

Emissions of volatile organic compounds from silage

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Emission of volatile organic compounds from silage

Sasha Hafner, Felipe Montes, Al Rotz
USDA-ARS, University Park, PA

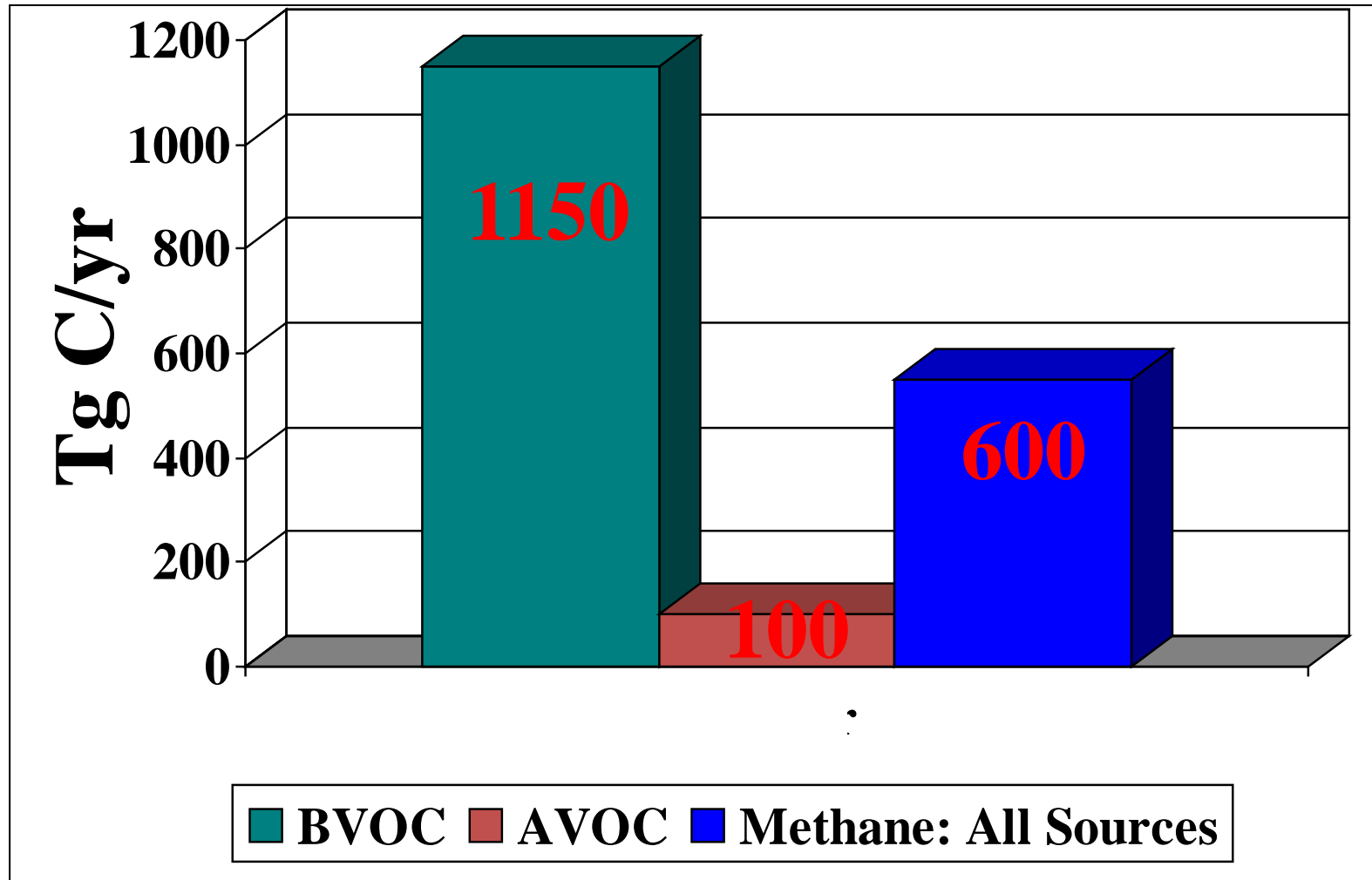
Howard, C. J., A. Kumar, I. A. Malkina,
P. G. Green, R. Flocchini, and M. Kleeman, UC
Davis

Shaw SL, Holzinger R, Goldstein AH.
UC Berkeley

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

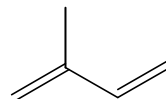


Biogenic Volatile Organic Compounds in Earth's Atmosphere

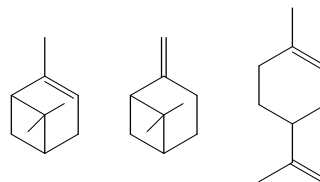
(BVOCs, 1000's of compounds)

Amount Known

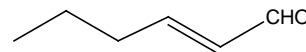
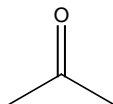
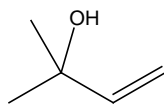
- Isoprene (C_5H_8)



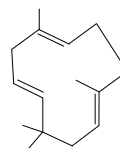
- Monoterpenes ($C_{10}H_{16}$)



- Oxygenated VOC



- Sesquiterpenes ($C_{15}H_{24}$)





Cattle feed is the leading VOC source on dairies

Table 4

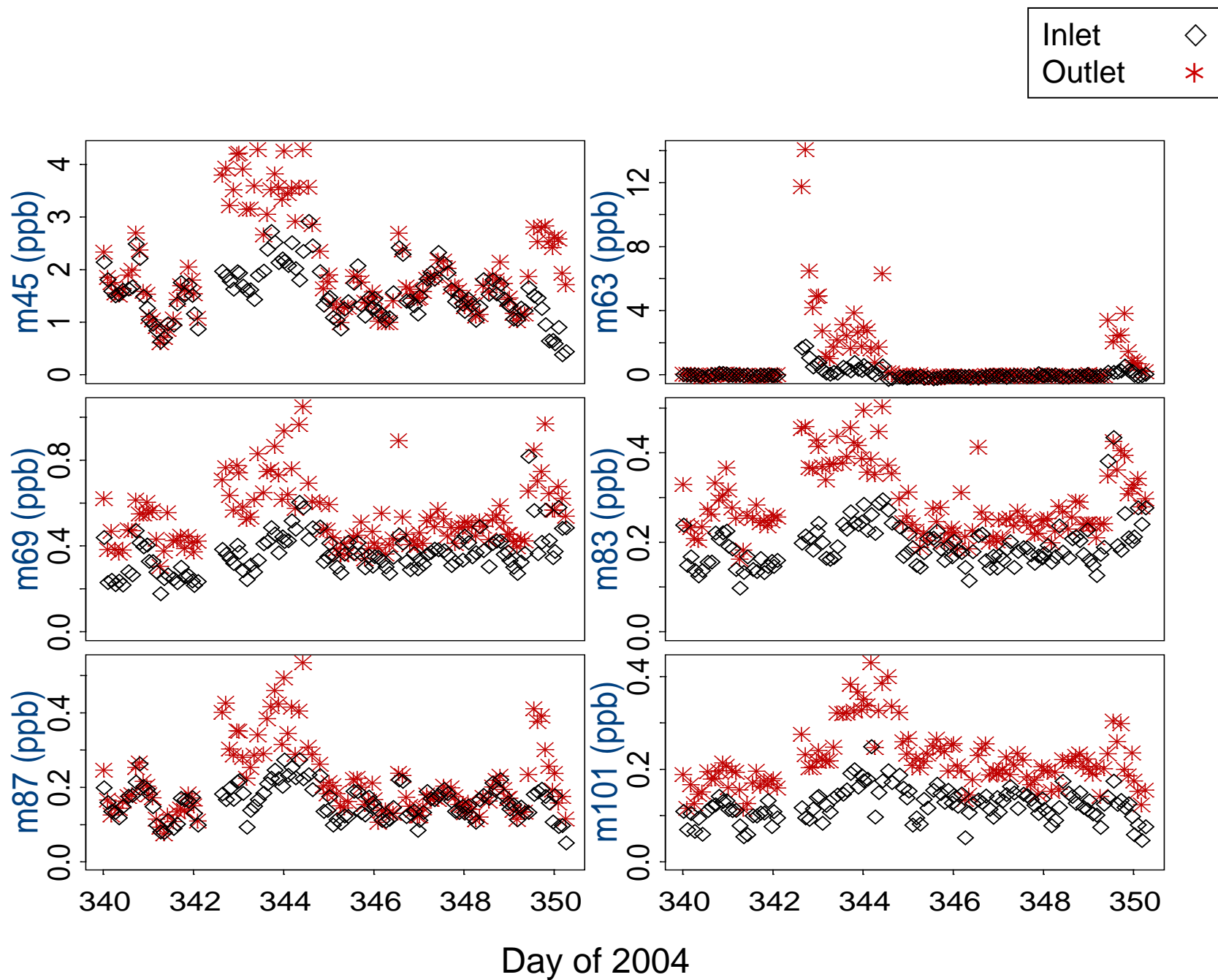
Estimated relative contribution of dairy sources to ozone formation.

Source	Estimated relative surface area/%	Relative contribution to ozone (MS)	Relative contribution to ozone (FID)
TMR	1	0.65	0.54
Silage	0.5	0.31	0.40
Flushing Lanes	0.8	4×10^{-5}	1×10^{-3}
Lagoon	69	0.04	0.03
Open Lot	27	9×10^{-3}	0.03
Bedding	1	1×10^{-4}	4×10^{-3}

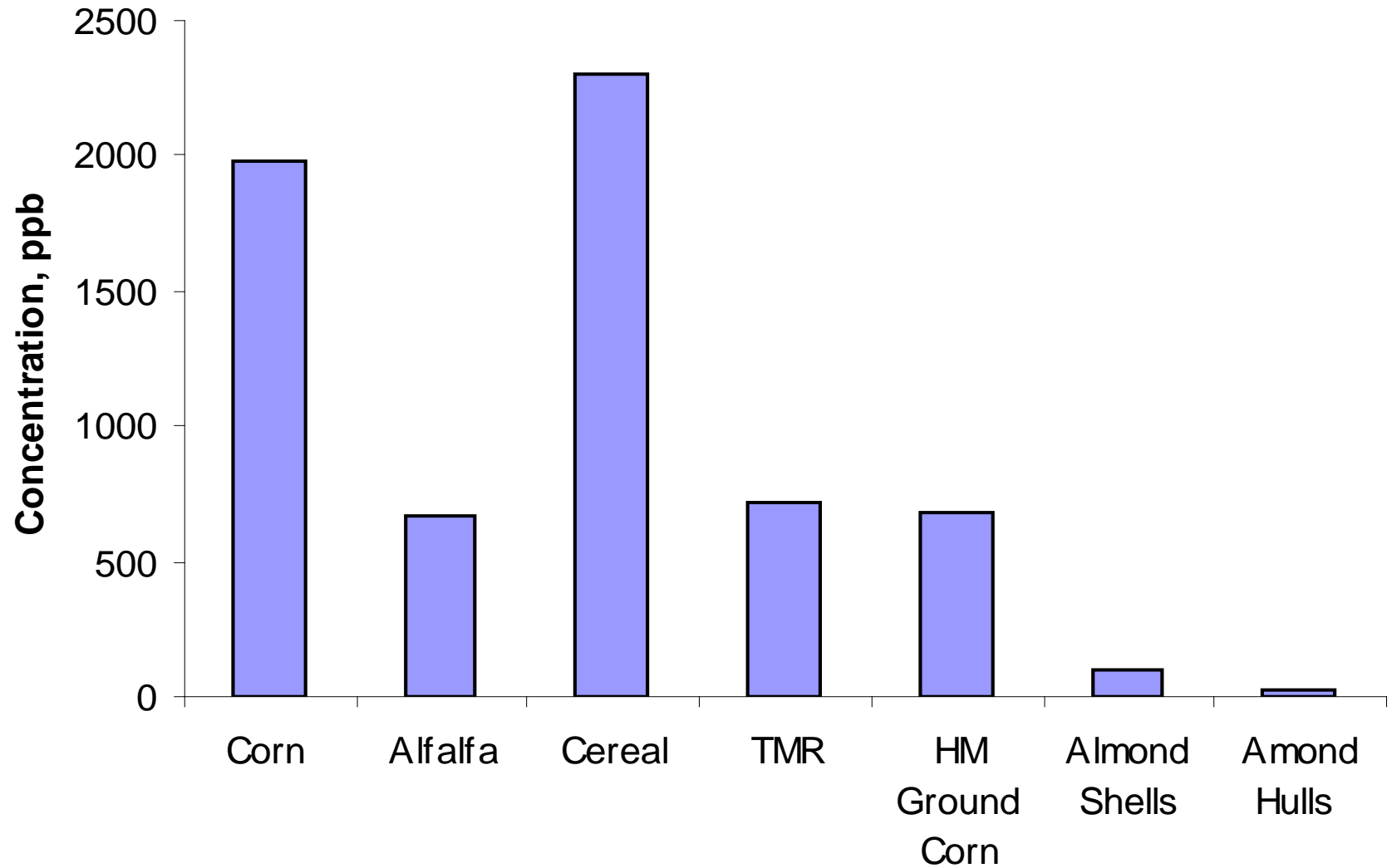
(Chung et al. 2009)



Which VOCs are present in
silage?



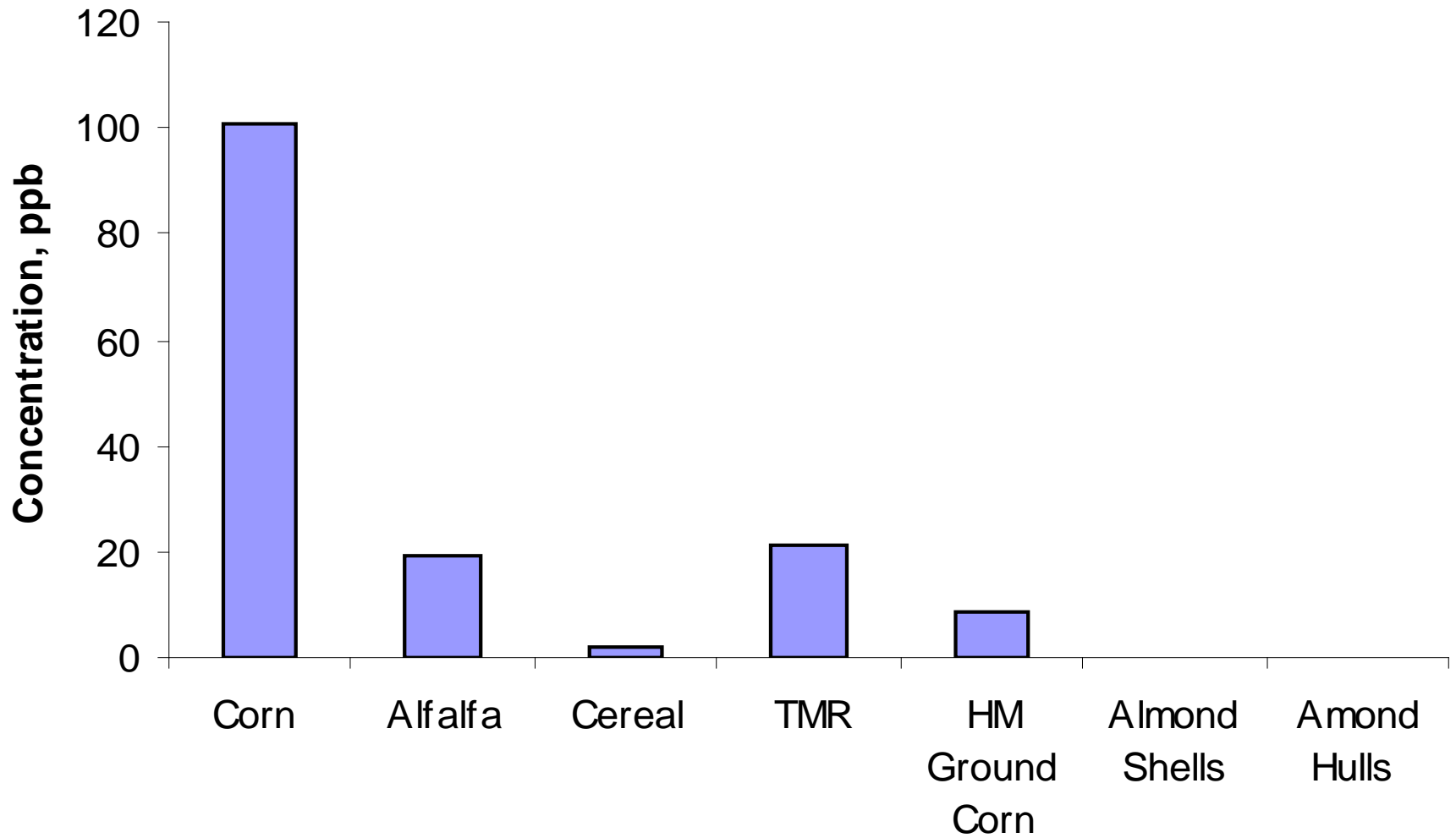
Alcohols



Alcohols

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

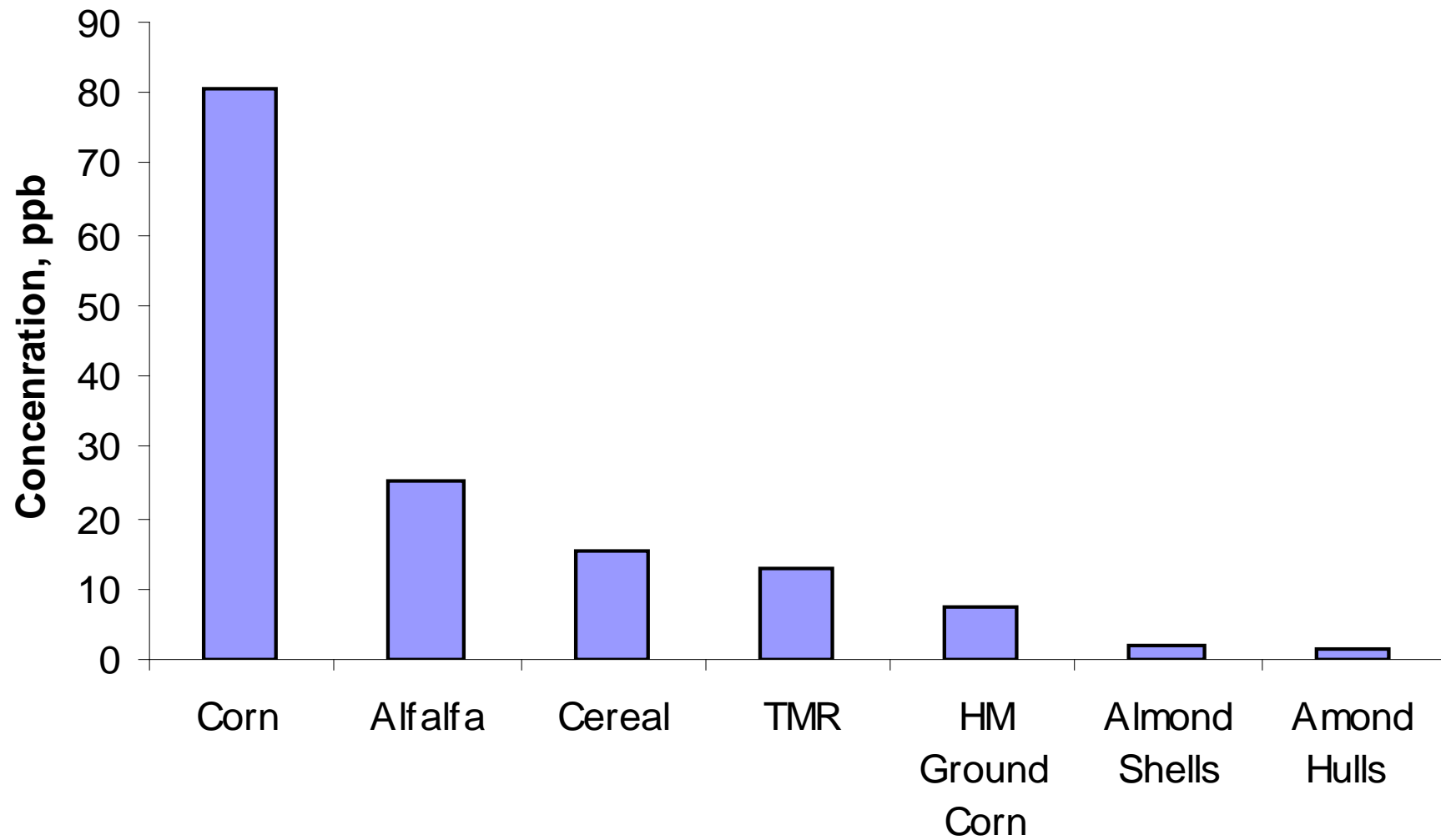
Esters



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

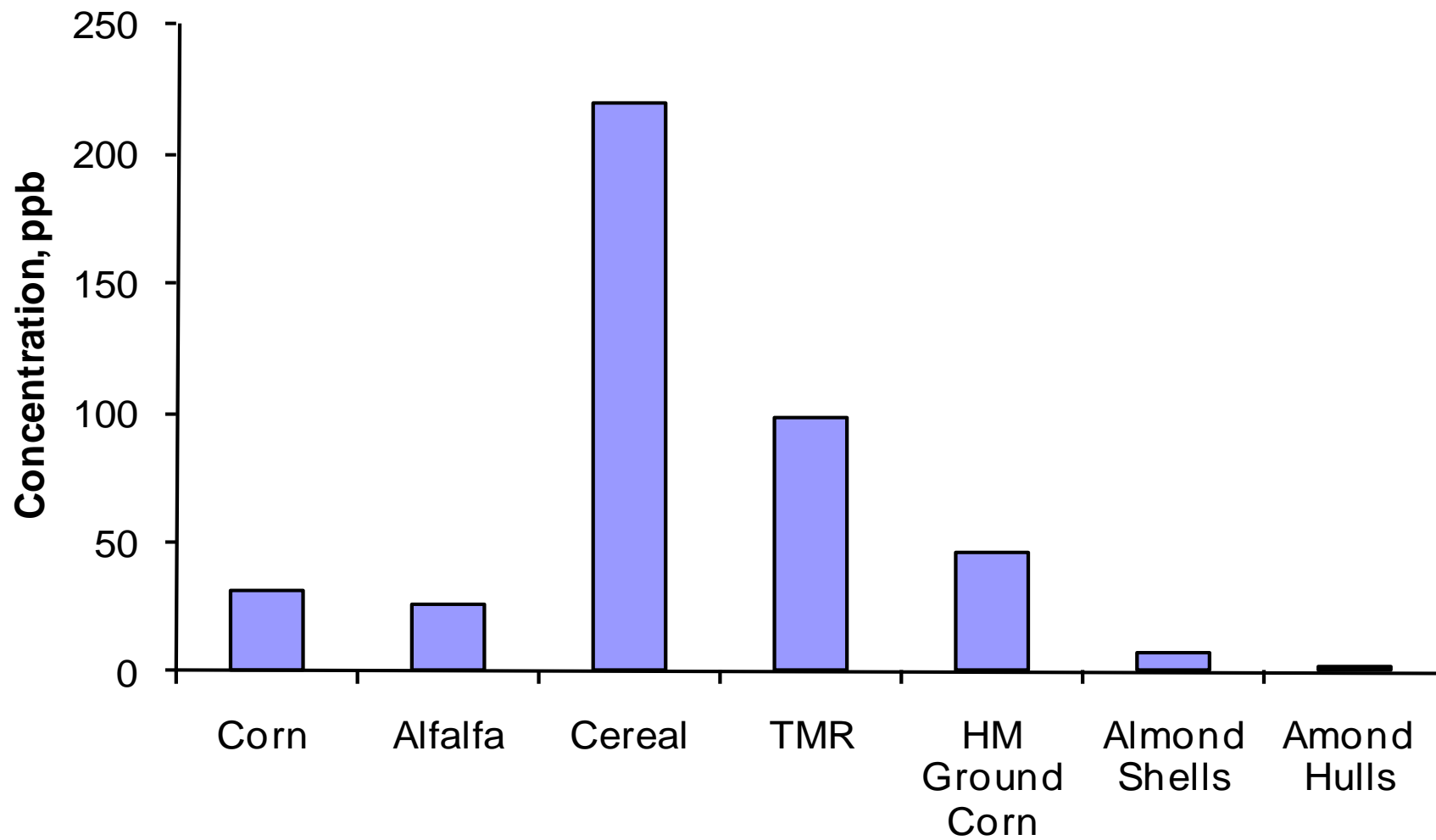
Alkenes



Alkenes

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

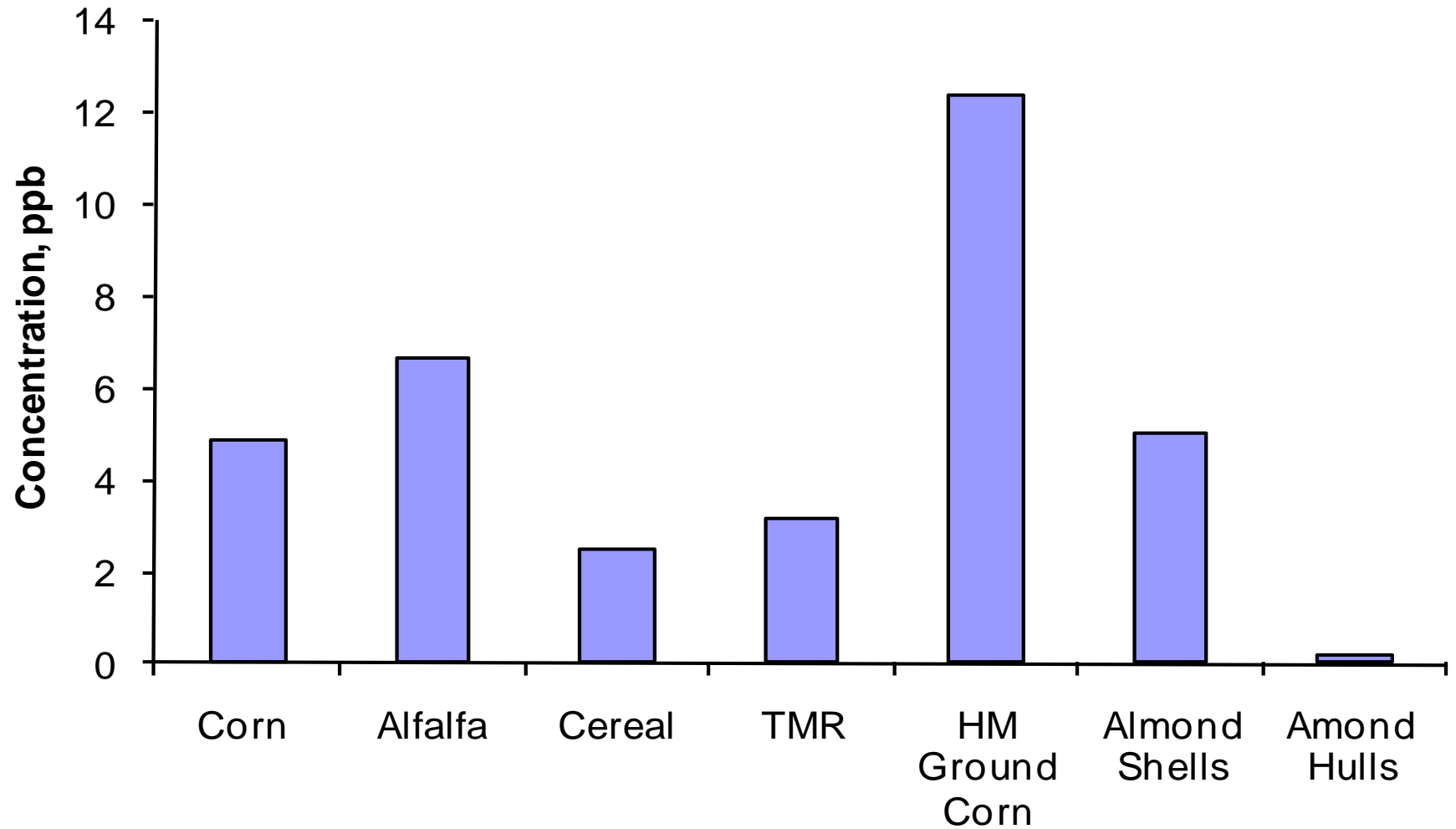
Aldehydes



Aldehydes

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

Ketones



Ketones

- Acetone
- 2-Pentanone
- 3-Pentanone
- Methylisobutyl ketone
- Cyclohexanone
- Octanone
- Methyl phenyl ketone

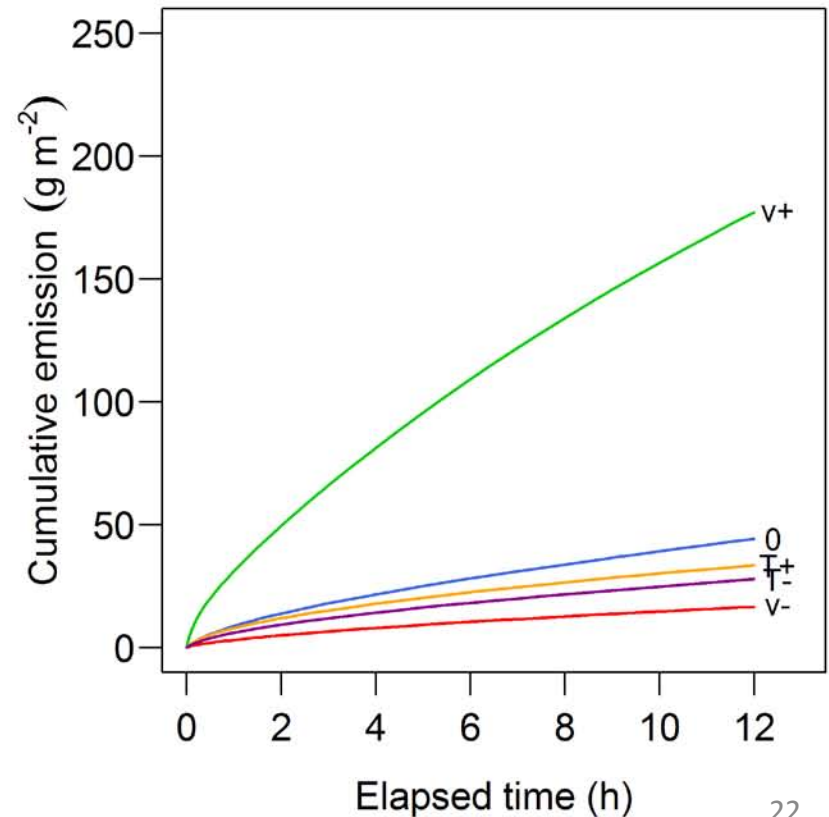
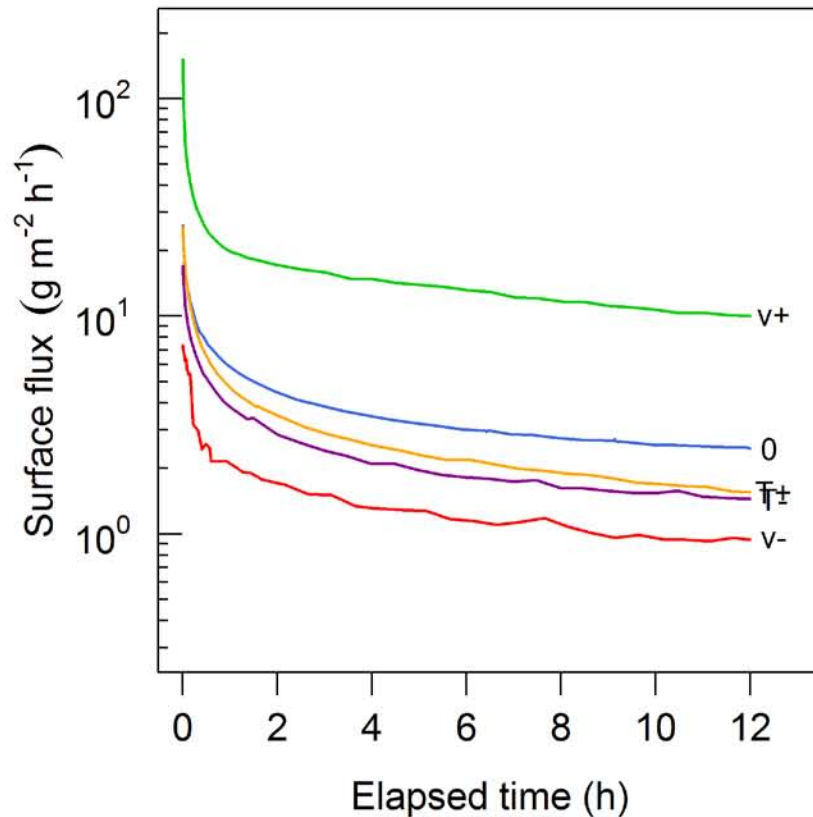
Carbonyl compound emissions (concentration, ppbV)

Compound	Corn Silage	Alfalfa Silage	Cereal Silage	TMR	High Moisture Ground Corn	Almond Shells	Almond Hulls
Formaldehyde	6.24	10.02	5.51	5.50	5.61	4.81	6.99
Acetaldehyde	178.84	172.59	249.72	385.79	55.62	3.33	4.42
Acrolein	0.83	3.84	0.50	1.40			
Acetone	20.28	24.79	10.07	20.21	34.92	4.20	4.82
Propionaldehyde	36.60	46.48	3.95	34.32	2.23	0.35	0.78
Crotonaldehyde (2- Butenal)			0.28				
Butylaldehyde	57.85	40.72	4.91	17.67	22.22		
Isovaleraldehyde	15.07	16.65	6.27	5.69	26.39	0.09	
Valeraldehyde	0.68			0.39			
Hexaldehyde	0.96	1.22	0.49	2.29	0.90	0.53	0.89
Benzaldehyde	17.96	1.42	1.87	1.69	0.72		0.24

What are important drivers for
silage VOCs?

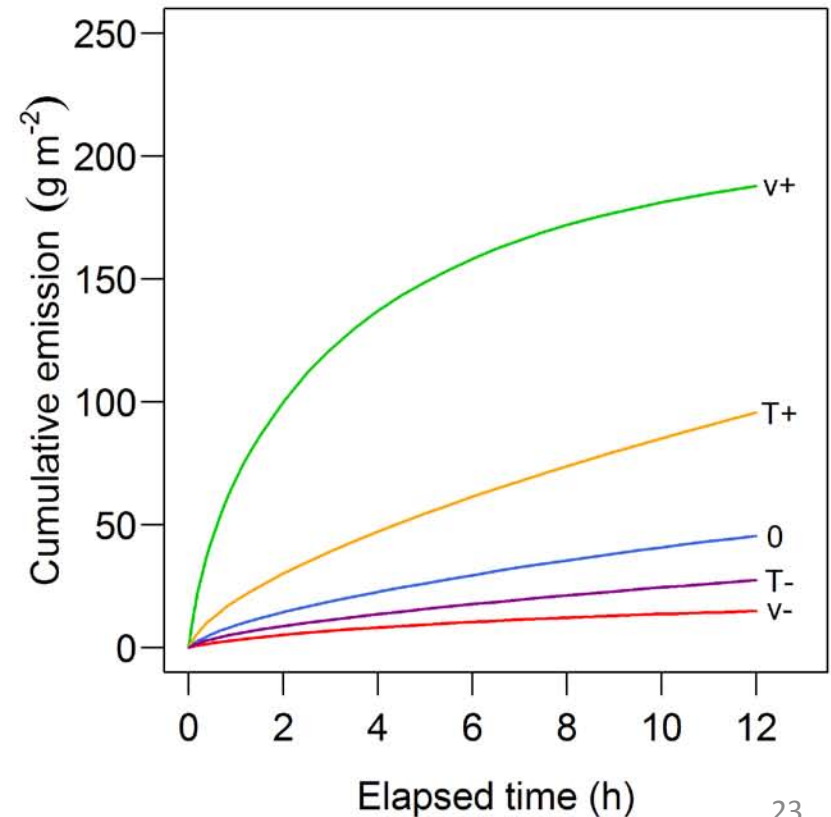
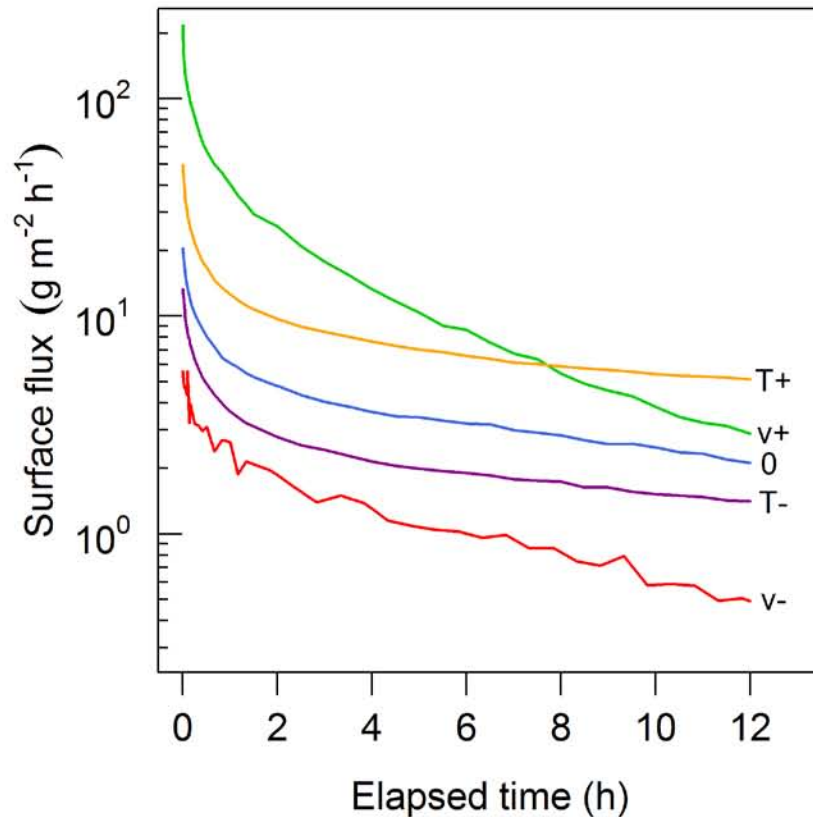
Ethanol emission rate is affected by several variables

Intact, packed corn silage



Ethanol emission rate is affected by several variables

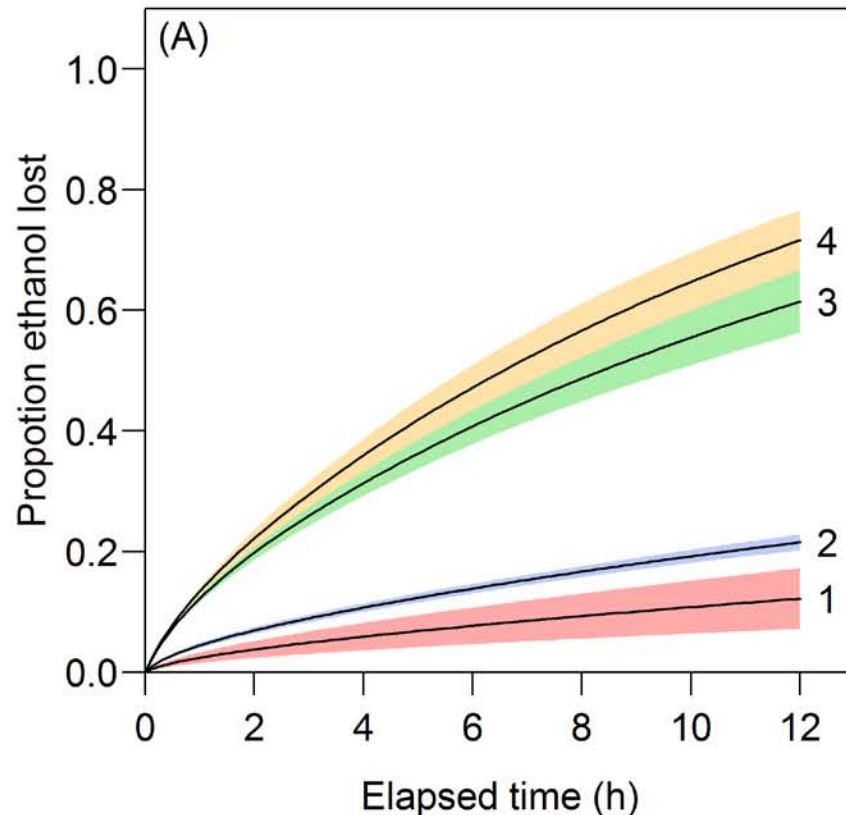
Loose corn silage



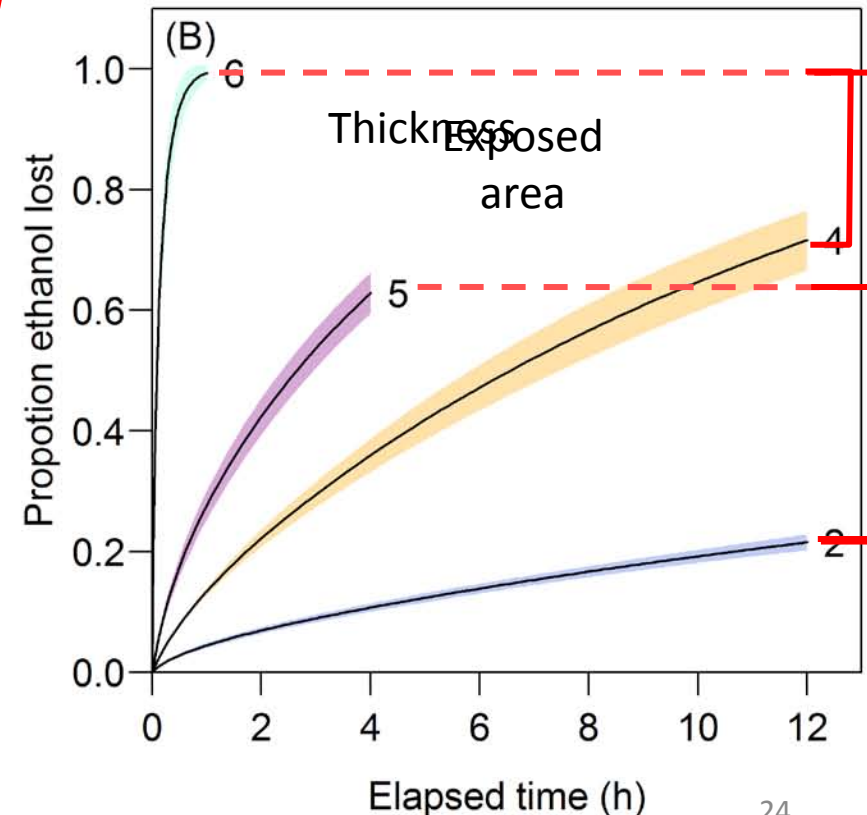
Emission rate is affected by permeability and exposed area

1. 15 cm intact B
2. 15 cm loose A
3. 15 cm loose C
4. 15 cm loose B

2. 15 cm loose A
4. 15 cm loose B
5. 3 cm loose A
6. Exposed particles A & B

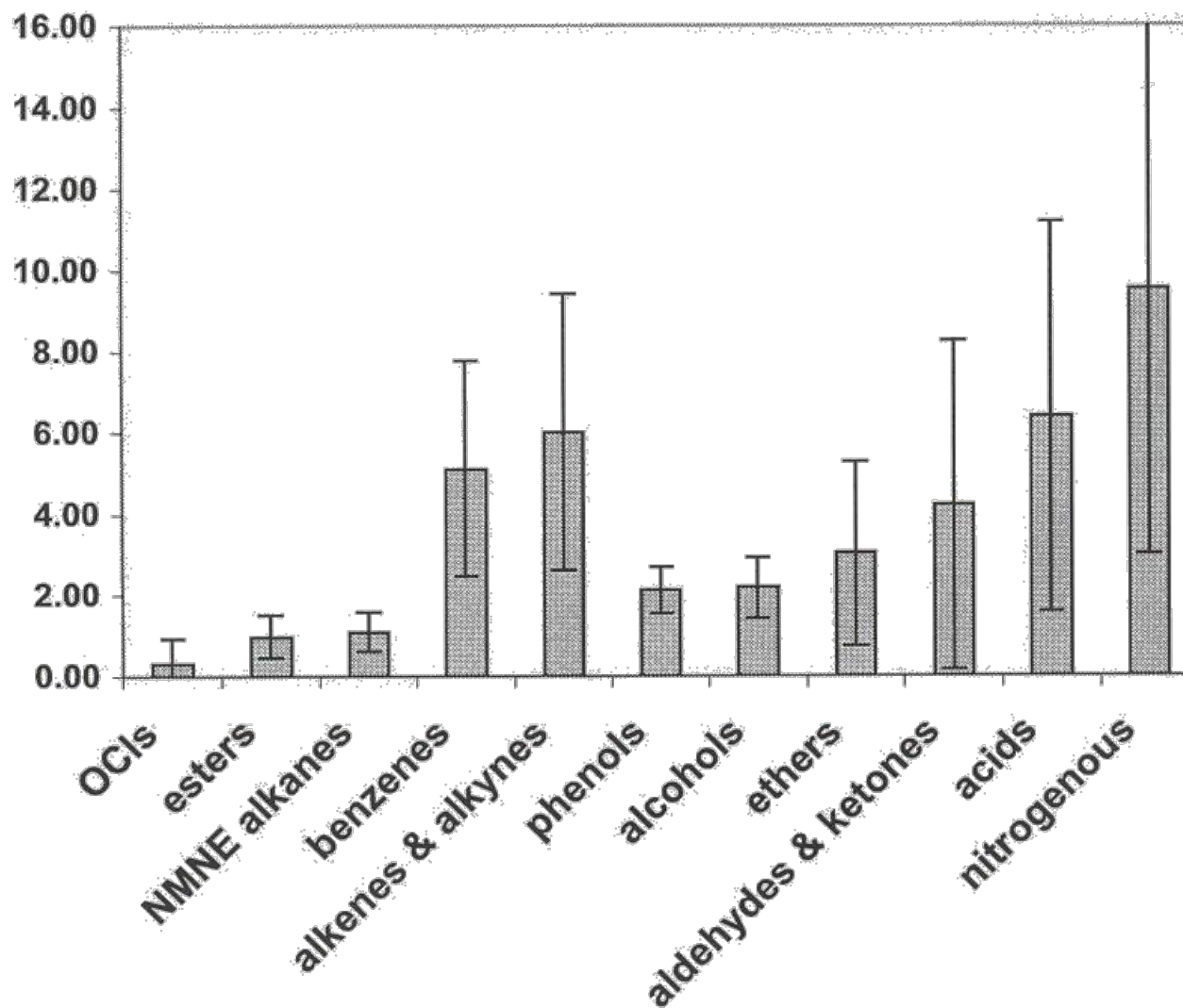


Density/
Particle
porosity
size



What is the ozone formation potential
of dairy emission sources?

Average MIR by Chemical Class



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

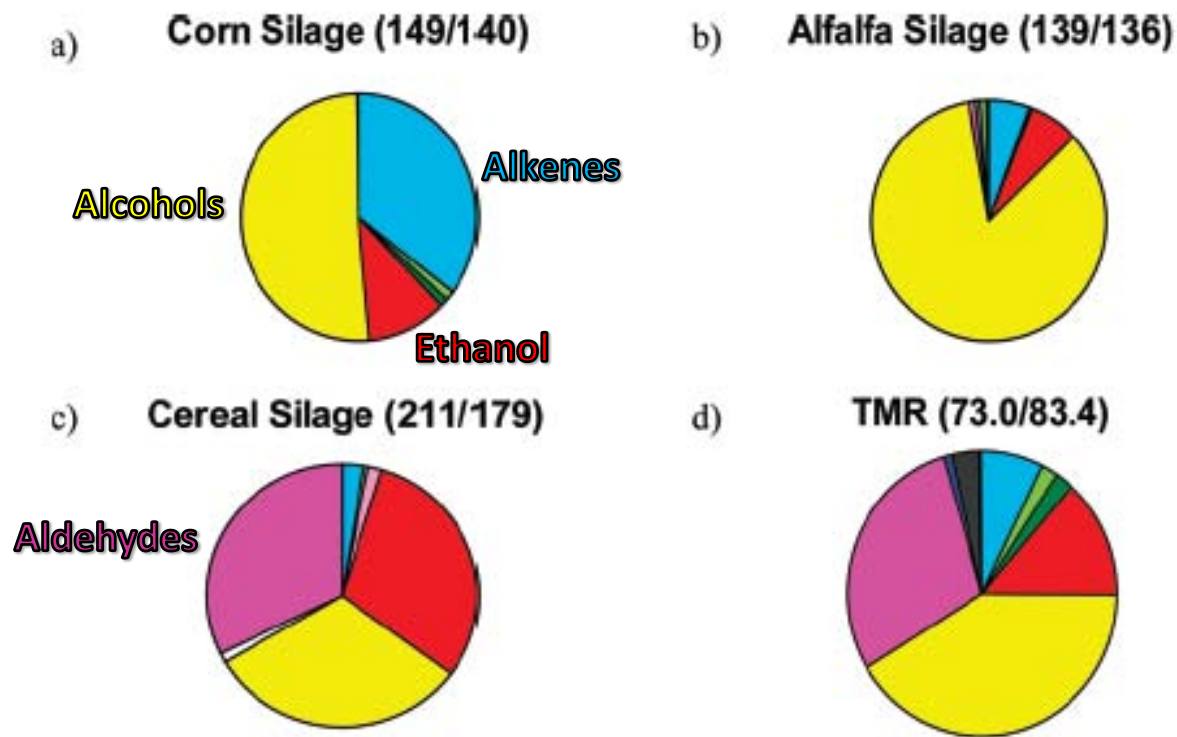
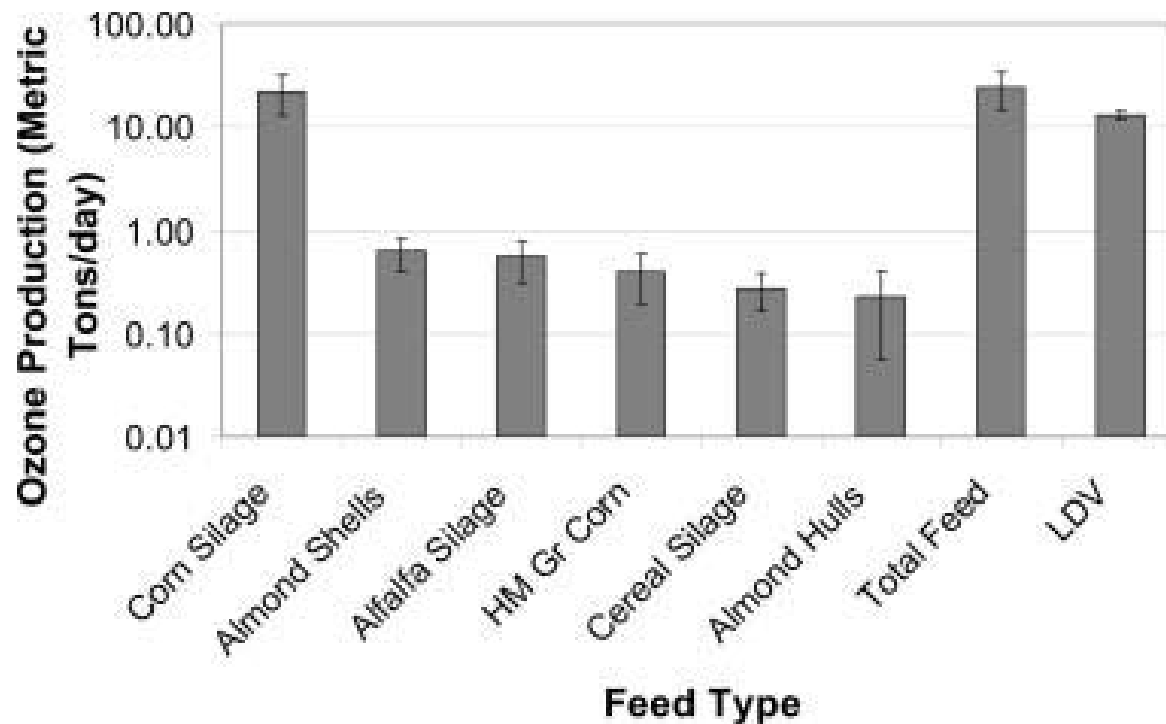


FIGURE 3. Contribution to total ozone formation from each lumped model species assuming additive behavior. Ozone formation associated with each species is calculated by removing that species from the ROG profile and observing the net reduction in ozone formation.

(Howard et al. 2010)



Ozone Production from Livestock Feed

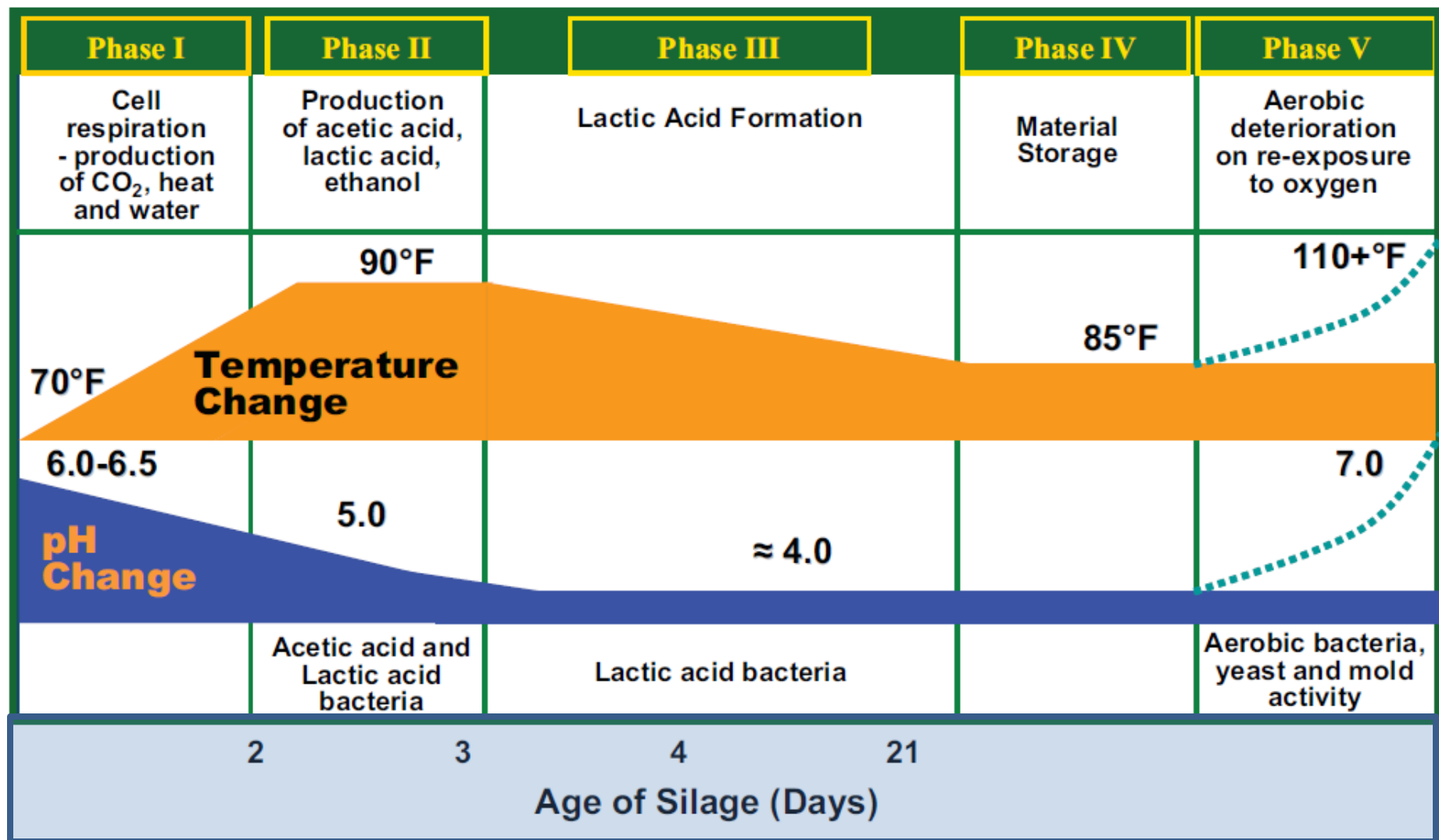


Howard et al., (2010)

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



Covering Corn Silage

Challenges at Covering



Storing Corn Silage

Storing Silage







Corn Silage Feedout

Smooth Face

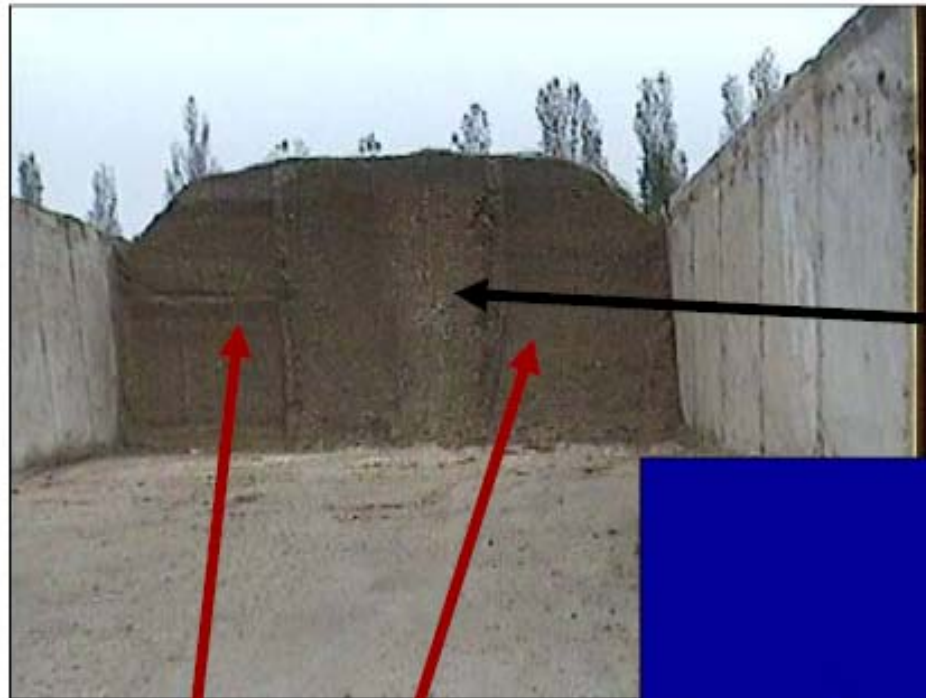
Prevent crack formation
that favors air penetration



Tight Face

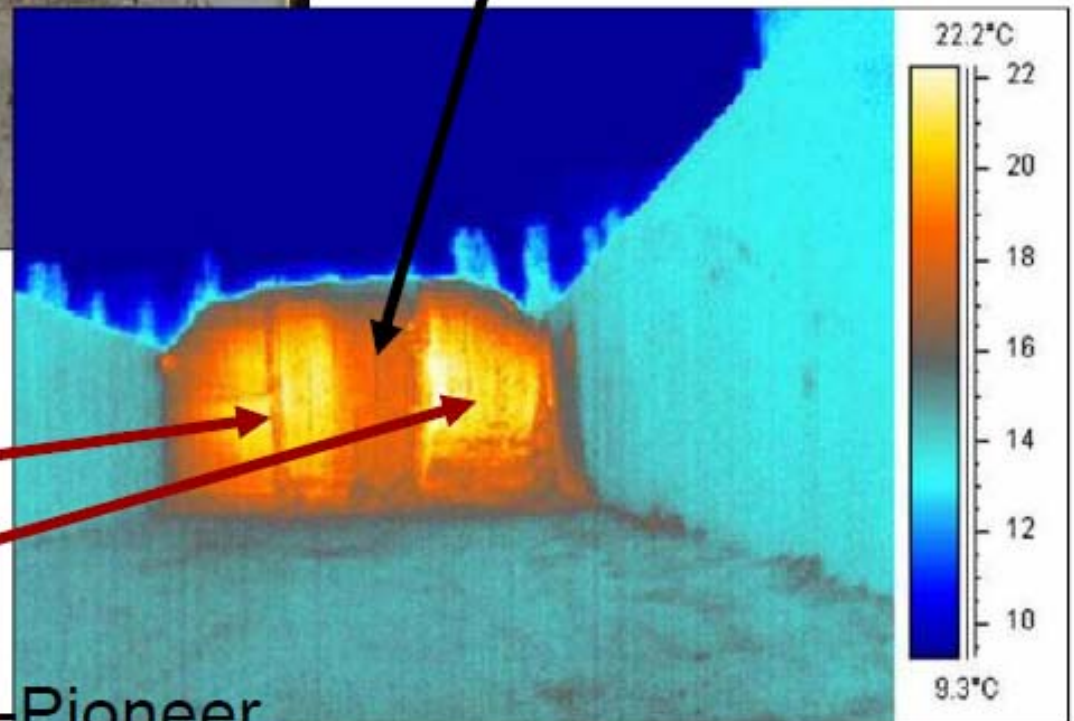
Keep air out of the
edges and seams





Notice area where last faced which is not as hot because aerobic bacteria just starting to multiply

Areas that have had more time for oxygen to penetrate and fuel growth of aerobic organisms causing heating



Source: Bill Mahanna-Pioneer



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.

Shaw SL, Mitloehner FM, Jackson W, DePeters EJ, Fadel JG, Robinson PH, Holzinger R, Goldstein AH. 2009. Volatile organic compound emissions from dairy cows and their waste as measured by proton-transfer-reaction mass spectrometry. *Env. Sci. Technol.* 41(4): 1310-6.

Howard, C. J., A. Kumar, I. A. Malkina, F. M. Mitloehner, P. G. Green, R. Flocchini, and M. Kleeman. 2010. Reactive Organic Gas Emissions from Livestock Feed Contribute Significantly to Ozone Production in Central California. *Env. Sci. & Technol.* 44(7): 2309-2314.

Montes, F., S. D. Hafner, C. A. Rotz, and F. M. Mitloehner. 2010. Temperature and air velocity effects on ethanol emission from corn silage with the characteristics of an exposed silo face. *Atmospheric Environment* 44:1987:1995

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

