Emission of volatile organic compounds from silage

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Emission of volatile organic compounds from silage

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USDA-ARS, University Park, PA

Howard, C. J., A. Kumar, I. A. Malkina, P. G. Green, R. Flocchini, and M. Kleeman, UC Davis

Shaw SL, Holzinger R, Goldstein AH. UC Berkeley
SJV Dairy Locations

North

South
California’s dairy industry

Number of Head in Dairies
Less than 500 head and
Greater than 500 head

What do we know about VOCs?

- VOC = 1000s individual reactive gases
- VOCs are compound groups like ketones, alcohols, aldehydes, acids, esters, amines, etc.
- VOCs plus NOx forms ozone (smog)
What do we know about VOCs?

- Natural (biogenic) sources of VOCs are significant
- Other main sources are combustion related
- Main biochemical processes that produce VOCs on dairies are fermentation and decomposition of organic material (feed and manure)
- VOC producing sources on dairies are the cow’s rumen, silage bags, lagoons, corral manure packs
Biogenic Versus Anthropogenic Volatile Organic Compound (VOC) Emissions

Guenther et al 1995, Singh and Zimmerman 1992
Biogenic Volatile Organic Compounds in Earth’s Atmosphere
(BVOCs, 1000’s of compounds)

- Isoprene (C5H8)
- Monoterpenes (C10H16)
- Oxygenated VOC
- Sesquiterpenes (C15H24)
Cattle feed is the leading VOC source on dairies

(Chung et al. 2009)

Table 4
Estimated relative contribution of dairy sources to ozone formation.

<table>
<thead>
<tr>
<th>Source</th>
<th>Estimated relative surface area/%</th>
<th>Relative contribution to ozone (MS)</th>
<th>Relative contribution to ozone (PID)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMR</td>
<td>1</td>
<td>0.65</td>
<td>0.54</td>
</tr>
<tr>
<td>Silage</td>
<td>0.5</td>
<td>0.31</td>
<td>0.40</td>
</tr>
<tr>
<td>Flushing Lanes</td>
<td>0.8</td>
<td>$4 \times 10^{-5}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Lagoon</td>
<td>69</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Open Lot</td>
<td>27</td>
<td>$9 \times 10^{-3}$</td>
<td>0.03</td>
</tr>
<tr>
<td>Bedding</td>
<td>1</td>
<td>$1 \times 10^{-4}$</td>
<td>$4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Which VOCs are present in silage?
**Alcohols**

![Bar chart showing concentrations of alcohols in various feed ingredients.](chart)

- **Corn**: 2500 ppb
- **Alfalfa**: 2000 ppb
- **Cereal**: 1500 ppb
- **TMR**: 1000 ppb
- **HM Ground Corn**: 1000 ppb
- **Almond Shells**: 500 ppb
- **Almond Hulls**: 100 ppb
Alcohols

- Ethanol
- Methanol
- Propanol
- Butanol
- Butanol Isopentyl alcohol
- Hexanol
Esters

- Methyl acetate
- Ethyl acetate
- Propyl acetate
- Butyl acetate
- Isoamyl acetate
- Hexyl acetate
- Ethyl propionate
- Propyl propionate

- Ethyl butyrate
- Propyl butyrate
- Butyl butyrate
- Ethyl hexanoate
- Propyl hexanoate
The bar chart illustrates the concentration, measured in parts per billion (ppb), of alkenes in various feed and feed ingredient samples. The y-axis represents the concentration, while the x-axis lists different categories:

- Corn
- Alfalfa
- Cereal
- TMR
- HM Ground Corn
- Almond Shells
- Almond Hulls

Corn has the highest concentration, with values exceeding 60 ppb, while the other categories show much lower values, with some close to or below 10 ppb.
Alkenes

- 1-Propene
- 2-methyl 2-Butene
- Isomer of Methylpropene
- Pentadiene Diene > C5
- Alkene > C6
- 1,4-Hexadiene
Aldehydes

Concentration, ppb

Corn, Alfalfa, Cereal, TMR, HM Ground Corn, Almond Shells, Almond Hulls
Aldehydes

- Acetaldehyde
- C4 Aldehyde
- Hexenal
- Hexanal Furaldehyde
- Heptanal
- Phenyl aceto aldehyde Benzaldehyde
- Octanal C8-C9
- Aldehydes isomers
- Decanal
Ketones

Concentration, ppb

Corn | Alfalfa | Cereal | TMR | HM Ground Corn | Almond Shells | Almond Hulls
--- | --- | --- | --- | --- | --- | ---
4 | 6 | 2 | 2 | 12 | 5 | 0.1
Ketones

- Acetone
- 2-Pentanone
- 3-Pentanone
- Methylisobutyl ketone
- Cyclohexanone
- Octanone
- Methyl phenyl ketone
Carbonyl compound emissions
(concentration, ppbV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Corn Silage</th>
<th>Alfalfa Silage</th>
<th>Cereal Silage</th>
<th>TMR</th>
<th>High Moisture Ground Corn</th>
<th>Almond Shells</th>
<th>Almond Hulls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>6.24</td>
<td>10.02</td>
<td>5.51</td>
<td>5.50</td>
<td>5.61</td>
<td>4.81</td>
<td>6.99</td>
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<tr>
<td>Acetaldehyde</td>
<td>178.84</td>
<td>172.59</td>
<td>249.72</td>
<td>385.79</td>
<td>55.62</td>
<td>3.33</td>
<td>4.42</td>
</tr>
<tr>
<td>Acrolein</td>
<td>0.83</td>
<td>3.84</td>
<td>0.50</td>
<td>1.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>20.28</td>
<td>24.79</td>
<td>10.07</td>
<td>20.21</td>
<td>34.92</td>
<td>4.20</td>
<td>4.82</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>36.60</td>
<td>46.48</td>
<td>3.95</td>
<td>34.32</td>
<td>2.23</td>
<td>0.35</td>
<td>0.78</td>
</tr>
<tr>
<td>Crotonaldehyde (2-Butenal)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butylaldehyde</td>
<td>57.85</td>
<td>40.72</td>
<td>4.91</td>
<td>17.67</td>
<td>22.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>15.07</td>
<td>16.65</td>
<td>6.27</td>
<td>5.69</td>
<td>26.39</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Hexaldehyde</td>
<td>0.96</td>
<td>1.22</td>
<td>0.49</td>
<td>2.29</td>
<td>0.90</td>
<td>0.53</td>
<td>0.89</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>17.96</td>
<td>1.42</td>
<td>1.87</td>
<td>1.69</td>
<td>0.72</td>
<td></td>
<td>0.24</td>
</tr>
</tbody>
</table>
What are important drivers for silage VOCs?
Ethanol emission rate is affected by several variables

Intact, packed corn silage
Ethanol emission rate is affected by several variables.
Emission rate is affected by temperature and air velocity

Intact, packed silage
Emission rate is affected by . . . temperature and air velocity

**Loose silage**

![Graph showing the relationship between normalized 12-hour emission, air velocity, and temperature.](image)
Emission rate is affected by permeability and exposed area.

1. 15 cm intact B
2. 15 cm loose A
3. 15 cm loose C
4. 15 cm loose B
5. 3 cm loose A
6. Exposed particles A & B
What is the ozone formation potential of dairy emission sources?
Average MIR by Chemical Class

- OCIs
- esters
- alkenes
- alkynes
- phenols
- alcohols
- ethers
- aldehydes & ketones
- acids
- nitrogenous
Mobile Ozone Chamber Assay (MOChA)

Graduate students Cody Howard and Doniche Derrick.
Mobile Ozone Chamber Assay (MOChA)

Separate lamp unit, with fans to aid temperature control.
Ethanol as a representative VOC

FIGURE 3. Contribution to total ozone formation from each lumped model species assuming additive behavior. Ozone formation associated with each species is calculated by removing that species from the ROG profile and observing the net reduction in ozone formation.

(Howard et al. 2010)
Ozone Production from Livestock Feed

Howard et al., (2010)
Summary

- Alcohols dominate the VOC spectrum by mass
- Acetone, VFAs, MeOH, EtOH are low in ozone formation potential
- Emissions of alkenes, alkynes, diene compounds, and aldehydes are abundant and reactive
- Volatilization of VOCs from silage reduces feed quality and has air quality impacts
# The Biology of Silage Preservation

<table>
<thead>
<tr>
<th>Phase</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Cell respiration - production of CO₂, heat and water</td>
</tr>
<tr>
<td>II</td>
<td>Production of acetic acid, lactic acid, ethanol</td>
</tr>
<tr>
<td>III</td>
<td>Lactic Acid Formation</td>
</tr>
<tr>
<td>IV</td>
<td>Material Storage</td>
</tr>
<tr>
<td>V</td>
<td>Aerobic deterioration on re-exposure to oxygen</td>
</tr>
</tbody>
</table>

### Temperature Change
- 70°F (21°C) to 90°F (32.2°C) to 110°F (43.3°C)

### pH Change
- 6.0-6.5 to 5.0 to ≈ 4.0 to 7.0

### Age of Silage (Days)
- 2
- 3
- 4
- 21

### Microorganisms
- Acetic acid and Lactic acid bacteria
- Lactic acid bacteria
- Aerobic bacteria, yeast and mold activity
Possible new directions

1. VOC production and consumption in silage—where do they come from, when and how quickly are they formed and destroyed?
2. Improvements in wind tunnel, portable design for field measurements
3. Equilibrium method for measurement of other VOCs in silage
4. Explore relationship between our approach and atmospheric measurements
5. Determination of the effects of management practices on total VOC emissions through farm level modeling and monitoring.


Hafner, SD, Montes, F., Rotz, CA, and Mitloehner, FM. Ethanol emissions from loose corn silage and exposed silage particles. Atmospheric Environment. IN PRESS