Dairy Farm Emissions in California: The Impact on Communities of Disadvantage

Brenna Biggs, Ph.D. Rowland-Blake Lab | UCI Chemistry Solutions that Scale Earth Day 2021



California Is Home























California Is a Leader

California leads the United States in sustainable practices and laws to reduce harmful emissions.

Incoming Solar Radiation



Outgoing Terrestrial Radiation

Greenhouse Gases Warm Earth

Incoming Solar Radiation



No atmosphere Earth ~ 0 °F

Outgoing Terrestrial Radiation

Incoming Solar Radiation



With atmosphere Earth ~ 60 °F



78% Nitrogen21% Oxygen1% Trace gases

Trace gases = argon, **carbon dioxide** (CO₂), **methane** (CH₄), helium, **nitrous oxide** (N₂O), **ozone** (O₃), **water** (H₂O), etc.



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Global Warming Potential (GWP)

 $CO_2 = 1$ $CH_4 = 28 - 36$ $N_2O = 265 - 298$

Trace Gases Cause Pollution and Odor



Trace gases in our environment don't just cause climate issues.

They can cause pollution (like ozone and particles) and odor.

 \downarrow visibility \uparrow physical and mental health problems







2005: Executive Order S-3-05

• We must \downarrow greenhouse gas emissions





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+ 2012: Senate Bill 535

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What is a disadvantaged community?



Disadvantaged communities are objectively defined with 20 parameters in 4 categories.

California Office of Environmental Health Hazard Assessment (2018)



- Cleanup sites
- Groundwater
- Hazardous waste
- Impaired water
- Solid waste



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ExposureOzone

- PM_{2.5}
- Diesel PM
- Drinking water
- Pesticides
- Toxic facilities
- Traffic



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Sensitive Populations

- Asthma rates
- Heart disease
- Low birth rate



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Socioeconomics

- Education
- Housing burden
- Linguistics
- Poverty
- Unemployment



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Methane Sources in California

Methane Sources in California



Methane Sources in California


Methane Sources in California



Methane Sources in California



Methane Sources in California



Summary of My Research

1. Dairy farm in Visalia, California

- Collect air samples upwind, downwind, on-site locations
- Explore seasonality
- Emissions and effect on communities

2. Remote and Airborne Data

- "Background" air entering California
- Effect of dairies on regional air quality





Remote coastal samples n = 512 from 1980 - 201834.5 - 40.0 °N in CA



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Dairy farm samples - n = 359 from 2018 – 2020 Visalia, CA



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Dairy farm samples n = 359 from 2018 – 2020 Visalia, CA

Regional airborne samples n = 336 from 2011, 2013, 2014, 2015, 2017 Pressure altitude < 3,000 feet San Joaquin Valley, CA



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Anatomy of the San Joaquin Valley





California Agricultural Statistics Review 2017-2018



fornia

Cows: 3,106 milk cows 386 dry cows 2,985 heifers

Campaigns (359 air samples):

September 2018 March 2019 June 2019 September 2019 January 2020

CalEnviroScreen Score: 85 – 90% (disadvantaged)







Enteric Emissions: Cows ruminate

Includes: Heifers/Calves Dry Cows Milk Cows

Manure Emissions: Decomposition

> Includes: Lagoons Slurries Bedding Processing Pit



Enteric Emissions: Cows ruminate

Includes: Heifers/Calves Dry Cows Milk Cows





<u> 2016: Senate Bill 1383</u>

- I Decrease methane to 40% below 2013 levels by 2030
 - Fines starting in 2024

Dairy farms make a lot of methane.

Farmers, who live in disadvantaged communities, will be fined for these emissions starting in 2024.













Sample Collection in the Rowland-Blake Lab



Canister

• Samples collected in 2-liter, evacuated, stainless steel canisters

Sample Collection in the Rowland-Blake Lab



- Samples collected in 2-liter, evacuated, stainless steel canisters
- Variety of sample locations (e.g., upwind, downwind)

Photos by Brenna Biggs & Alicia Hoffman (2018).



Canister


































Gas Chromatogram



Select Gases in Whole Air Samples

Alkanes: Methane Ethane Propane i/n-Butane i/n-Pentane n-Hexane Cyclohexane 2,3-Dimethylbutane 2,2-Dimethylbutane Methylcyclopentane n-Heptane Methylcyclohexane 2,4-Dimethylpentane 2-Methylhexane 3-Methylhexane n-Octane 2,2,4-Trimethylpentane n-nonane

Alcohols: 2-Butanol Ethanol Isopropanol Methanol **Aromatics:** 1,2,4-Trimethylbenzene 1,3,5-Trimethylbenzene Ethylbenzene i-Propylbenzene n-Propylbenzene m+p-Xylene o-Xylene Toluene m-Ethyltoluene o-Ethyltoluene p-Ethyltoluene Benzene **Extra Greenhouse Gases:** Nitrous Oxide

Carbon Dioxide

Alkenes: 1-Butene i-Butene α-Pinene β-Pinene Isoprene Limonene Myrcene γ-Terpinene α-Terpinene 3-Carene Propene trans-2-butene *cis*-2-butene **Sulfur Species:** Carbon Disulfide **Dimethyl Disulfide** Dimethyl Sulfide Carbonyl Sulfide

Halocarbons: Tetrachloroethylene Chloroform **CFC-11 CFC-12** Dichloromethane Trichloroethylene Carbon Tetrachloride **Methyl Chloroform** Methyl Chloride 1,2-Dichloroethene **Bromoform** Ketones: Acetone Butanone Methylisobutylketone **Aldehydes:** Acetaldehyde **Butanal**

Select Gases in Whole Air Samples

Alkanes: **Methane** Ethane Propane i/n-Butane i/n-Pentane n-Hexane Cyclohexane 2,3-Dimethylbutane 2,2-Dimethylbutane Methylcyclopentane n-Heptane Methylcyclohexane 2,4-Dimethylpentane 2-Methylhexane 3-Methylhexane n-Octane 2,2,4-Trimethylpentane n-nonane

Alcohols: 2-Butanol Ethanol Isopropanol **Methanol Aromatics:** 1,2,4-Trimethylbenzene 1,3,5-Trimethylbenzene Ethylbenzene i-Propylbenzene n-Propylbenzene m+p-Xylene o-Xylene Toluene m-Ethyltoluene o-Ethyltoluene p-Ethyltoluene Benzene **Extra Greenhouse Gases: Nitrous Oxide**

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Summary of Findings

Issue	Dairy	Suggestions
CH_4		
N_2O		
DMS		
OCS		
Pollution		
Odor		

"Background" Methane Entering CA



Coastal samples (34.5 to 40.0 °N) 1980 – 2018

↑ methane over time

Now 1.931 ppm CH₄

Samples with $CH_4 > 1.931$ ppm assumed to be enhanced by inland sources.

Methane at the Visalia Dairy Farm



How much from cows? How much from manure?

Coastal CH₄ was 1.931 ppm.

 International Panel for Climate Change (IPCC) 2006 Guidelines for National Greenhouse Gas Inventories gives emission factor methodology for manure management

Tier	What You Need		
1	Average annual air temperature of the region Number of animals		
2	Specific animal and temperature characteristics Manure management practices		
3	Measurements Models	Ţ	

Increasing complexity

 International Panel for Climate Change (IPCC) 2006 Guidelines for National Greenhouse Gas Inventories gives emission factor methodology for manure management

	Tier	What You Need	
Environmental Protection Agency (EPA) uses these to calculate our GHG inventory	1	Average annual air temperature of the region Number of animals	
	2	Specific animal and temperature characteristics Manure management practices	Increasing complexity
	3	Measurements Models	

EPA Tier 2 formula: $EF = VS * B_0 * MCF * \rho_{CH4} * MDP$



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$EF = VS * B_0 * MCF * \rho_{CH4} * MDP$

EF = methane emission factor, in (kg CH₄/month) VS = volatile solids entering the lagoon each month, in (kg VS) B₀ = maximum CH₄-producing capacity of manure, in (m³ CH₄/kg VS) MCF = temperature-dependent methane conversion factor ρ_{CH4} = 0.662, the density of CH₄ at 25 °C, in (kg CH₄/m³ CH₄) MDP = manure management and design practices factor

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EPA Tier 2 formula:

$$EF = VS * B_0 * MCF * \rho_{CH4} * MDP$$

MCF = temperature-dependent methane conversion factor

Directly proportional to the amount of methane that can be produced.



Modelled Liquid Manure Temperatures

Modified van't Hoff-Arrhenius explains biological systems

$$f = \exp\left[\frac{E(T_2 - T_1)}{RT_1T_2}\right] \longrightarrow$$
Safley &
Westerman
(1990)

Modelled Liquid Manure Temperatures

Modified van't Hoff-Arrhenius explains biological systems

How bacteria make methane in manure



Liquid temperatures, not air temperatures, would ideally be used as T_2 to calculate MCF.

MCF Temperature Requirements

Method	Type of Temperature Data Needed	Example
IPCC Tier 1	Average annual air temperature of a region	SJV annually
EPA Tier 2	Average monthly air temperature of a county	Tulare per month
This study	Modelled daily lagoon/slurry temperatures	Daily for liquid manure

Modelled Lagoon and Slurry Temperatures

$$TL_{i} = \frac{TA_{i}\alpha_{i} + TA_{i-1}\alpha_{i-1} + \dots + TA_{i-n}\alpha_{i-n}}{\alpha_{i} + \alpha_{i-1} + \dots + \alpha_{i-n}}$$

 TL_i = lagoon or slurry temperature (°C) for day *i* TA_i = mean air temperature (°C) for day *i* α = e^{-bt}, a weight factor that simulates the response of the lagoon to air temperature b = constant t = number of days (0, 1, 2, ..., 365)

This study uses daily air temperatures in Visalia to calculate lagoon and slurry temperatures at the dairy farm.

Methane Emission Factor Calculation

$$\mathbf{TL}_{i} = \frac{\mathrm{TA}_{i}\alpha_{i} + \mathrm{TA}_{i-1}\alpha_{i-1} + \dots + \mathrm{TA}_{i-n}\alpha_{i-n}}{\alpha_{i} + \alpha_{i-1} + \dots + \alpha_{i-n}}$$
Plug **TL** into **MCF** equation
$$\mathbf{MCF} = \exp\left[\frac{\mathrm{E}(\mathrm{TL} - \mathrm{T}_{1})}{\mathrm{RT}_{1}\mathrm{TL}}\right]$$
Plug **MCF** into Emission Factor **EF** equation
$$\mathbf{EF} = \mathrm{VS} * \mathrm{B}_{0} * \mathbf{MCF} * \rho_{CH4} * \mathrm{MDP}$$

Methane Emission Factors Calculated from Liquid Temperature MCF



- The EPA and IPCC use air temperatures and longer temperature averages.
- They **underestimate** methane emissions from manure management.

This dairy releases 350 metric tonnes of CH₄ annually from manure management.

Manure Management Methane Will Increase with Climate Change



Assume Representative Concentration Pathway 4.5

Predicts average temperature increases:

- 1.4 °C between 2046 and 2065
- 1.8 °C between 2081 and 2100

Important for counties with many cows, like Tulare.

Thomson et al. (2011) Moss et al. (2008, 2010)

Enteric Methane Estimates at the Dairy Farm

Tior	What You Need	Milk Cow EF (kg CH ₄ hd ⁻¹ yr ⁻¹⁾)	
ner		IPCC (2006)	EPA (2020)
1	Number and type of animals	128	146
2	Information about cows' lifestyle	$EF = \frac{GE * \left(\frac{Y_{m}}{100}\right) * 365}{55.65}$	-

where

EF = emission factor, in (kg CH₄ hd⁻¹ yr ⁻¹)

GE = gross energy intake, in (MJ hd⁻¹ day⁻¹), which depends on various other parameters

 Y_m = methane conversion factor (i.e., the % of gross energy in the feed that is converted to methane) 55.65 = energy content of methane, in (MJ/kg CH₄)

365 = days in a year, in (day/yr)

Enteric Methane Estimates at the Dairy Farm

Category	Enteric EF (kg CH ₄ hd ⁻¹ yr ⁻¹)	# Cows
Milk Cow	134	3106
Dry Cow	53	386
Heifer (15 months)	55	2985
^a Eggleston et al. (2006)		

^b EPA (2020c)

This dairy releases 600 metric tonnes of CH₄ annually from enteric emissions.

Total methane at the dairy = 954 metric tonnes CH_4 annually.

Summary of Findings

Issue	Dairy	Suggestions
CH₄	CH₄ EFs calculated 954 metric tonnes CH₄/yr ↑ T ↑ CH₄	Use liquid T
N ₂ O		
DMS		
OCS		
Pollution		
Odor		

Nitrous Oxide at the Dairy Farm



Data from AGAGE (Prinn et al., 2018)

- Nitrous oxide steadily increasing
- ↑ 7,300 Gg N₂O/yr
- Currently 331 ppb N₂O
- Over 298 times stronger GHG than CO₂
- Lifetime ~120 years

126% since 1990 from manure management sources only (CARB, 2019)

Nitrous Oxide at the Dairy Farm



Average = 356±16 ppb

Most enhanced N₂O found near manure management.

"Background" is 331 ppb N_2O (Prinn et al., 2018) $N_2O > 331$ ppb is "enhanced"

Nitrous Oxide at the Dairy Farm



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N ₂ O	Most enhanced near manure management	Count lagoons in inventory
DMS		
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DMS and OCS at the Dairy



Coastal "background:" 560±24 ppt OCS and 50±30 ppt DMS

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DMS primarily an "ocean gas" Important for climate and particles

Hobbs et al. (1998) Hobbs & Mottram (2000)

- Cows with high protein diets expel excess sulfur as DMS
- Mixing ratios of 0 to 25 ppm DMS in cow breath

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OCS primarily an "ocean gas" Important for aerosol layer Used as proxy for CO_2 calculations

Lennartz et al. (2017) Missing OCS source: Between 230 and 800 Gg S/yr
DMS Estimates for the SJV from Enteric Milk Cow Emissions

- DMS from cow breath at dairy farms in SJV was calculated:
 - 4,600 metric tonnes DMS/yr
- Global DMS flux (Aumont et al. 2002; Bopp et al., 2003; Kloster et al., 2006):
 - 15.4 28.0 Tg S/yr

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Milk cows in the SJV could contribute:

- Up to 15.4% of the global DMS flux
- Up to 5% particles in the SJV

Bad for health and air quality of the disadvantaged communities.

Bovine Activity Contribution to OCS Missing Source

- OCS from bovine activities was calculated:
 - 39.5 Gg S/yr from dairy cows worldwide
 - 28.2 Gg S/yr from other cattle worldwide
 - 11.3 Gg S/yr from manure management worldwide
- Missing OCS Source (Suntharalingam et al., 2008; Berry et al., 2013; Kuai et al., 2015; Glatthor et al., 2015):
 - 230 800 Gg S/yr; previously assumed to come from the ocean

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Bovine activities worldwide may contribute up to 34% of the missing OCS source.

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N ₂ O	Most enhanced near manure management	Count lagoons in inventory
DMS	Cow breath Particle/aerosol formation Air quality concern	Study SJV inland sources
ocs	Possible contribution to missing source Cow breath/manure	Include cow breath as possible source
Pollution		
Odor		

Air Pollution in the San Joaquin Valley

California

As of March 31, 2021:

SJV: nonattainment zone for ozone and particulate matter (PM)

Air Pollution in the San Joaquin Valley



As of March 31, 2021:

SJV: nonattainment zone for ozone and particulate matter (PM) O_3 depends on VOC and NO_x concentrations.

Ozone (O₃) formation: $NO_2 + hv (\lambda \le 420 \text{ nm}) \rightarrow NO + O(^3P)$ $O(^3P) + O_2 + M \rightarrow O_3 + M$

Air Pollution in the San Joaquin Valley



As of March 31, 2021:

SJV: nonattainment zone for ozone and particulate matter (PM) O_3 depends on VOC and NO_x concentrations.

Ozone (O₃) formation: $\rightarrow NO_2 + hv (\lambda \le 420 \text{ nm}) \rightarrow NO + O(^3P)$ $O(^3P) + O_2 + M \rightarrow O_3 + M$

With volatile organic compounds (VOC): $O_3 + hv (\lambda \le 310 \text{ nm}) \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2 \cdot OH$

$$\begin{array}{c} \mathsf{CH}_4 + \bullet \mathsf{OH} \to \bullet \mathsf{CH}_3 + \mathsf{H}_2\mathsf{O} \\ \bullet \mathsf{CH}_3 + \mathsf{O}_2 + \mathsf{M} \to \mathsf{CH}_3\mathsf{OO} \bullet + \mathsf{M} \\ \mathsf{CH}_3\mathsf{OO} \bullet + \mathsf{NO} \to \mathsf{CH}_3\mathsf{O} \bullet + \mathsf{NO}_2 \\ \mathsf{CH}_3\mathsf{O} \bullet + \mathsf{O}_2 \to \mathsf{HCHO} + \mathsf{HOO} \bullet \\ \mathsf{HOO} \bullet + \mathsf{NO} \to \bullet \mathsf{OH} + \mathsf{NO}_2 \end{array}$$

Ozone Formation from Dairies

Ozone formation potential (OFP)
$$\left(\frac{\mu g}{m^3}\right) = \text{VOC} (\text{ppb}) * \frac{\text{molecular weight} \left(\frac{g}{\text{mol}}\right)}{22.4 \text{ mol}^{-1}} * \text{POCP}$$

Shin et al. (2013) Derwent et al. (2007)

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O₃ Contributors at the Dairy Farm:

Oxygenates: Methanol, Ethanol, 2-Butanol, Acetaldehyde, Acetone **Alkenes:** Limonene, Isoprene

Likely sources:



Shin et al. (2013) Derwent et al. (2007)

Aerosol Formation from Dairies

To form secondary organic aerosols (SOA):

- They participate in heterogenous chemistry and contribute particles (bad air pollution)

SOA formation potential
$$\left(\frac{ng}{m^3}\right) = \text{VOC} (\text{ppb}) * \text{SOA yield} \left(\frac{\mu g}{\text{ppm m}^3}\right) * \frac{1 \text{ ppm}}{1000 \text{ ppb}} * \frac{1000 \text{ ng}}{1 \mu g}$$

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SOA Contributors at the Dairy Farm:

Aromatics: Toluene, Benzene Sulfur: DMS

Likely sources:



Shin et al. (2013) Turpin & Huntzicker (1995)

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OCS	Possible contribution to missing source Cow breath/manure	Include cow breath as possible source
Pollution	Silage, enteric, manure form O ₃	Study SJV inland sources
Odor		

Odor from the Dairy Farm



Odor from the Dairy Farm



Reduction Factor (RF):

 $RF = \frac{maximum mixing ratio (ppb)}{odor threshold (ppb)}$

Odor from the Dairy Farm

 Schiffman et al. (1995): livestock odors ↑ tension, depression, anger, fatigue, and confusion
 Mental Health Concerns

 Schiffman (1998): livestock odors ↑ teary eyes, headaches, dry eyes, congestion, and nasal irritation
 Physical Health Concerns

Reduction Factor (RF):

 $RF = \frac{\text{maximum mixing ratio (ppb)}}{\text{odor threshold (ppb)}}$

53

Gases with RF > 1	RF _{max}	Odor	Likely Source
Limonene	132	Citrus	Feed, croplands
DMS	26	Decayed cabbage	Cows
Ethanol	14	Sweet, alcoholic	Feed
Butanal	7	Sweet, rancid	Regional

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DMS	Cow breath Particle/aerosol formation Air quality concern	Study SJV inland sources	
OCS	Possible contribution to missing source Cow breath/manure	Include cow breath as possible source	
Pollution	Silage, enteric, manure form O_3	Study SJV inland sources	
Odor	Cow breath, cows, feed, regional	-	



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Could this work in the SJV?





Bessie

Bessie Fun Facts:

- Weighs 1,500 pounds
- Eats 3% of her body weight daily (45 pounds!)
- Would need 2 pounds of seaweed daily



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1.5 million Bessies



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1.5 million Bessies



- 1 x 10¹⁰ pounds of seaweed needed in SJV daily!
- This seaweed is tropical
- Costs of growing and hauling
- Nutritional side effects
- No incentive for farmers

- California government funding dairies to install digestors to prepare for SB-1383
- Feasible for large dairies (~2,000 cows)
- Visalia dairy farm will install (2021) for \$5 million
 - Will reduce GHG emissions by nearly 200,000 MT CO₂e over a 10-year period





Most projects create RCNG

Can be added to our existing natural gas pipeline

CDFA DDRDP (CDFA, 2020)



- Tulare, Kings, Kern counties most participation
- Counties with few cows per dairy look for other options



Solution: Alternative Manure Management



- California funds non-digester manure management practices
- Remove solids from the manure before lagoon storage



\downarrow GHG emissions

Counties where this is still not feasible may consider flaring the methane like landfills.

Summary of Research and Suggestions



CH₄, N₂O, DMS, OCS, pollution, odor





Proposed solutions for scientists:

- Use liquid system temperature and short time intervals, not air temperature over long intervals, when calculating emissions
- Count N₂O from lagoons in future GHG inventories
- Further explore sulfur contribution from bovine-related activities

Proposed solutions for farmers:

- Focus on reducing manure emissions rather than enteric emissions
- Use CA funds!
 - Install anaerobic digesters
 - Implement alternative manure management practices

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