84-1	2,2,4-Trimethylpentane	74-84-0	Ethane
589-34-4	3-Methylhexane	74-98-6	Propane
107-83-5	2-Methylpentane	75-28-5	i-Butane
565-75-3	2,3,4-Trimethylpentane	104-51-8	n-Butylbenzene
589-81-1	3-Methylheptane	100-42-5	Styrene
124-18-5	n-Decane	74-85-1	Ethene
96-14-0	3-Methylpentane	96-37-7	Methylcyclopentane
109-66-0	n-Pentane	74-86-2	Acetylene
591-76-4	2-Methylhexane	115-07-1	Propene
589-43-5	2,4-Dimethylhexane	78-79-5	Isoprene
141-93-5	1,3-Diethylbenzene	624-64-6	t-2-Butene
611-14-3	2-Ethyltoluene	106-98-9	1-Butene
592-13-2	2,5-Dimethylhexane	590-18-1	c-2-Butene
622-96-8	4-Ethyltoluene	109-67-1	1-Pentene
78-78-4	i-Pentane	646-04-8	t-2-Pentene
565-59-3	2,3-Dimethylpentane	627-20-3	c-2-Pentene
1120-21-4	Undecane	75-83-2	2,2-Dimethylbutane
620-14-4	3-Ethyltoluene	287-92-3	Cyclopentane
108-67-8	1,3,5-Trimethylbenzene	79-29-8	2,3-Dimethylbutane
98-82-8	i-Propylbenzene	80-56-8	a-Pinene
103-65-1	n-propylbenzene	127-91-3	b-Pinene

Method TO-15

Method TO-15¹⁴ is a GC method that uses a mass spectrometer (MS) detector for compound identification. Identification by GC/MS has a higher certainty in identifying individual hydrocarbon species than other detectors and, because of this, data from this analytical method is principally used to identify TACs for health risk evaluation. Gas samples for TO-15 are taken from the same canister as TO-14 and delivered to the GC/MS in an identical fashion. Method detection limits for most compounds were below 1 ppbv. The analytes sampled for in Method TO-15 are shown in Table 3.4.

¹⁴ US EPA, "Air Method, Toxic Organics-15 (TO-15): Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)." EPA 625/R-96/010b, 1999.

Table 3.4: Gas Phase Analytes – U.S. EPA TO-15.

CAS No.	Compound	CAS No.	Compound
71-43-2	Benzene	100-41-4	Ethylbenzene
108-88-3	Toluene	179601-23-1	m,p-xylene
95-47-6	o-xylene	87-68-3	Hexachlorobutadiene
142-82-5	n-Heptane	76-13-1	Freon 113
622-96-8	4-Ethyltoluene	75-09-2	Dichloromethane
95-63-6	1,2,4-Trimethylbenzene	156-60-5	trans-1,2-Dichloroethene
67-64-1	Acetone	1634-04-4	Methyl tert butyl ether
110-82-7	Cyclohexane	75-34-3	1,1-Dichloroethane
78-93-3	2-Butanone	141-78-6	Ethyl acetate
108-67-8	1,3,5-Trimethylbenzene	74-97-5	Bromochloromethane
108-88-3	Toluene-d8	109-99-9	Tetrahydrofuran
75-15-0	Carbon disulfide	156-59-2	cis-1,2-Dichloroethene
100-42-5	Styrene	67-66-3	Chloroform
67-63-0	2-propanol	71-55-6	1,1,1-Trichloroethane
591-78-6	2-Hexanone	107-06-2	1,2-Dichloroethane
108-10-1	4-Methyl-2-pentanone	78-87-5	1,2-Dichloropropane
75-35-4	1,1-Dichloroethene	123-91-1	1,4-Dioxane
64-17-5	Ethanol	79-01-6	Trichloroethene
91-20-3	Naphthalene	75-27-4	Bromodichloromethane
75-71-8	Dichlorodifluoromethane	10061-01-5	cis-1,3-Dichloropropene
74-83-9	Bromomethane	10061-02-6	trans-1,3-Dichloropropene
108-05-4	Vinyl acetate	79-00-5	1,1,2-Trichloroethane
80-62-6	Methyl methacrylate	124-48-1	Dibromochloromethane
74-87-3	Chloromethane	106-93-4	1,2-Dibromoethane
100-44-7	Benzyl chloride	127-18-4	Tetrachloroethene
56-23-5	Carbon tetrachloride	108-90-7	Chlorobenzene
95-50-1	1,2-Dichlorobenzene	75-25-2	Bromoform
76-14-2	Freon 114	79-34-5	1,1,2,2-Tetrachloroethane
75-01-4	Vinyl chloride	541-73-1	1,3-Dichlorobenzene
106-99-0	1,3-Butadiene	106-46-7	1,4-Dichlorobenzene
75-00-3	Chloroethane	120-82-1	1,2,4-Trichlorobenzene
75-69-4	Trichlorofluoromethane		

ASTM Methods 1945 and 3416

The fixed gases including carbon dioxide and methane were determined by ASTM Methods 1945¹⁵ and 3416¹⁶, respectively. ASTM Method 1945 is a GC thermal conductivity method (TCD) which is commonly used for carbon dioxide, and the method detection limit is 0.01% or 121 parts per million, volume (ppmv). ASTM Method 3416 is a GC/FID method like TO-14, and the method detection limit is 0.01 ppmv. Samples for fixed gas analysis are also taken from the canister sample. The analytes sampled for in ASTM Methods 1945 and 3416 are shown in Table 3.5.

Table 3.5: Gas Phase Analytes – ASTM D 3416/1946.

CAS No.	Compound	Test Method
74-82-8	Methane	ASTM D 3416
124-38-9	Carbon Dioxide	ASTM D 1946

Method 1664

US EPA Method 1664¹⁷ is typically used for water treatment compliance for regulatory purposes. Method 1664 quantifies the amount of total oil found in the produced water. This liquid analysis method was included in the liquid sampling program to provide a data set consistent with facility records which can be used to link study data to historic facility data. The method uses an extraction of sample using normal hexane (n-hexane) and the amount of oil and grease in the sample is determined by gravimetric analysis. Liquid samples are collected, stored and shipped in amber color, 64 fluid ounce glass jars. The method detection limit is less than 1 mg/L. The analytes sampled for in U.S. EPA Method 1664 are shown in Table 3.6.

Table 3.6: Liquid Phase Analytes – U.S. EPA Method 1664.

CAS No.	Compound
N/A	Total Oil

¹⁵ ASTM D1945 – 14, Standard Test Method for Analysis of Natural Gas by Gas Chromatography, Active Standard D03.07.

¹⁶ ASTM D3416, Method of Test for Total Hydrocarbons, Methane, and Carbon Monoxide (Gas Chromatographic Method), Inactive Standard D3416-78.

¹⁷ US EPA, Method 1664, Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, February 2010.

Method 8260b

Dissolved VOCs in produced water were determined by using Method 8260b¹⁸, which includes collecting liquid sample in volatile organic analysis (VOA) vials with septa lids that seal in the sample and dissolved sample gases. Sample aliquots are taken by syringe through the septa vial lids and injected into a heated sampling port on the GC/MS instrument. The method detection limit for most compounds is less than 1 µg/L. The analytes sampled for in U.S. EPA Method 8260b are shown in Table 3.7.

Table 3.7: Liquid Phase Analytes – U.S. EPA Method 8260b.

CAS No.	Compound	CAS No.	Compound
71-43-2	Benzene	124-48-1	Dibromochloromethane
100-41-4	Ethylbenzene	96-12-8	1,2-Dibromo-3-chloropropane
108-88-3	Toluene	106-93-4	1,2-Dibromoethane
1330-20-7	Total Xylenes	74-95-3	Dibromomethane
179601-23-1	p- & m-Xylenes	95-50-1	1,2-Dichlorobenzene
95-47-6	o-Xylene	541-73-1	1,3-Dichlorobenzene
95-63-6	1,2,4-Trimethylbenzene	106-46-7	1,4-Dichlorobenzene
91-20-3	Naphthalene	75-71-8	Dichlorodifluoromethane
103-65-1	n-Propylbenzene	75-34-3	1,1-Dichloroethane
108-67-8	1,3,5-Trimethylbenzene	107-06-2	1,2-Dichloroethane
98-82-8	Isopropylbenzene	75-35-4	1,1-Dichloroethene
99-87-6	p-Isopropyltoluene	156-59-2	cis-1,2-Dichloroethene
104-51-8	n-Butylbenzene	156-60-5	trans-1,2-Dichloroethene
135-98-8	sec-Butylbenzene	78-87-5	1,2-Dichloropropane
1634-04-4	Methyl t-butyl ether	142-28-9	1,3-Dichloropropane
96-18-4	1,2,3-Trichloropropane	594-20-7	2,2-Dichloropropane
98-06-6	tert-Butylbenzene	563-58-6	1,1-Dichloropropene
79-01-6	Trichloroethene	10061-01-5	cis-1,3-Dichloropropene
127-18-4	Tetrachloroethene	10061-02-6	trans-1,3-Dichloropropene
108-90-7	Chlorobenzene	87-68-3	Hexachlorobutadiene
108-86-1	Bromobenzene	75-09-2	Methylene chloride
74-97-5	Bromochloromethane	100-42-5	Styrene
75-27-4	Bromodichloromethane	630-20-6	1,1,1,2-Tetrachloroethane
75-25-2	Bromoform	79-34-5	1,1,2,2-Tetrachloroethane
74-83-9	Bromomethane	87-61-6	1,2,3-Trichlorobenzene
56-23-5	Carbon tetrachloride	120-82-1	1,2,4-Trichlorobenzene
75-00-3	Chloroethane	71-55-6	1,1,1-Trichloroethane
67-66-3	Chloroform	79-00-5	1,1,2-Trichloroethane
74-87-3	Chloromethane	75-69-4	Trichlorofluoromethane
95-49-8	2-Chlorotoluene	76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane
106-43-4	4-Chlorotoluene	75-01-4	Vinyl chloride

¹⁸ US EPA, Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, December 1996.

3.5 Quality Control and Quality Assurance

To ensure the accuracy of sample data, sampling equipment was cleaned after each sample. The flux chamber and liquid dipper were both cleaned via soap and water after each use. The sample lines were purged with sweep gas for 2 minutes. Finally, the liquid dipper was conditioned prior to sample collection by rinsing with produced water from the sample location prior to collecting each sample.

In addition to the 95 samples, 11 field blanks and 17 replicate samples were collected to meet QA/QC objectives, resulting in a total of 123 samples collected during the program. Field blank canister samples were collected by filling canisters with ultra-pure air and submitting them as blind QC samples for analysis. Blank samples were collected at a frequency of 5% or more. Likewise, liquid blank samples were collected by filling the liquid sample containers with distilled water and submitting the blank samples for analysis as blind field blank samples. Field replicates were second samples collected in the field immediately after the primary sample in the same location. The results of the replicate sample were compared with the primary sample to provide information on consistency and reproducibility of field sampling procedures. Field replicates were also collected at a 5% rate (i.e. 1 duplicate per 20 samples) or more. The QC data presentation for all sample data is found in Appendix B.

In general, the data quality was determined to be acceptable with several noted exceptions. Analytes were detected in Phase 1 method blanks and field blanks for gaseous samples, and were therefore quality control was not acceptable. The lab was unable to document the source of the analytes, but the lab resolved the contamination issue by the time they analyzed all of the subsequent samples. Analysis of all subsequent method blanks and field blanks resulted in analyte non-detects. Since the goal for Phase 1 was to identify the ponds with the largest potential to emit for further study, the results were deemed acceptable for qualitative purposes. All quantitative analyses were performed exclusively on Phase 2 data.

The majority of results for replicate samples (over 55%) did not meet the acceptable 30% error margin, approximately 27% due to the flux chamber¹⁹ and 5% due to the summa cannister²⁰. The laboratory control standards and laboratory control standard duplicates were reviewed and were confirmed to be well within the laboratory determined acceptable error margin of 25%. The standard operating procedures for flux chambers and summa canisters were followed rigorously. The difference in samples may be due to the fact that replicate samples were generally collected from locations in

¹⁹ US EPA. 1985, Measurement of Gaseous Emission Rates From Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide. EPA Environmental Monitoring Systems Laboratory, Las Vegas , Nevada . NTIS No. PB-86-223161.

²⁰ Biermann, H. and Barry, T. 1999, Evaluation of Charcoal Tube and SUMMA Canister Recoveries for Methyl Bromide Air Sampling. State of California, Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring and Pest Management Branch, Environmental Hazards Assessment Program, 830 K St. Sacramento, California 95814-3510. EH 9-02.

the pond where water was either entering or exiting the system, therefore causing turbulent flow. With a constant influx of produced water from a variety of sources and formations, the concentration near the inlet or outlet (where the samples were collected) is likely to be in a constant state of fluctuation. However, due to the volatility of the analytes studied, it was important to try and obtain a sample that most accurately represented source-produced water. As such, this required collection as close to the inlet as possible. Given these circumstances, the lack of agreement between the replicate field samples is not believed to be an indication of poor field sampling procedures, but rather a result of constant introduction of heterogeneous fluids.

Chapter 4 – Results and Data Analysis

4.1 Data Set Overview

This data set consisted of 95 unique liquid and gas samples were collected and analyzed for 129 compounds. A general summary of the gas phase data are presented in Table 4.1 and the liquid phase data are presented in Table 4.2. All data collected during the study can be found in Appendices A, B, and C. Non-detected values were excluded from Tables 4.1. Since a large amount of compounds were analyzed in both gaseous and liquid samples, the percent detects for all test methods are compiled in Tables 4.3-4.5.

Table 4.1: Gas Phase Concentration Average and High Values (Phase 2 Facilities).

Compound	Units	Average	High
Total Non-Methane Hydrocarbon	C1 $\mu\text{g}/\text{m}^3$	50,700	1,223,000
TO-15 BTEX			
Benzene	$\mu\text{g}/\text{m}^3$	990	16,000
Toluene	$\mu\text{g}/\text{m}^3$	2,800	59,000
Ethylbenzene	$\mu\text{g}/\text{m}^3$	360	2,850
m,p-Xylene	$\mu\text{g}/\text{m}^3$	1,200	11,500
o-Xylene	$\mu\text{g}/\text{m}^3$	740	5,600
Total Xylene	$\mu\text{g}/\text{m}^3$	1,800	17,100
Carbon Dioxide	%	0.1	0.2
Methane	ppmv	94.5	633

Table 4.2: Liquid Phase Concentration Average and High Values (All Facilities).

Compound	Units	Average	High
EPA Method 1664	mg/L	17,710	660,000
BTEX			
Benzene	$\mu\text{g}/\text{L}$	125	1,650
Toluene	$\mu\text{g}/\text{L}$	151	1,900
Ethylbenzene	$\mu\text{g}/\text{L}$	46	1,000
m,p-Xylene	$\mu\text{g}/\text{L}$	102	1,400
o-Xylene	$\mu\text{g}/\text{L}$	55	790
Total Xylene	$\mu\text{g}/\text{L}$	159	2,200
Total BTEX	$\mu\text{g}/\text{L}$	437	4,745

Table 4.3: Liquid Phase (8260b) Compounds Sorted by Frequency of Detection.

Species	Percent of Total Detected*	Species	Percent of Total Detected*
o-Xylene	95%	p-Isopropyltoluene	47%
Toluene	93%	Sec-Butylbenzene	39%
Benzene	91%	n-Butylbenzene	26%
p- & m-Xylenes	89%	tert-Butylbenzene	3%
Ethylbenzene	86%	Tetrachloroethene	3%
1,2,4-Trimethylbenzene	86%	Chlorobenzene	2%
1,3,5-Trimethylbenzene	73%	Methyl t-butyl ether	1%
Naphthalene	67%	Trichloroethene	1%
n-Propylbenzene	65%	1,2,3-Trichloropropane	1%
Isopropylbenzene	63%		

*The percentages are based on the number of total detects from all Phases after removing blanks.

Table 4.4: Gas Phase (TO-14) Compounds Sorted by Frequency of Detection.

Species	Percent of Total Detected*	Species	Percent of Total Detected*
Ethane	97%	Ethene	34%
n-Pentane	93%	2,4-Dimethylhexane	33%
Benzene	86%	3-Methylpentane	33%
Toluene	86%	i-Butane	29%
n-Hexane	86%	1,2,3-Trimethylbenzene	28%
n-Octane	84%	2,5-Dimethylhexane	28%
Propane	83%	2,3,4-Trimethylpentane	24%
m,p-Xylene	76%	2,3-Dimethylpentane	24%
n-Nonane	76%	d-Limonene	24%
1,2,4-Trimethylbenzene	74%	b-Pinene	22%
1,3,5-Trimethylbenzene	74%	a-Pinene	21%
Undecane	74%	n-Butylbenzene	21%
Ethylbenzene	72%	2,2,4-Trimethylpentane	19%
Dodecane	72%	2,3-Dimethylhexane	16%
n-Butane	72%	2-Ethyltoluene	16%
n-Decane	72%	3-Ethyltoluene	14%
o-xylene	71%	t-2-Pentene	12%
n-Heptane	67%	c-2-Pentene	9%
3-Methylhexane	66%	1-Pentene	7%
2-Methylhexane	64%	Cyclohexane	7%
4-Ethyltoluene	53%	Styrene	7%
i-Pentane	52%	1-Butene	5%
2,4-Dimethylpentane	43%	Methylcyclopentane	5%
1,3-Diethylbenzene	40%	2,2-Dimethylbutane	3%
1,4-Diethylbenzene	40%	2,3-Dimethylbutane	3%
i-Propylbenzene	40%	Acetylene	2%
2-Methylpentane	38%	Cyclopentane	2%
Methylcyclohexane	38%	Isoprene	2%
2-Methylheptane	36%	Propene	2%
3-Methylheptane	36%	t-2-Butene	2%
n-propylbenzene	36%		

*The percentages are based on the number of total detects from Phase 2 after removing blanks.

Table 4.5: Gas Phase (TO-15) Compounds Sorted by Frequency of Detection.

Species	Percent of Total Detected*	Species	Percent of Total Detected*
Benzene	88%	n-Heptane	9%
Acetone	81%	1,1,2-Trichloroethane	3%
Toluene	79%	Ethanol	3%
m,p-Xylenes	66%	Styrene	3%
Ethylbenzene	60%	Tetrachloroethene	3%
2-Butanone	60%	trans-1,3-Dichloropropene	3%
o-Xylenes	53%	1,1,2,2-Tetrachloroethane	2%
1,2,4-Trimethylbenzene	48%	1,2-Dibromoethane	2%
Naphthalene	45%	1,2-Dichlorobenzene	2%
4-Ethyltoluene	31%	1,4 Dioxane	2%
1,3,5-Trimethylbenzene	28%	Benzyl chloride	2%
2-propanol	28%	Chlorobenzene	2%
2-Hexanone	22%	Chloromethane	2%
4-Methyl-2-pentanone	21%	Cyclohexane	2%
Carbon disulfide	21%	Vinyl acetate	2%

*The percentages are based on the number of total detects from Phase 2 after removing blanks.

4.2 Produced Water Characteristics

In addition to the laboratory data for the liquid samples, field data consisting of water temperature, conductivity (reported as TDS), and pH were also measured. These parameters give a basic understanding of the quality of produced water at the facilities studied. Also, water temperature, TDS, and pH give some insights into the origin and treatment of the produced water prior to entering the facility. Only Phase 2 facilities are presented in Figures 4.1-4.3 to characterize the variability of field data with time. A full suite of the temperature, TDS, and pH data can be found in Appendix C. Values presented in Figures 4.1-4.3 are an average of all measurements from a facility on a sampling day. In October 2017, no evaporation/percolation ponds were measured at R5S3 due to sample priority being concentrated on cleaning ponds to quantify the worst case scenario. In October 2018, R5S1B was not sampled due to lack of remaining samples in the contract test plan.

Temperature

The temperature variation within and among facilities sampled in Phase 2 are shown in Figure 4.1. At all facilities, the evaporation/percolation ponds are cooler than the cleaning ponds. This is expected because water in the evaporation/percolation ponds are generally characterized by longer residence times and the water has had time to cool. The cleaning pond(s) are where water first enters the system from the formation and/or fields and in this region many operators utilize thermal enhanced oil recovery methods. Hence water temperature in cleaning ponds is expected to be higher than evaporation/percolation ponds.

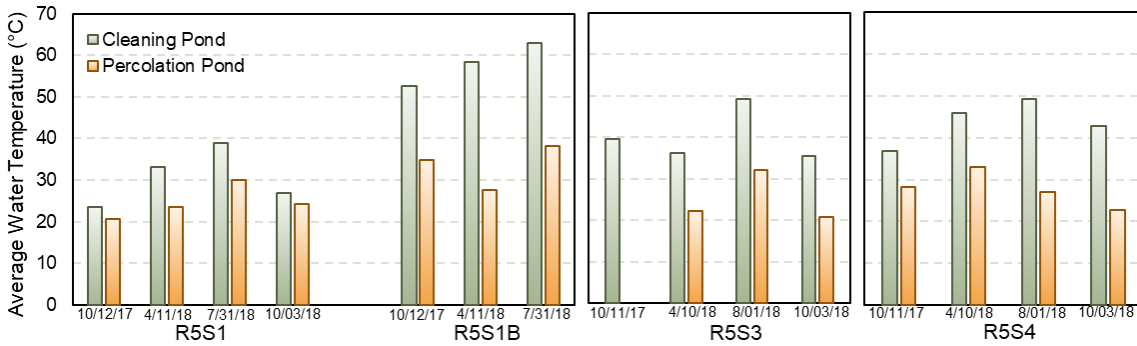


Figure 4.1: Phase 2 field water temperature measurements.

TDS

The variability in TDS within and among facilities sampled during Phase 2 is shown in Figure 4.2. The TDS concentration of the produced water in the cleaning ponds is representative of the baseline value as it is where the produced water first enters the facility from the field before evaporation and/or percolation has had time to occur. If evaporation is occurring, TDS in the evaporation/percolation ponds will be higher compared to the cleaning ponds. Understanding the relationship between evaporation and percolation could be an indicator of the potential emissions to expect at a facility.

TDS concentrations of produced water measured at the produced water pond facilities is brackish to salty, consistent with water coming up from oil-bearing formations. The average TDS of cleaning ponds at all Phase 2 facilities were 15,181 mg/L TDS and the average TDS of evaporation/percolation ponds at all Phase 2 facilities were 17,268 mg/L, an indication that evaporation is occurring.

The highest TDS measurement was in produced water from facility R5S1. At R5S1, the TDS concentrations of both the cleaning pond(s) and evaporation/percolation pond(s) are similar except for the measurements in July 2018, where TDS concentration in the evaporation/percolation ponds(s) is about 5,000 mg/L greater, indicating that evaporation (rather than percolation) is the dominate process in the summer months.

The overall trend in TDS concentration is very different between R5S1 and R5S1B, as the TDS concentration of ponds at R5S1B is nearly half of the TDS concentration of ponds at R5S1. At R5S1 it appears that dry, hot summer weather causes an increase in evaporation. However at R5S1B evaporation is prevalent in both winter and summer months. The R5S3 facility has intermediate TDS concentrations, ranging from 12,900 mg/L to 22,343 mg/L TDS and when compared to other Phase 2 facilities, evaporation was prevalent year round. The R5S4 facility had the lowest TDS concentration of all Phase 2 facilities, and similar to facility R5S1 there is an increase in evaporation during the summer. Facility R5S4 also has the smallest range in TDS concentrations.

From this data it is clear that season and outdoor air temperature are not the only controlling factors on evaporation rate. For example, residence times of produced water in evaporation/percolation ponds are not known. Longer residence times could correspond with more concentrated TDS due to the water having more time to evaporate.

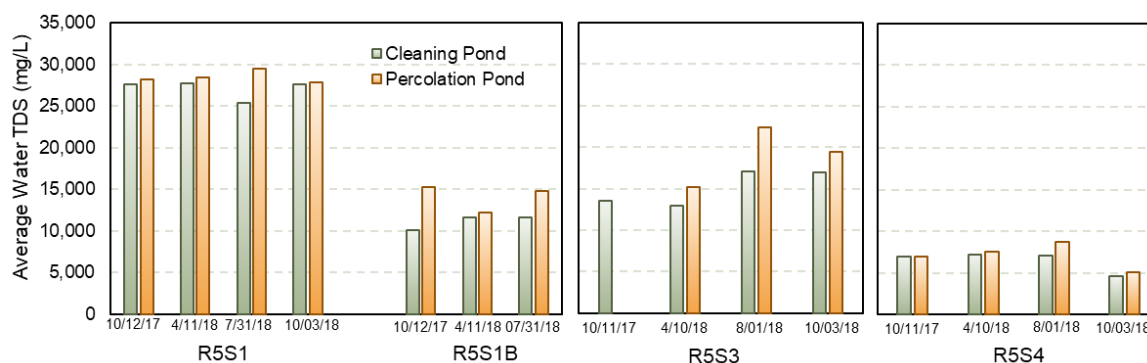


Figure 4.2: Phase 2 field water TDS measurements.

pH

The pH variability within and among Phase 2 facilities is shown in Figure 4.3. pH is another metric that shows the variability of water (and potentially emissions) entering a facility. pH can also indicate produced water source. Facilities R5S1, R5S1B, and R5S3 all have slightly alkaline pH values, which is consistent with known groundwater type of calcium-magnesium to calcium-sodium bicarbonate type waters in the region²¹. Facility R5S4 had the largest range in pH of all the facilities, with the lowest and highest pH values of all facilities measured on the same day. The neutral pH values in the R5S4 cleaning ponds could indicate that water entering the system could have a higher portion of surface water, driving the alkaline pH down. The average pH for cleaning ponds is 7.2 and the average pH for evaporation/percolation ponds is 8.2. This

²¹ Central Valley Regional Water Quality Control Board. 2006, Irrigated Lands Discharge Program Draft Existing Conditions Report, accessed 4/1/2019.
https://www.waterboards.ca.gov/centralvalley/water_issues/irrigated_land/archives/exist_cond_rpt/draft_existing_conditions_rpt/ch04_pt3.pdf

difference could be caused by the natural microbes carrying out anaerobic digestion in the evaporation/percolation ponds^{22,23}.

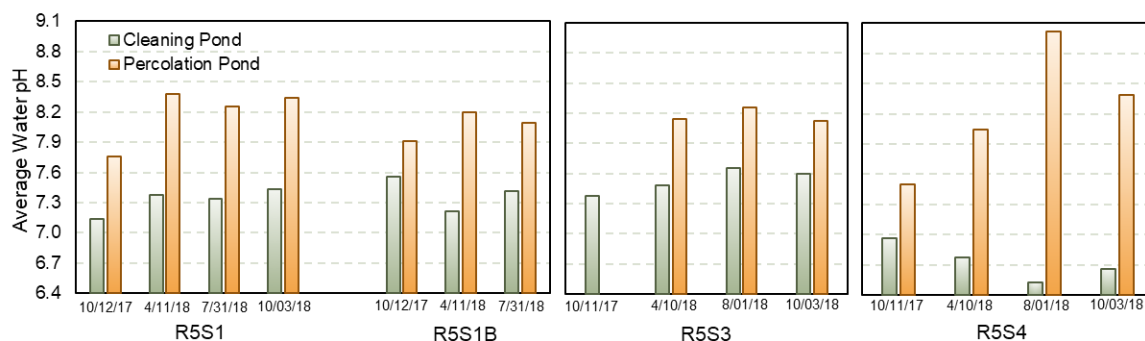


Figure 4.3: Phase 2 field water pH measurements.

Using these field water data to gain a basic understanding of produced water quality at these facilities serves two purposes: 1) knowing where produced water originates and what enhanced oil recovery processes it may have undergone, allows for predictions as to what pollutants to expect in the water and ultimately the air; and 2) measuring physical and chemical characteristics of produced water is necessary information when modeling the partitioning and mass transfer behavior of toxics from the water to the air.

4.3 Emissions Estimates and Variability

A major goal of this study was to understand the impact of produced water treatment and disposal facilities on air quality. Since flux was directly measured at these facilities, emissions were estimated as follows: 1) PTE was estimated for all facilities but was only used qualitatively in Phase 1 to select facilities for further study in Phase 2. The PTE assumes that all ponds at a given facility are full to capacity and emitting; 2) “actual emissions” are estimates calculated when adequate data points were collected from a facility. Only Phase 2 facilities had enough data points to calculate actual emissions. The active surface area of the ponds within the produced water facility at the time of testing was used to calculate actual emissions.

²² Cioabla, A. E., et al. 2012, Comparative study on factors affecting anaerobic digestion of agricultural vegetal residues. *Biotechnol Biofuels*, 5:39. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3431276/>

²³ U.S. Department of the Interior Bureau of Reclamation. 2014, *Produced Water Treatment Primer: Case Studies of Treatment Applications*, accessed 7/9/2019. https://www.usbr.gov/research/projects/download_product.cfm?id=1214

Potential to Emit

Due to the QA/QC issues encountered with the Phase 1 data, the PTE results were only used in a qualitative manner. Most results were not depicted graphically since PTE data was only used as a screening measure, however a brief discussion is still included below.

PTE values were estimated for TNMHC, methane, and total BTEX compound groups for all facilities. The lowest overall PTE (including TNMHC, methane, and total BTEX) was measured at facilities that utilized tanks, which were the northern California gas well facilities and R4S1. Furthermore, the northern California gas well facilities had the lowest BTEX and TNMHC of all facilities tested, demonstrating that water produced with dry natural gas has less hydrocarbons compared to water produced with oil. While the highest PTE values are observed at the four facilities sampled during Phase 2, they also have the highest surface area. Some R3 facilities have especially high PTE values, considering the small surface area. This is illustrated for total BTEX in Figure 4.4.

Generally, TNMHC were the compounds with the highest PTE at most facilities, especially in R3 and R4. In R5, only 2 facilities had TNMHC PTE values significantly higher (two orders of magnitude) than methane or total BTEX; while the rest of R5 facilities show similar PTE estimates for TNMHC and methane. Methane PTE was highest at R5 facilities followed by R3 facilities. Total BTEX PTE was highly variable at all facilities spanning several orders of magnitude, except for the northern California gas wells (Figure 4.4). Of the top 5 facilities with the highest total BTEX PTE, four were from R5.

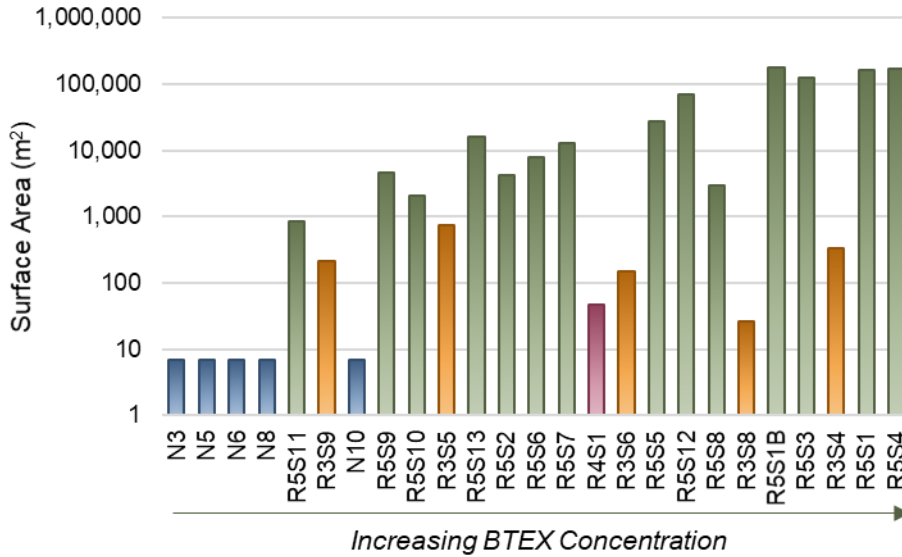


Figure 4.4: Ranked Phase 1 total BTEX flux versus total surface area of a facility. Regions are differentiated by color.

PTE was also estimated for northern California natural gas production facilities. Natural gas production facility produced water collection and treatment is different from crude oil produced water treatment. Produced water passes through a separator (which removes water from the natural gas), and the produced water is then transferred to a storage tank where it is stored for offsite disposal. Air emission measurements were made at five natural gas produced water facilities, all showing low level emissions from produced water with no significant air emissions released from the system. The PTE of methane was proportionally (compared to other compound groups) highest at these facilities, but low compared to methane PTE associated with wastewater from crude oil production.

Actual Emissions

Phase 2 data was used to calculate actual emissions for TNMHC, methane, and total BTEX (Figure 4.5). Samples came from multiple cleaning ponds or evaporation/percolation ponds. Actual emissions for a facility were averaged for a sampling day. Results show variability in actual emissions at all facilities, for all compound groups, and these range over several orders of magnitude. The largest variability is exhibited in the methane results, with emissions spanning nearly three orders of magnitude across all Phase 2 samples. Total BTEX emissions by comparison were relatively consistent at most facilities, generally varying one order of magnitude or less within a facility. Except for the methane emissions in July 2018 at R5S1B, both TNMHC and methane emissions increased at facilities over Phase 2. The change in total BTEX emissions was variable over Phase 2. Facilities R5S3 and R5S4 saw small decreases in total BTEX emissions over Phase 2, between 26-32% decrease. Total

BTEX emissions increased at R5S1 and R5S1B, however the most dramatic change in total BTEX emissions of all facilities during Phase 2 was at R5S1B where emissions increased by 1,800%. The concentration of compounds in the gas phase changed over time, but shows no seasonal trend.

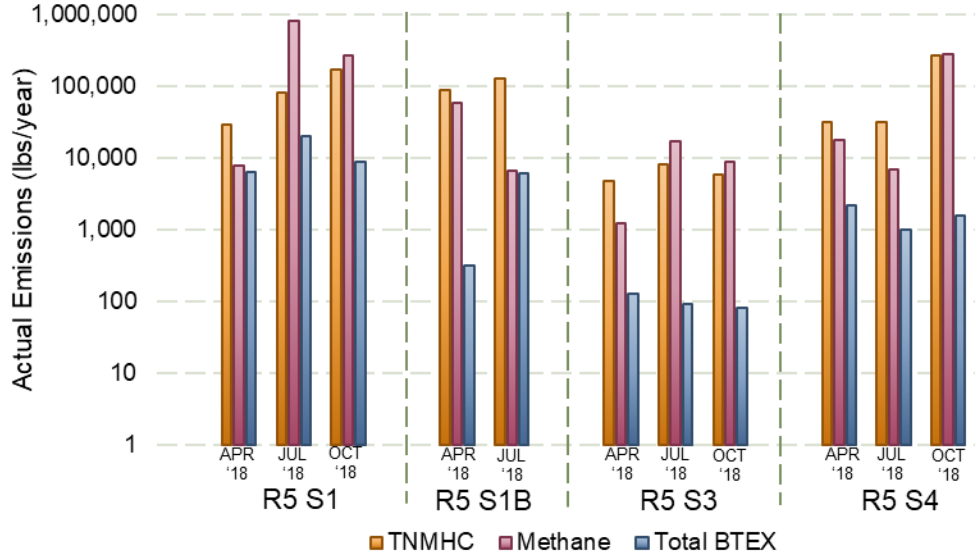


Figure 4.5: Actual emissions calculated for all Phase 2 facilities. Dotted lines separate different Phase 2 facilities. Detailed actual emissions calculations can be found in Appendix C. R5S1B was the only facility that was not sampled in the fall of 2018.

Variability in actual emissions at Phase 2 facilities is dependent on the facility, not the compound (Figure 4.6). R5S1 showed the most variability among all three compound groups, while R5S3 showed the least variability among the three compound groups. R5S3 had the lowest and most consistent emissions of all Phase 2 facilities.

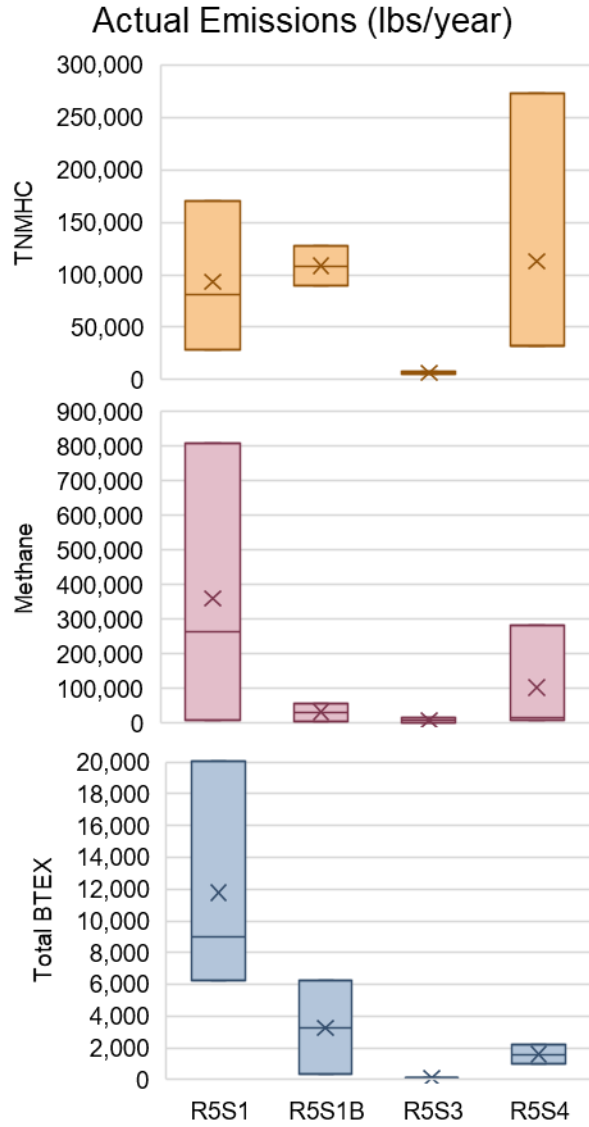


Figure 4.6: Box plots showing the variability in actual emissions for TNMHC, methane, and total BTEX at Phase 2 facilities.

The actual emissions data was also used to quantify the variability within a facility, especially the variability between various evaporation/percolation ponds (Figure 4.7). Relative percent difference (RPD) was calculated to estimate the amount of variability between two samples*. At facility R5S4, samples were taken from adjacent ponds, samples 104 and 105 in October 2018 and 301 and 302 in April 2018; on both dates there were large discrepancies between adjacent ponds with RPDs approaching 200% in benzene emissions in adjacent evaporation/percolation ponds. Since produced water becomes cleaner as it moves throughout the facility, this variability is expected. However, adjacent evaporation/percolation ponds at facilities R5S1 and R5S1B show similar benzene emissions at different evaporation/percolation ponds within a facility, demonstrating the unique nature of each facility.

*Relative Percent Difference (RPD) = $(|V_1 - V_2| \div [(V_1 + V_2) \div 2]) \times 100$

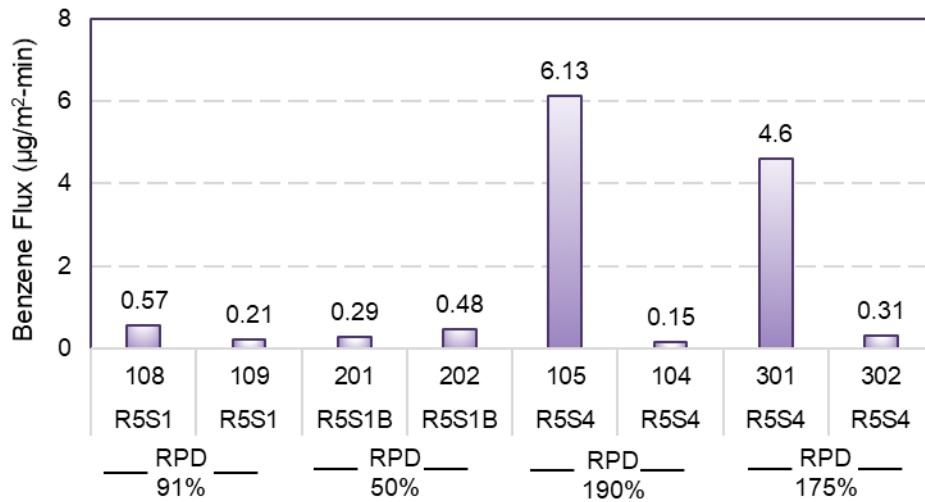


Figure 4.7: Variability of benzene emissions expressed as relative percent difference (RPD) in adjacent evaporation/percolation ponds. Three digit sample ID locations can be found in Appendix C.

In addition, samples from within a single evaporation/percolation pond were analyzed for variability. Evaporation/percolation ponds can be very large at these facilities, potentially causing variability within a pond itself as it may take time for water entering the pond to fully mix. In some cases, multiple samples were taken on opposite sides (e.g. front and back), but within a single evaporation/percolation pond (Figure 4.8). The data show less variability within a pond compared to variability between ponds. The data from this study indicates that water within an evaporation/percolation pond is well mixed and that sampling location within a pond is inconsequential.

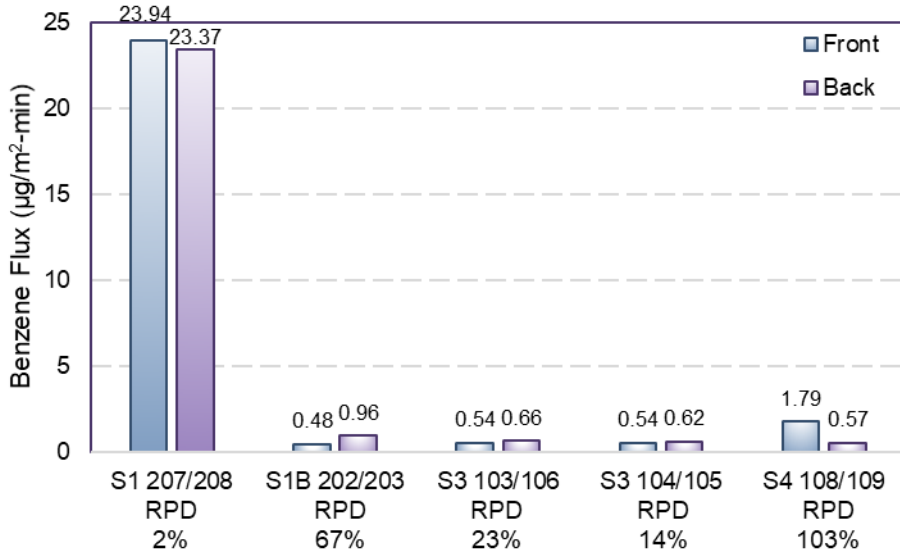


Figure 4.8: Benzene variability, expressed as relative percent difference (RPD), within evaporation/percolation ponds within Region 5. Front is defined as near where water enters the pond and back is the location furthest away from where water enters the pond. Three digit sample ID locations can be found in Appendix C.

4.4 Predictive Gas Phase/Liquid Phase Partitioning

Collecting water samples is simpler and less time-intensive than measuring air flux. Therefore, if air emissions can be effectively predicted by measuring the liquid phase concentration, emissions can be estimated with less complication²⁴.

Air emissions (flux rate) can be estimated from liquid phase concentrations using equation 1:

$$(1) r_v = K_t A C_{Le}$$

where r_v is the air emission in g/s, K_t is the overall mass transfer coefficient in m/s, A is the area in m², and C_{Le} is the liquid phase concentration in g/m³.

The overall mass transfer coefficient is derived from equation 2:

$$(2) K_t = \frac{1}{\frac{1}{k_l} + \frac{1}{Hk_g}}$$

where k_l is the liquid phase mass transfer coefficient in m/s, H is the gas/liquid partition coefficient in g/m³ gas per g/m³ liquid, and k_g is the gas phase mass transfer coefficient.

In this study, k_l will be much larger than k_g for all compounds, therefore:

$$K_t = k_l$$

If the liquid phase concentration and surface area are divided into the flux rate, equation 1 can be rearranged:

$$(3) k_l = \frac{r_v}{A C_{Le}}$$

Equation 3 generates the mass transfer coefficient, which should be constant for similar environmental conditions. Co-located air and water samples from Phase 2 were plotted together to quantify how well the liquid concentration predicts flux at facilities with cleaning and evaporation/percolation ponds open to the atmosphere (Figure 4.9). Note that facilities such as the northern California gas wells and R4 S1 were excluded because produced water at these facilities is generally stored in covered tanks and produced water does not interact significantly with the atmosphere. For all BTEX compounds, water concentration shows a moderate to high correlation with

²⁴ United States Environmental Protection Agency. 1994, Air Emissions Models for Waste and Wastewater, accessed 4/24/2019.

https://www3.epa.gov/ttn/chief/software/water/air_emission_models_waste_wastewater.pdf

corresponding air concentration. Benzene, ethylbenzene, and toluene all show a high correlation ($R^2 > 0.8$), while (m,p-) and (o-) xylenes show a moderate correlation ($R^2 \approx 0.5$). It has been demonstrated that in systems similar to produced water pond facilities, xylenes have lower solubility than benzene, ethylbenzene, and toluene²⁵. As cleaning ponds and evaporation/percolation ponds were not distinct from one another, all air and water data, regardless of pond type, were utilized in the following regression analysis.

Since a moderate to strong correlation was found between air and water concentration for BTEX compounds, a regression model was developed to estimate flux (equations provided in Figure 4.9). The modeled flux estimates were compared to the measured flux values (Figure 4.10). At high flux rates, the model neither over predicts nor under predicts measured flux values. At low flux rates ($< 100 \mu\text{g}/\text{m}^2\text{-min}$ for benzene, toluene, ethylbenzene, and $< 10 \mu\text{g}/\text{m}^2\text{-min}$ for m-,p-,o-xylenes), the model generally over predicted flux compared to measured values for all BTEX compounds.

Total oil was also evaluated as a predictive variable for all methane and benzene emissions. However, no correlation was found in the data, with an R^2 for benzene of 0.27 and an R^2 of 0 for methane (results not shown).

²⁵ Njobuenwu, D. O., et al., 2005, Dissolution Rate of BTEX Contaminants in Water. The Canadian Journal of Chemical Engineering, v. 83, p. 985-989.

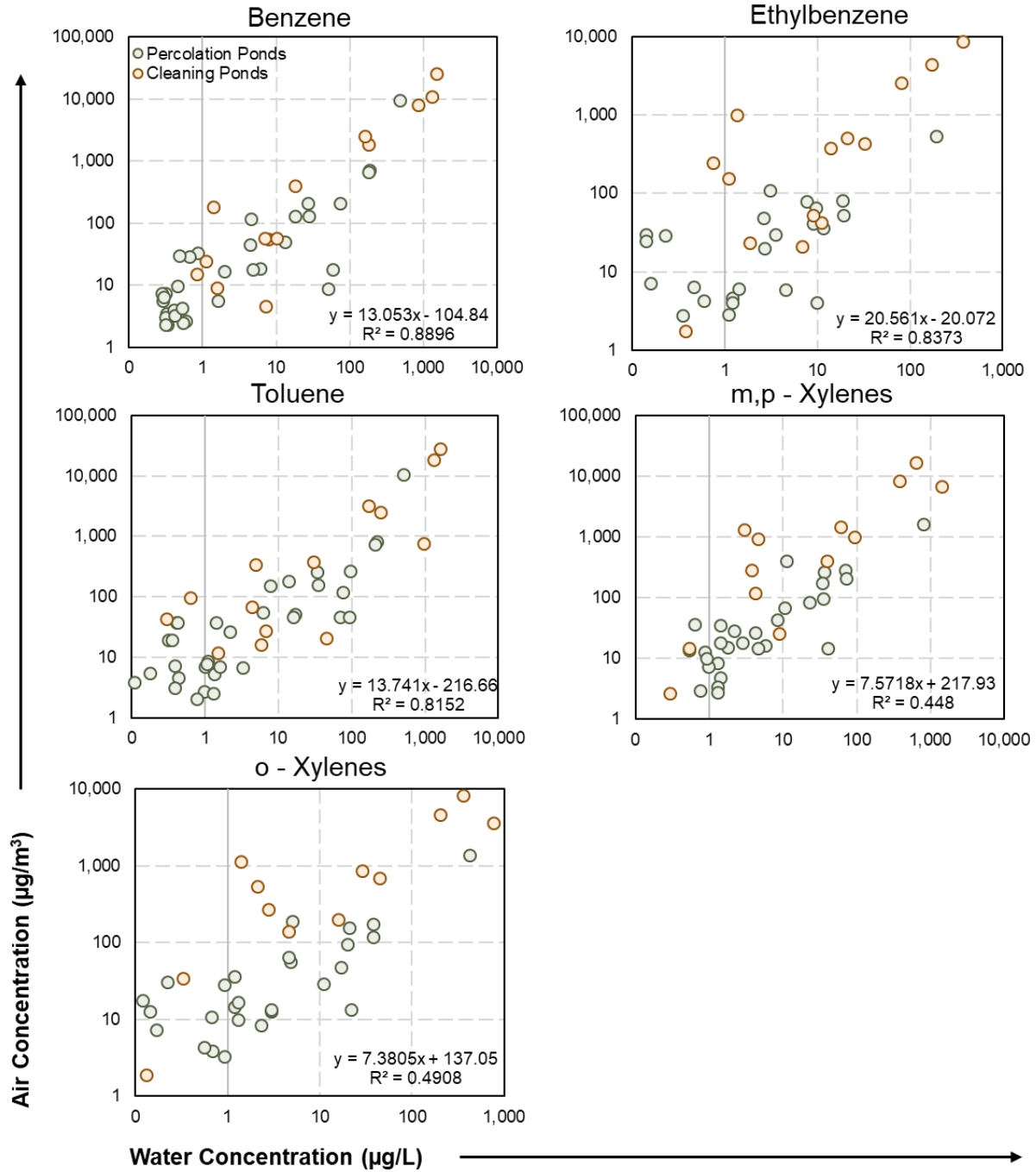


Figure 4.9: Correlation of BTEX compounds in Phase 2 co-located water and air samples.

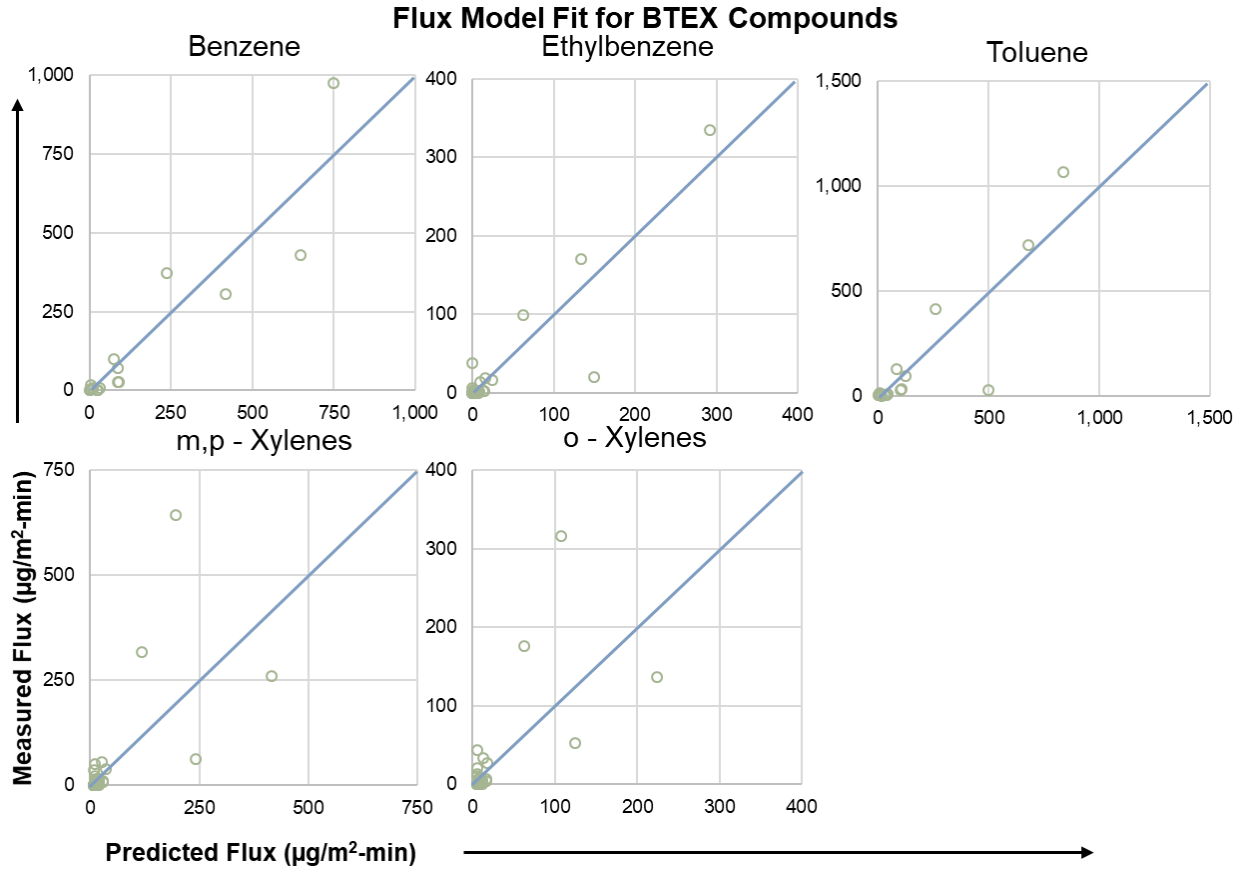


Figure 4.10: BTEX predicted flux using regression model and measured BTEX liquid concentration versus the flux measured in the field. The blue line is a 1:1 line representing a perfect model fit.

Chapter 5 – Discussion

5.1 Emission Impacts

Estimates of total BTEX and methane emissions from produced water pond facilities are presented in Table 5.1 due to the potential public health and climate implications of these compounds. BTEX compounds compose the majority of TACs identified during this study. Due to the variable nature of the air emissions, multiple scenarios were calculated, considering differences in the fullness of ponds within a facility (i.e. the amount of the facility actively being used to hold water) and how concentrated total BTEX and methane emissions were. Based on field observations, facilities generally operate between 50% and 100% surface area capacity. These calculations were made for Phase 2 facilities only, due to aforementioned issues with Phase 1 data.

Table 5.1: Estimated emissions of Total BTEX and Methane from Phase 2 Produced Water Pond Facilities. High and low estimates were calculated by using the highest and lowest flux values measured, respectively, and applying that value to the facility surface area. The average estimate was calculated by averaging all flux values measured at a facility and applying that value to the facility area.

Facility % Capacity	BTEX (lbs/yr) High	BTEX (lbs/yr) Average	BTEX (lbs/yr) Low	Methane (lbs/yr) High	Methane (lbs/yr) Average	Methane (lbs/yr) Low
100%	984,207	162,961	59	5,387,320	1,240,407	26,946
50%	492,104	81,480	29	2,694,164	620,707	13,977

Since all four Phase 2 facilities are in the SJV Air Basin, calculated emissions were compared to other sources of BTEX emissions in the SJV Air Basin (Figure 5.1). Estimated total BTEX emissions from the four Phase 2 produced water pond facilities can be significant, representing 1-2% of the toxics inventory²⁶. Currently, emissions from produced water pond facilities are not included in the inventory. Note that these data only include the estimated emissions from facilities sampled during Phase 2; this estimate will increase if all facilities in the state are considered.

A similar analysis was completed for methane emissions. However, results indicated that methane emissions from produced water ponds may be insignificant compared to other major sources of methane in the SJV Air Basin and the state.

²⁶ California Air Resources Board, California Toxics Inventory. <https://ww3.arb.ca.gov/toxics/cti/cti.htm>. (accessed 8/6/2019)

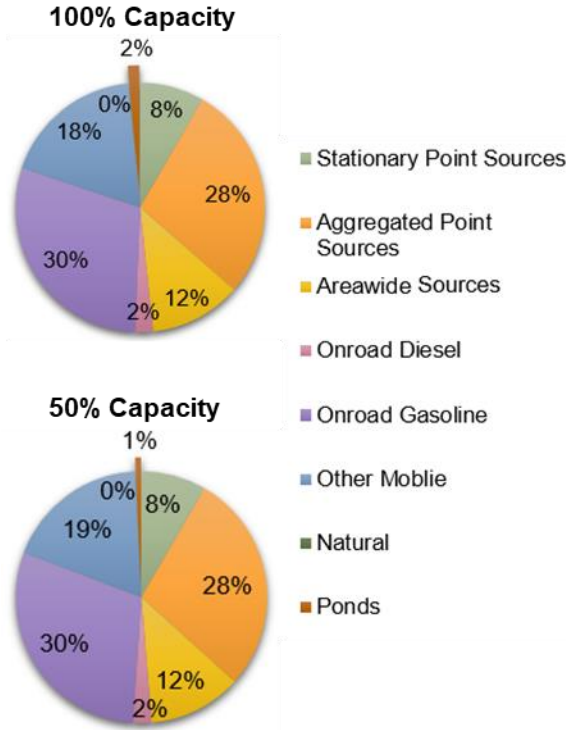


Figure 5.1: San Joaquin Valley Air Basin total BTEX emissions sources compiled from the 2010 California Toxics Inventory²⁶ and estimated average total BTEX from Phase 2 facilities. The natural category indicates emissions from native tar pits and seeps present in the air basin, accounting for 0.03% of total BTEX emissions.

5.2 Variability and Predictions

The goal of this work was to better understand the impacts of produced water pond facilities on air quality. Measurements of TACs and other compounds varied considerably among produced water facilities statewide. Produced water entering these facilities comes from different oil fields, different formations, and potentially may have been used for enhanced oil recovery. Since incoming produced water quality can be different over time and among ponds within a facility, the extent of air emissions from these facilities cannot be accurately quantified from a limited number of samples. Also, since emissions change over time, additional air samples should be acquired to obtain a more accurate quantification of the emissions over the course of a year. Specific facility testing generates a day-of-testing “snapshot” of air emissions which can be used to monitor facility TAC/VOC/fixed gas emissions (lb/yr), and an aggregate of facility data can be used to generate emission factors (lb/yr-surface area) that can be used for statewide emission estimation.

While studies of produced water ponds are limited, in 2014, CARB conducted sampling at some of the same produced water pond facilities⁷ (R5S1 and R5S1B, Table 2.1).

Compared to the current study, results from the 2014 study were significantly higher. This change is likely due to operational and potential treatment changes upstream prior to entering the facility.

Measuring the liquid field parameters (temperature, TDS, and pH) gives a first order understanding of where produced water is coming from (i.e. thermal enhanced recovery projects, formation water versus surface water, etc.) and the fate of the water once it is on site (i.e. evaporating or percolating). These metrics are quick to measure and provide valuable data.

Liquid-air mass transfer models indicate that for benzene, ethylbenzene, and toluene it may be possible to estimate emissions from the concentrations measured in the produced water. However, agreement in the xylene model was not as evident.

Since equations 1-3 are based on an ideal system, the model could be improved by correction for non-ideal parameters. Mass transfer coefficients are dependent on particular physical and chemical properties and are usually derived in a laboratory setting (pure water at 25°C)²⁷. In some cases, it may be possible to correct for non-ideal parameters, such as sample temperature. Also, additional measurements, such as major ion chemistry would improve the predictability of the model. Finally, the presence of suspended oil is known to create a film which could also affect partitioning behavior. However, these corrections are outside the scope of the work and are not developed here.

The preliminary measurements from this study show that in general, the concentration of BTEX compounds in produced water may provide a good estimate of the expected air emissions. The collection of more data, especially samples with BTEX concentrations between 100 µg/L and 1,000 µg/L, could improve the model by creating a more even distribution of the data. The regression model could also be further improved by collecting additional data to correct for non-ideal parameters.

²⁷ Sander, R. 2015, Compilation of Henry's law constants (version 4) for water as solvent. Atmos. Chem. Phys., 15, 1399-4981.

5.3 Conclusions

This study provides information to increase understanding of how oil and gas produced water facilities may impact air quality in the state. Data from this study shows that produced water pond facilities can be a significant source of BTEX emissions, especially in the SJV Air Basin. Data also show that these facilities are not significant sources of methane emissions. Flux was found to be variable over time, with no clear patterns to explain variability. Regression analysis showed that benzene, ethylbenzene, and toluene emissions have the potential to be estimated from the concentration of these compounds in produced water samples. Future work could involve more regular monitoring of facilities by taking flux chamber measurements from multiple ponds within a facility at regular intervals to get a more thorough characterization of how emissions change over time.