Emissions of volatile organic compounds from silage

Pacific SW Organic Residuals Symposium, Sept 14-15, 2010

Frank Mitloehner, PhD

Assoc Professor & Air Quality Specialist

Dept of Animal Science

University of California, Davis

Emission of volatile organic compounds from silage

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

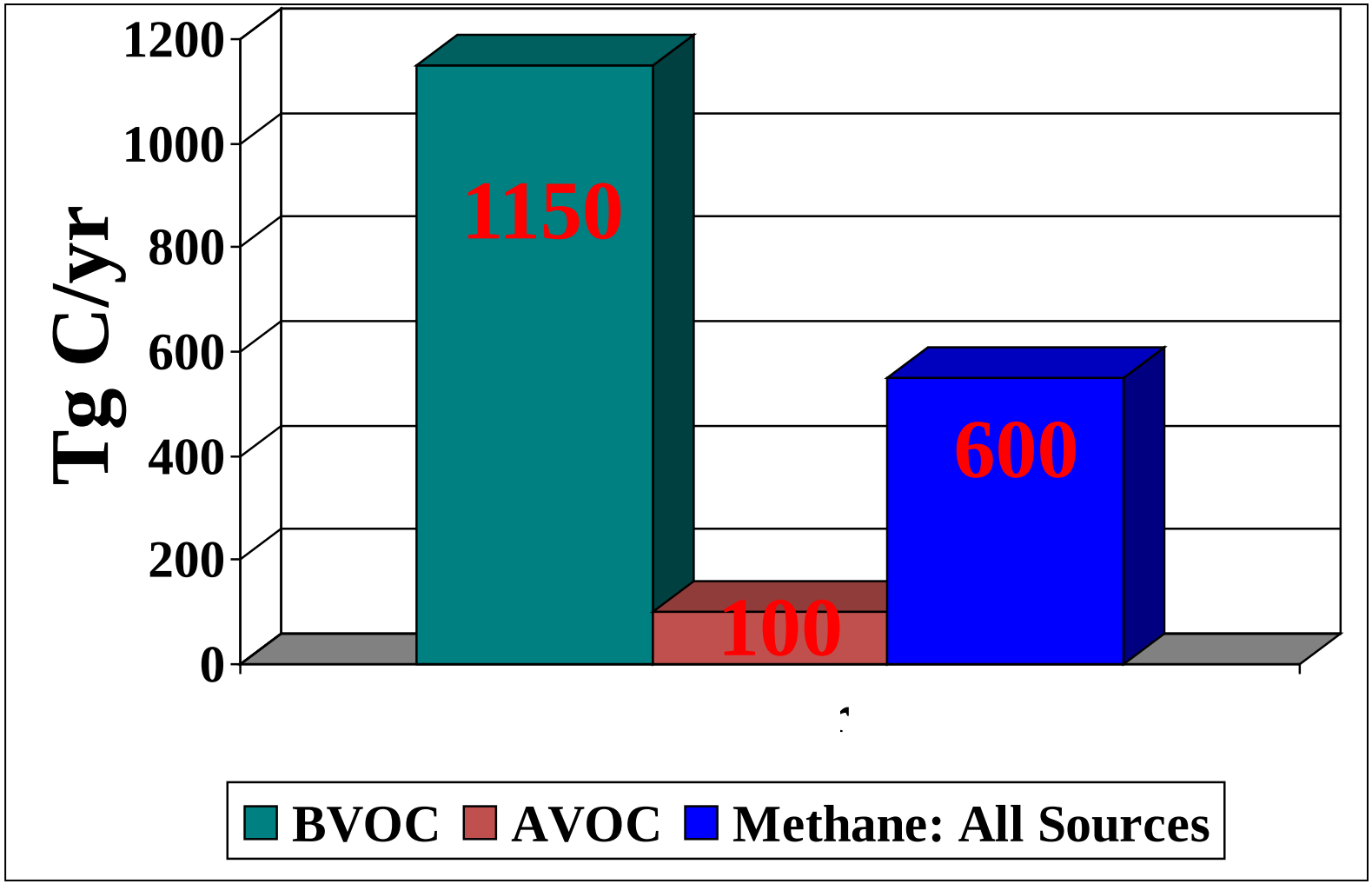
Howard, C. J., A. Kumar, I. A. Malkina,
P. G. Green, R. Flocchini, and M. Kleeman, UC Davis

Shaw SL, Holzinger R, Goldstein AH.
UC Berkeley

What <u>do we know</u> 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



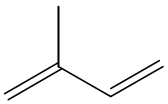
Guenther et al 1995, Singh and Zimmerman 1992

Biogenic Volatile Organic Compounds in Earth's Atmosphere

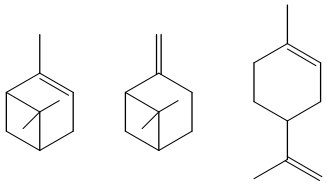
(BVOCs, 1000's of compounds)

Amount Known

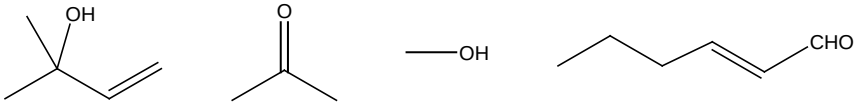
- Isoprene (C5H8)



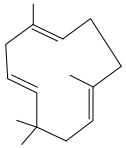
- Monoterpenes (C10H16)



- Oxygenated VOC



- Sesquiterpenes (C15H24)

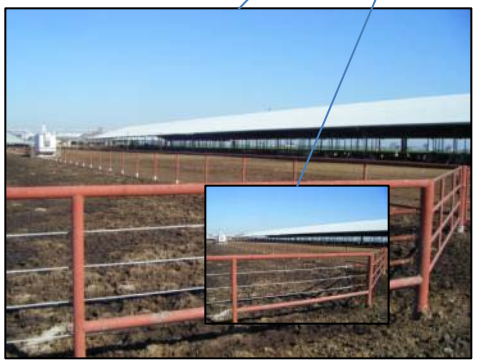


Cattle feed is the leading VOC source on dairies

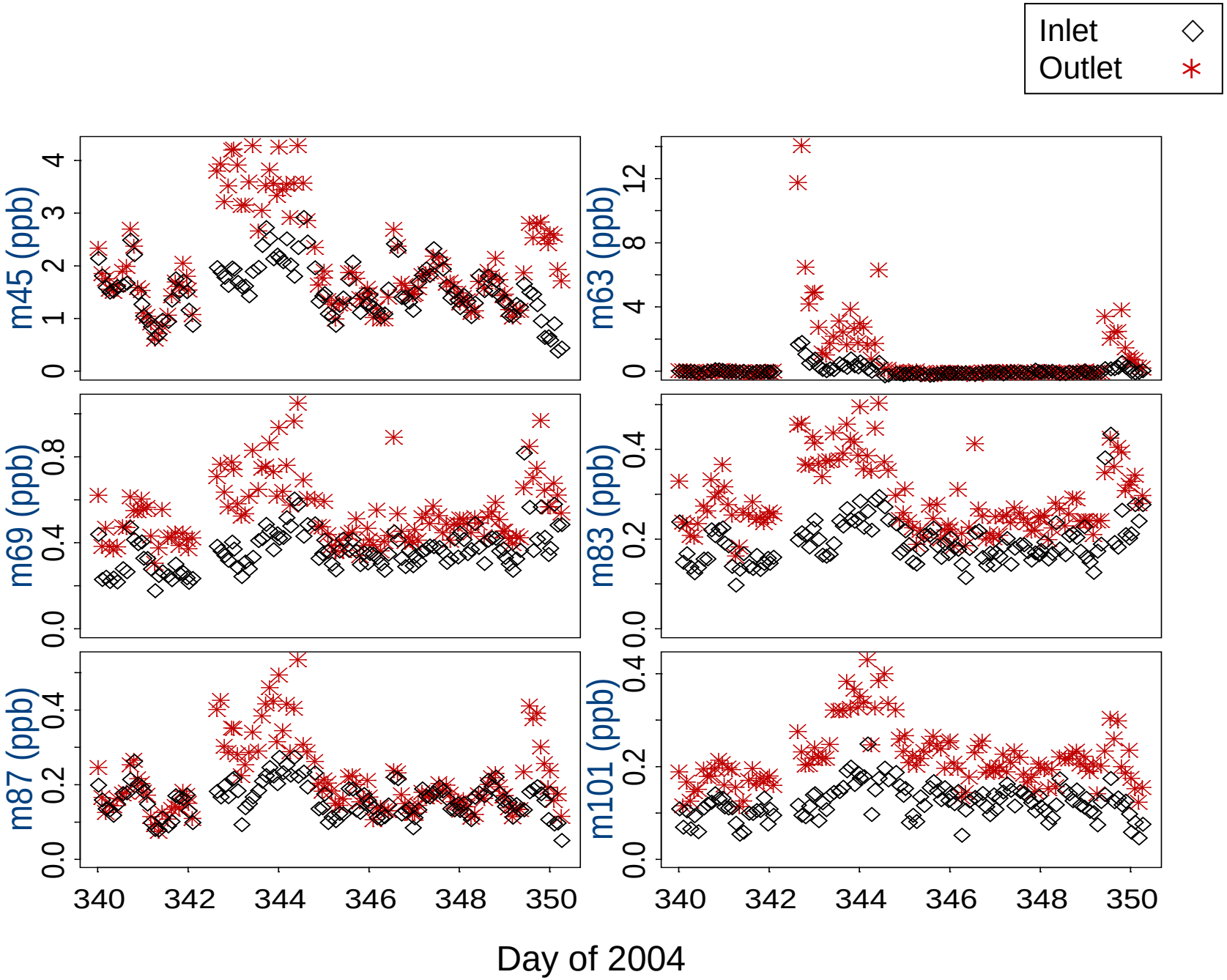
Table 4
Estimated relative contribution of dairy sources to ozone formation.

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}

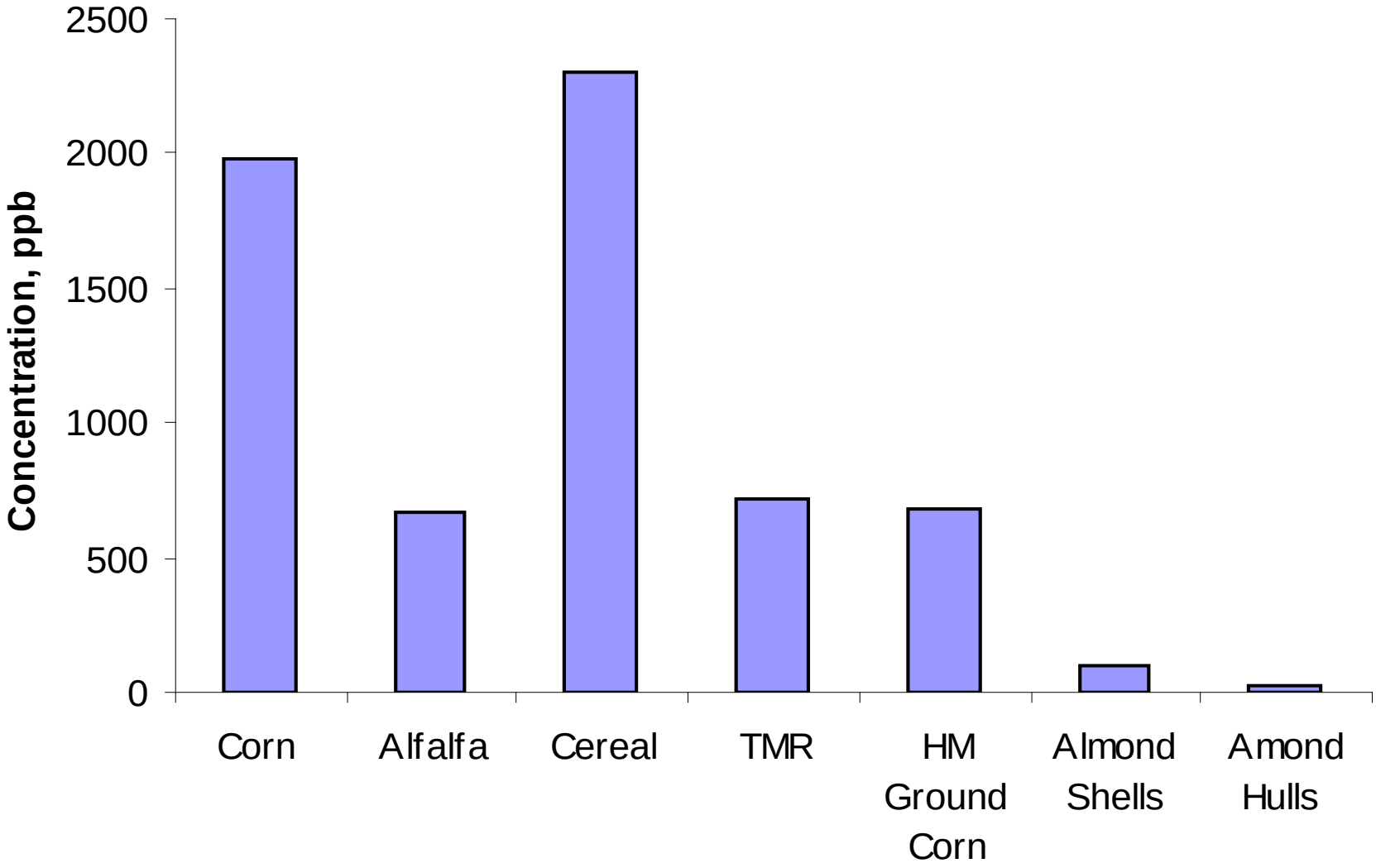
(Chung et al. 2009)



Which VOCs are present in silage?


Inlet
Outlet
m45 (ppb)
m63 (ppb)
m69 (ppb)
m83 (ppb)
m87 (ppb)
m101 (ppb)
0
1
2
3
4
0
4
8
12
0.0
0.4
0.8
0.0
0.2
0.4
0.0
0.2
0.4
0.0
0.2
0.4
340
342
344
346
348
350
Day of 2004

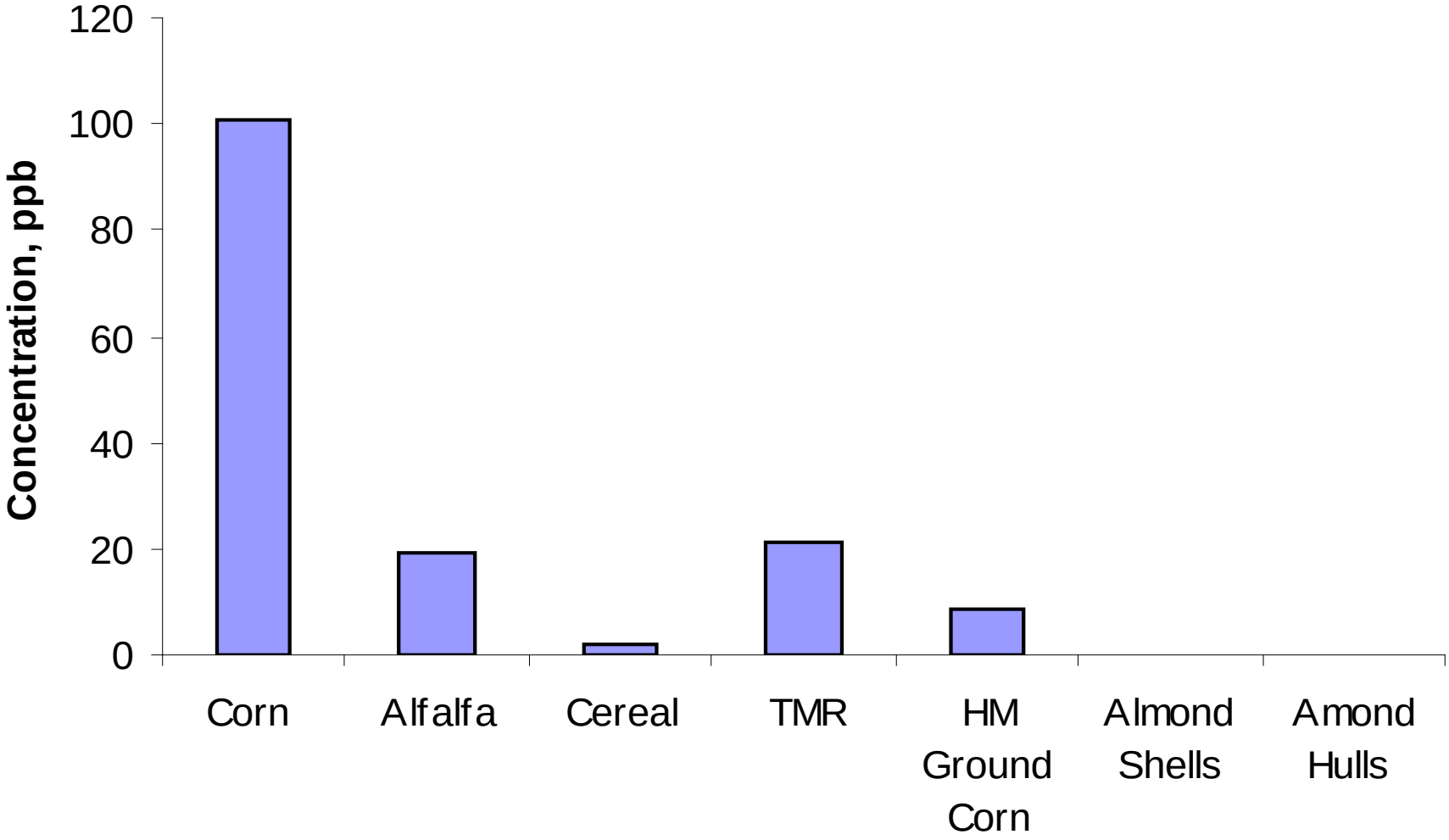
Alcohols


Concentration, ppb
2500
2000
1500
1000
500
0
Corn
Alfalfa
Cereal
TMR
HM Ground Corn
Almond Shells
Amond Hulls

Alcohols

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

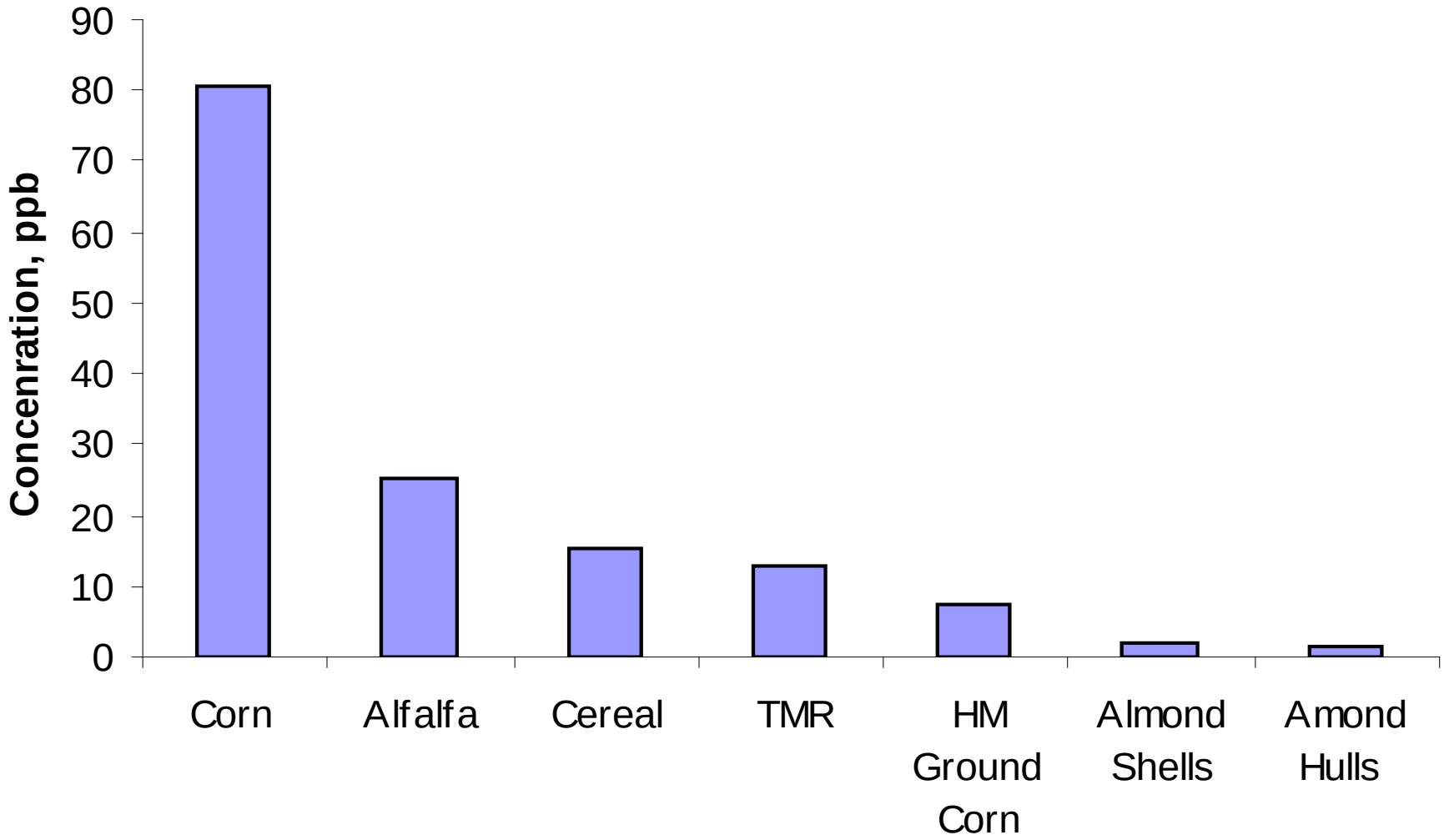
Esters


Concentration, ppb
120
100
80
60
40
20
0
Corn
Alfalfa
Cereal
TMR
HM Ground Corn
Almond Shells
Amond Hulls

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

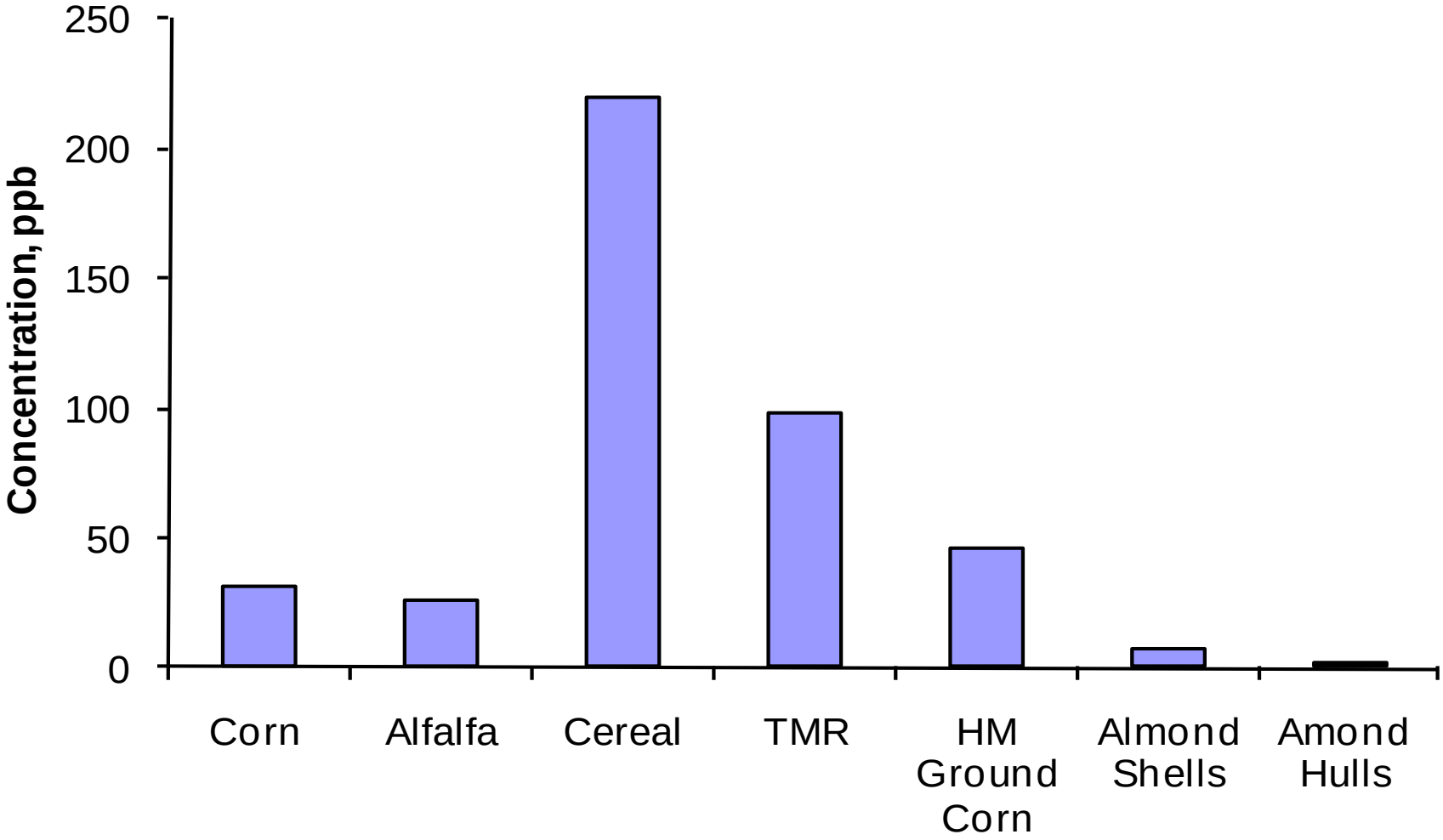
Alkenes


Concenration, ppb
90
80
70
60
50
40
30
20
10
0
Corn
Alfalfa
Cereal
TMR
HM Ground Corn
Almond Shells
Amond Hulls

Alkenes

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

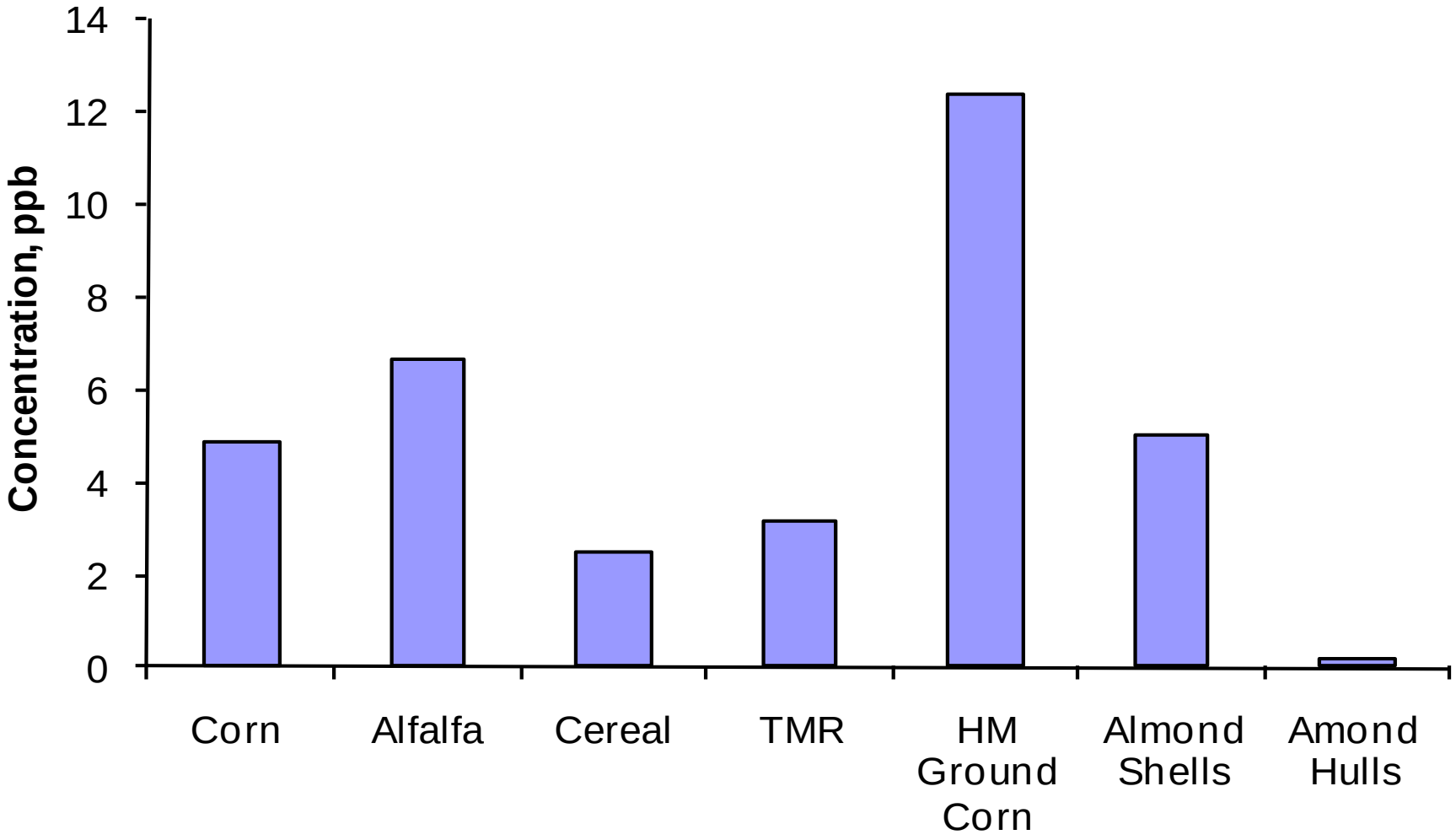
Aldehydes


Concentration, ppb
250
200
150
100
50
0
Corn
Alfalfa
Cereal
TMR
HM Ground Corn
Almond Shells
Amond Hulls

Aldehydes

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

Ketones


Concentration, ppb
14
12
10
8
6
4
2
0
Corn
Alfalfa
Cereal
TMR
HM Ground Corn
Almond Shells
Amond Hulls

Ketones

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

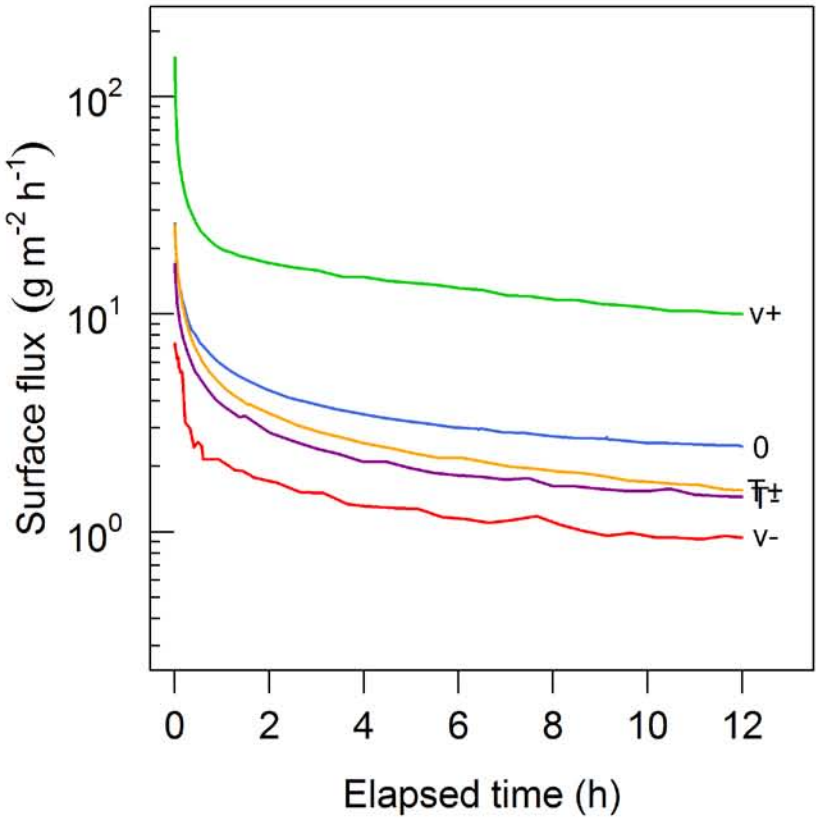
Carbonyl compound emissions (concentration, ppbV)

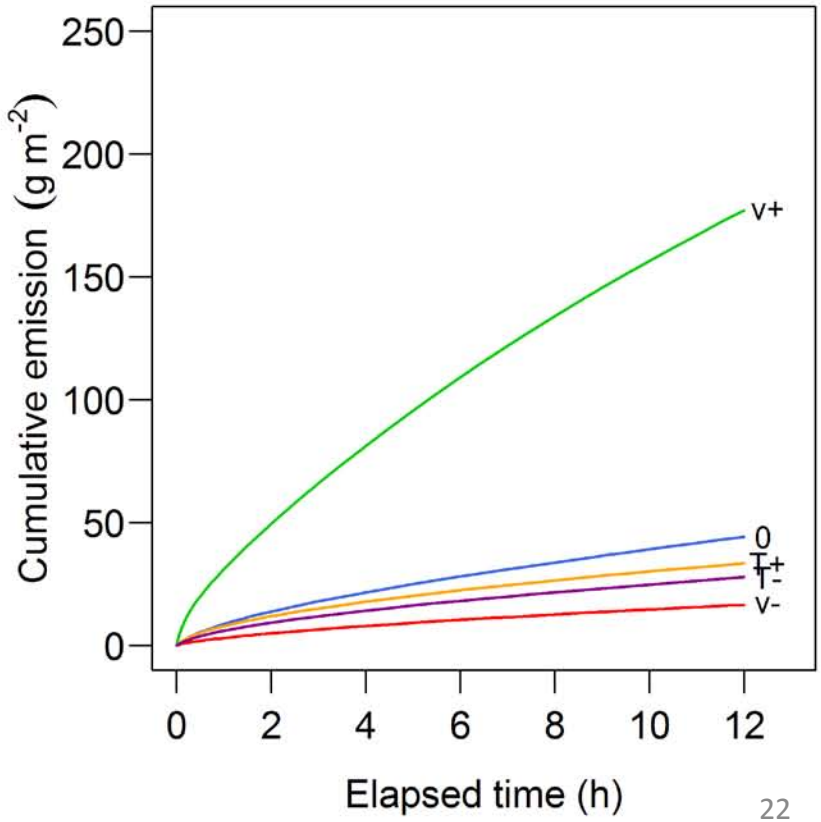
Compound	Corn Silage	Alfalfa Silage	Cereal Silage	TMR	High Moisture Ground Corn	Almond Shells	Almond Hulls
Formaldehyde	6.24	10.02	5.51	5.50	5.61	4.81	6.99
Acetaldehyde	178.84	172.59	249.72	385.79	55.62	3.33	4.42
Acrolein	0.83	3.84	0.50	1.40			
Acetone	20.28	24.79	10.07	20.21	34.92	4.20	4.82
Propionaldehyde	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

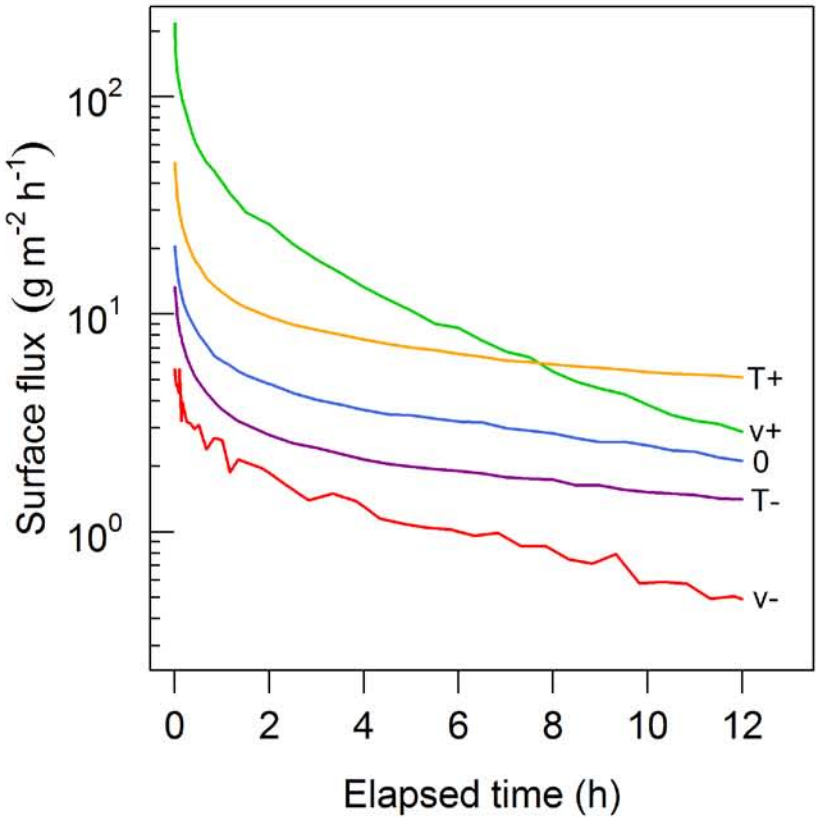
Intact, packed corn silage

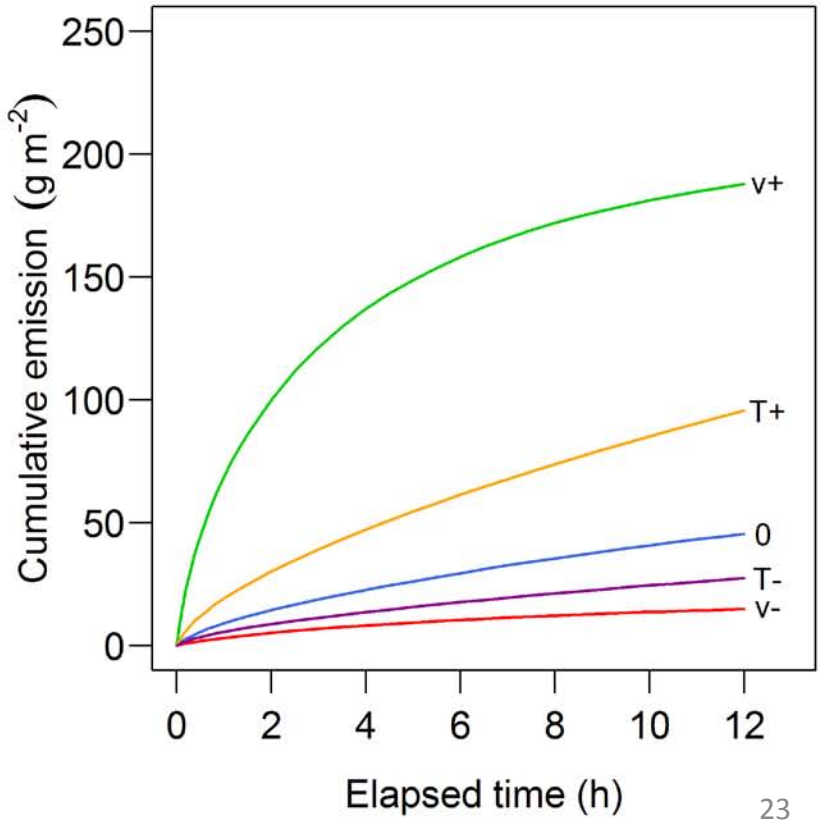




Ethanol emission rate is affected by several variables

Loose corn silage





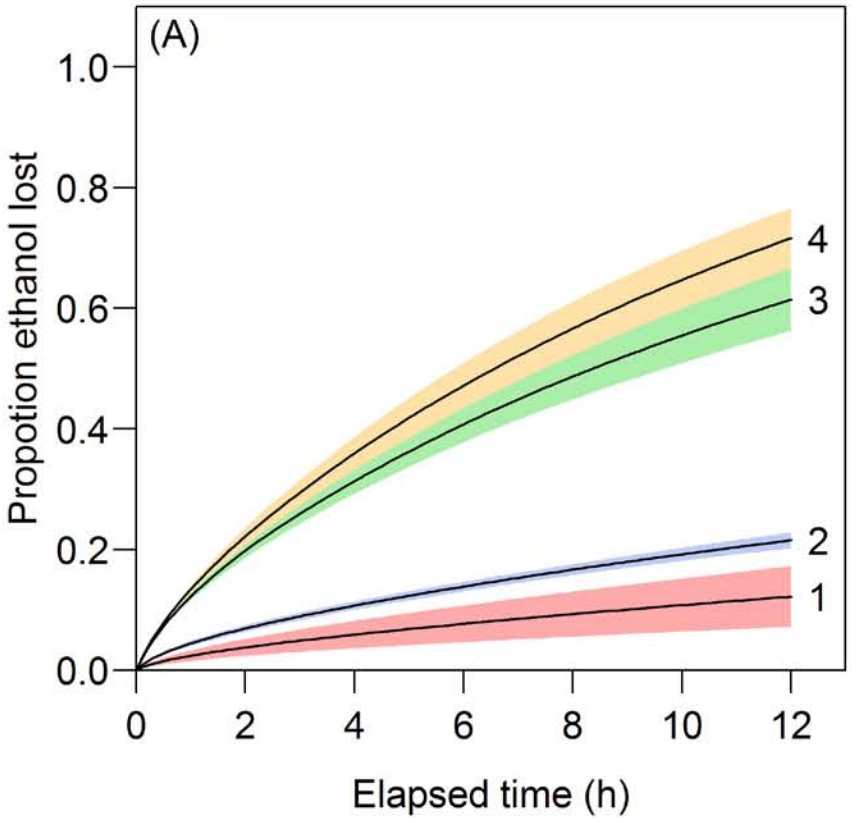
Emission rate is affected by permeability and exposed area

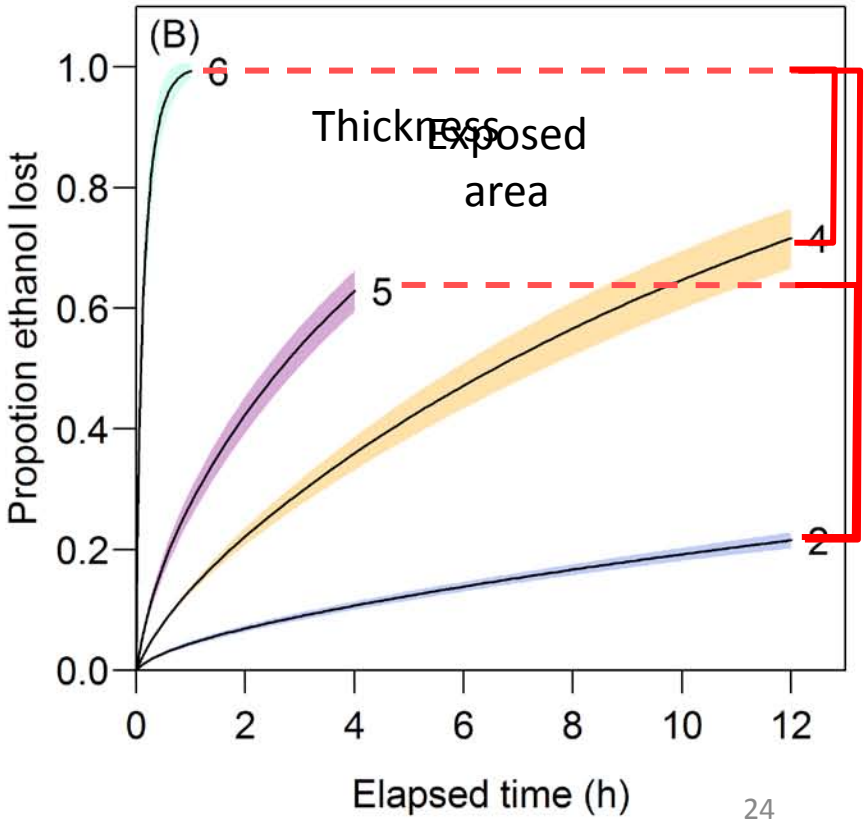
1. 15 cm intact B
2. 15 cm loose A
3. 15 cm loose C
4. 15 cm loose B

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

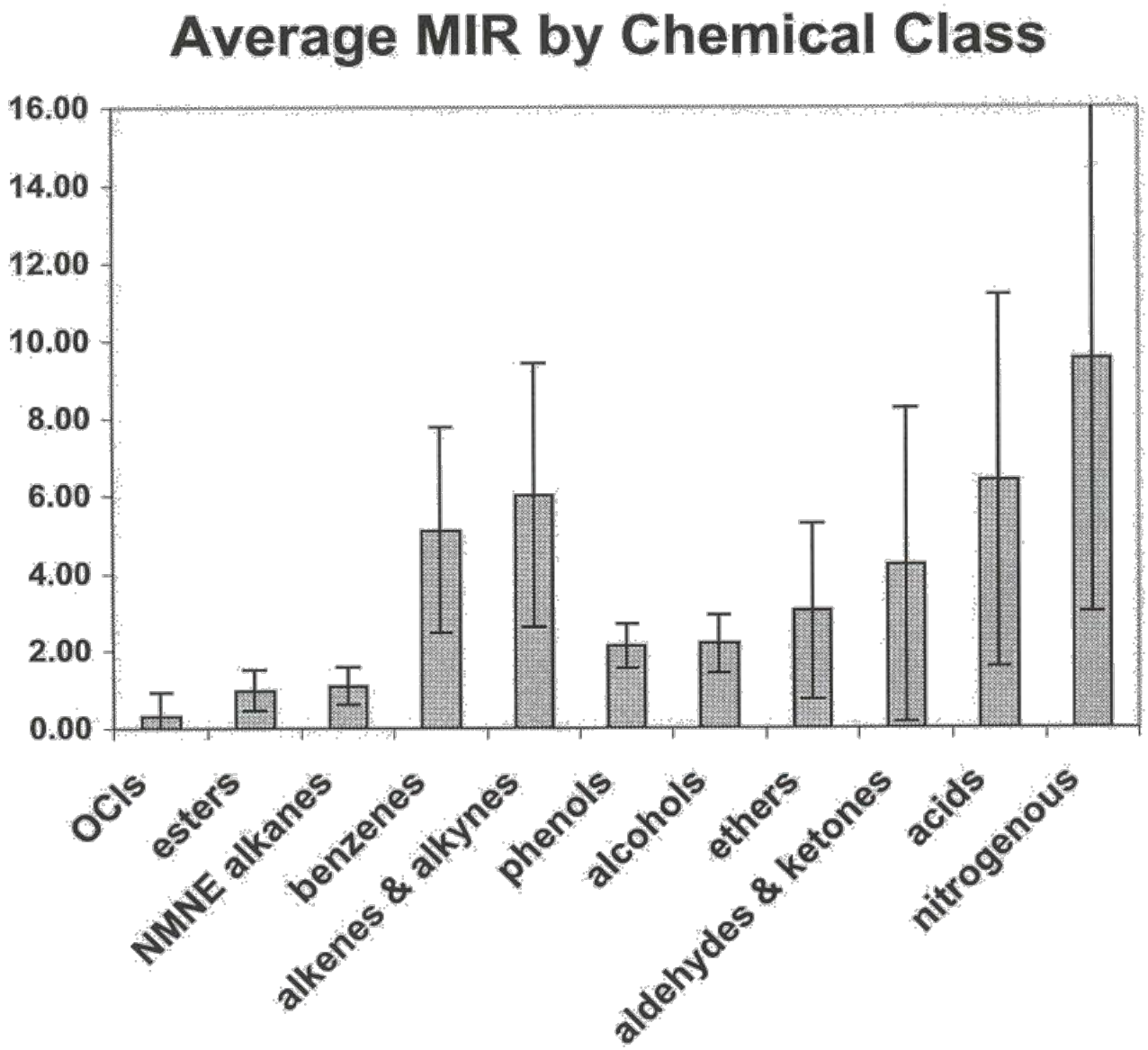
Density/ porosity

Particle size





What is the ozone formation potential of dairy emission sources?


Average MIR by Chemical Class
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
OCIs
esters
NMNE alkanes
benzenes
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

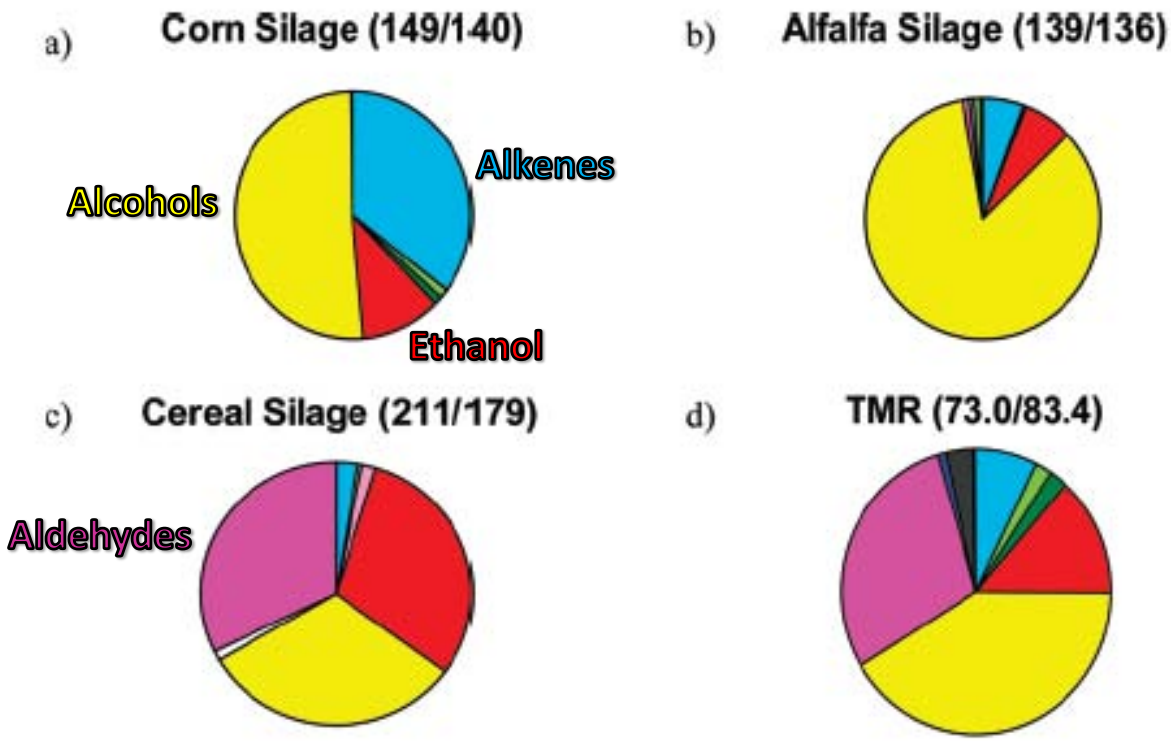
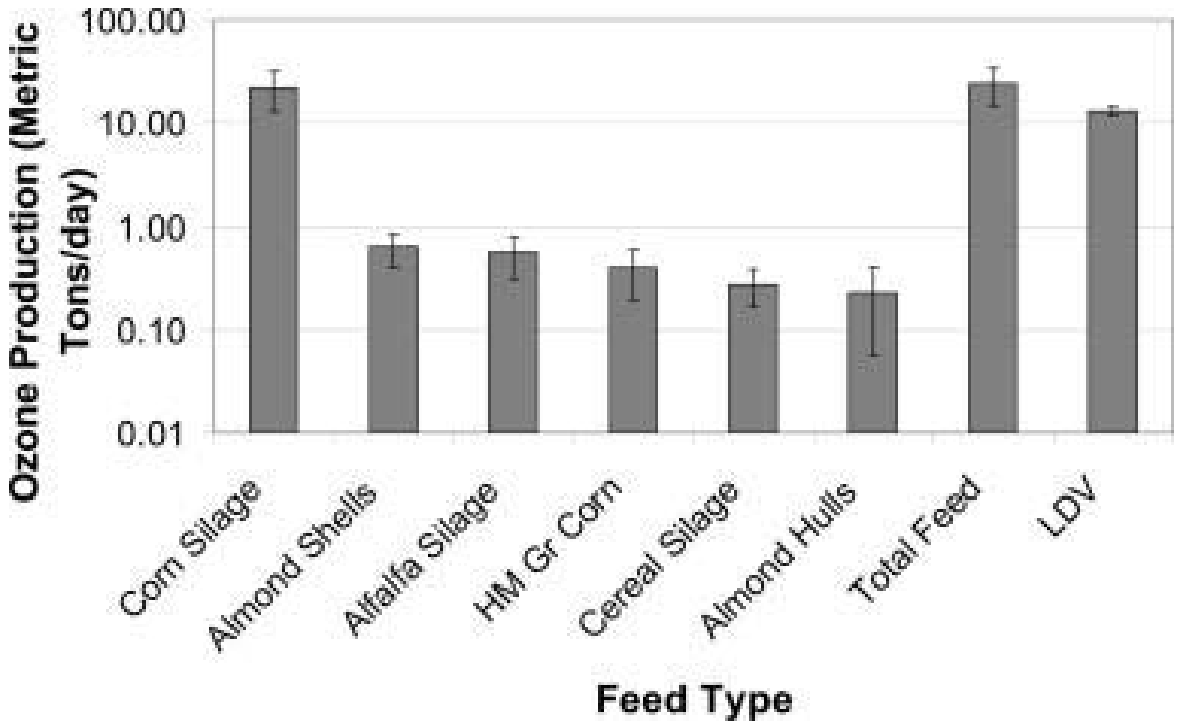


FIGURE 3. Contribution to total ozone formation from each lumped model species assuming additive behavior. Ozone formation associated with each species is calculated by removing that species from the ROG profile and observing the net reduction in ozone formation.

(Howard et al. 2010)

Ozone Production from Livestock Feed

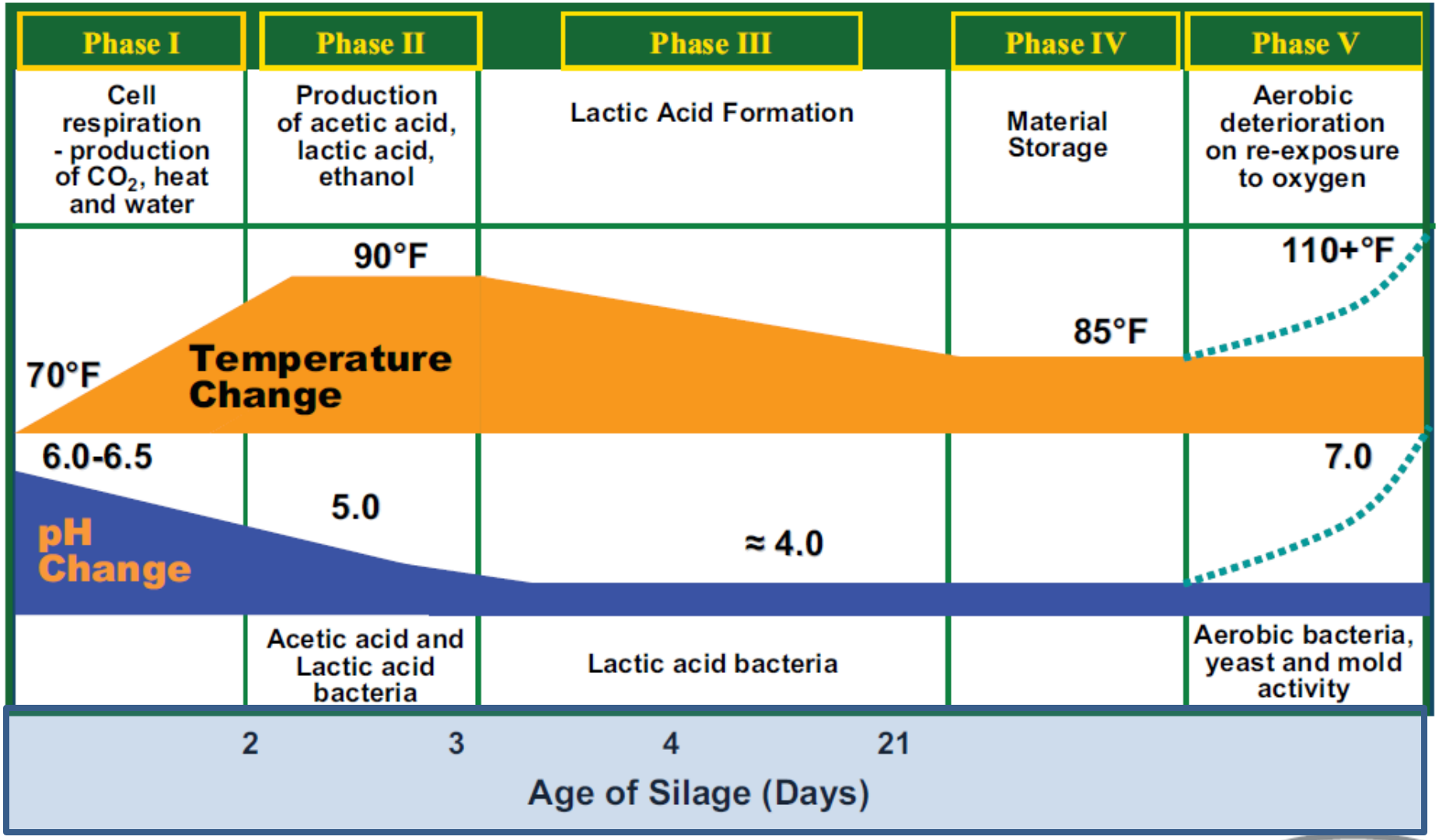


Howard et al., (2010)

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



Covering Corn Silage

Challenges at Covering

Storing Corn Silage

Storing Silage

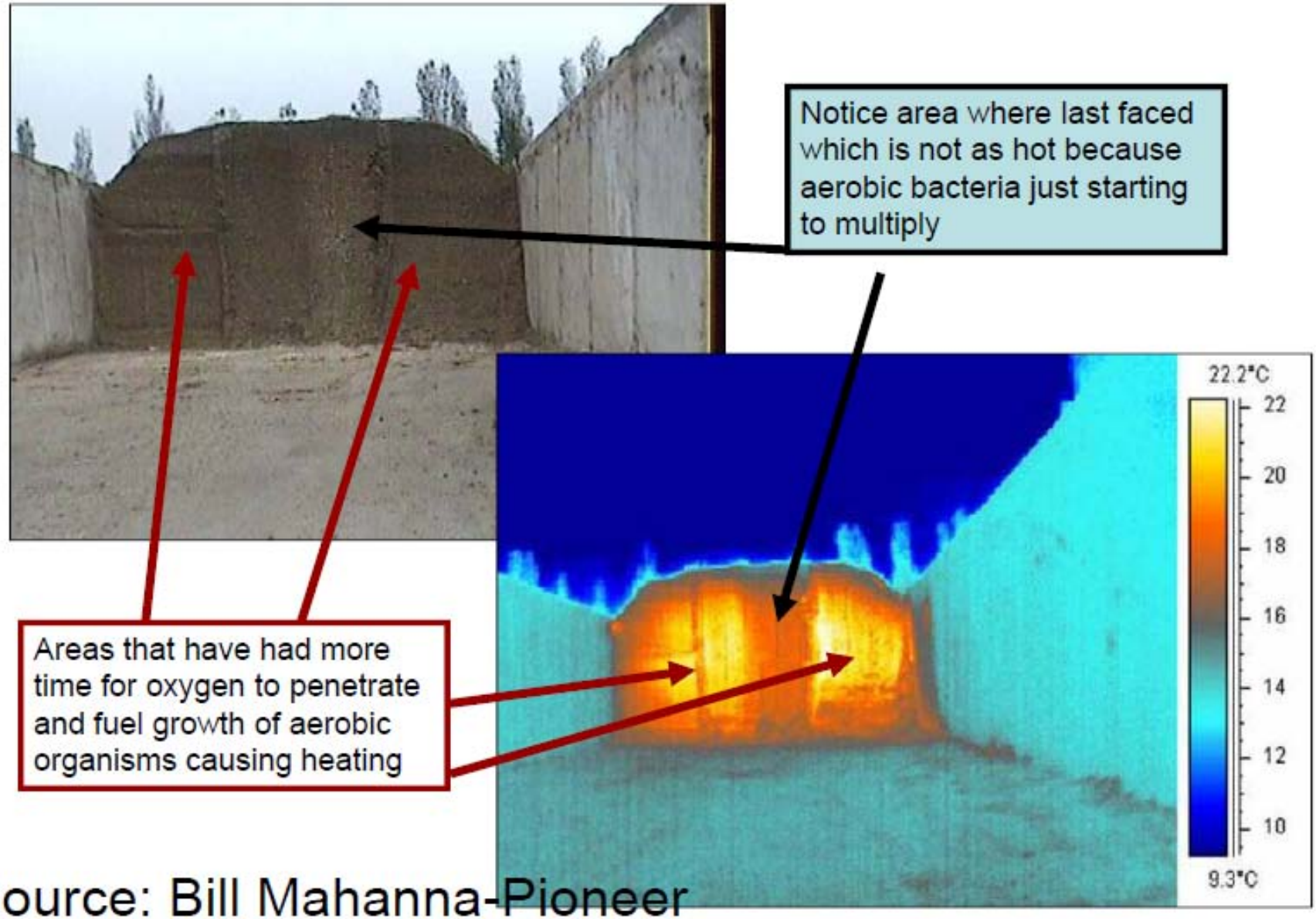
Corn Silage Feedout

Smooth Face

Prevent crack formation that favors air penetration

Tight Face

Keep air out of the edges and seams



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

THE UNIVERSITY OF CALIFORNIA
A
LET THERE BE LIGHT
1868