Volatile organic compounds and silage: sources, emission, and mitigation

S. D. Hafner*, M. Bühler, A. Feilberg, R. B. Franco, C. Howard, F. Montes, R. E. Muck, C. A. Rotz, K. Weiß

International Silage Conference

Bonn, Germany

25 July 2018

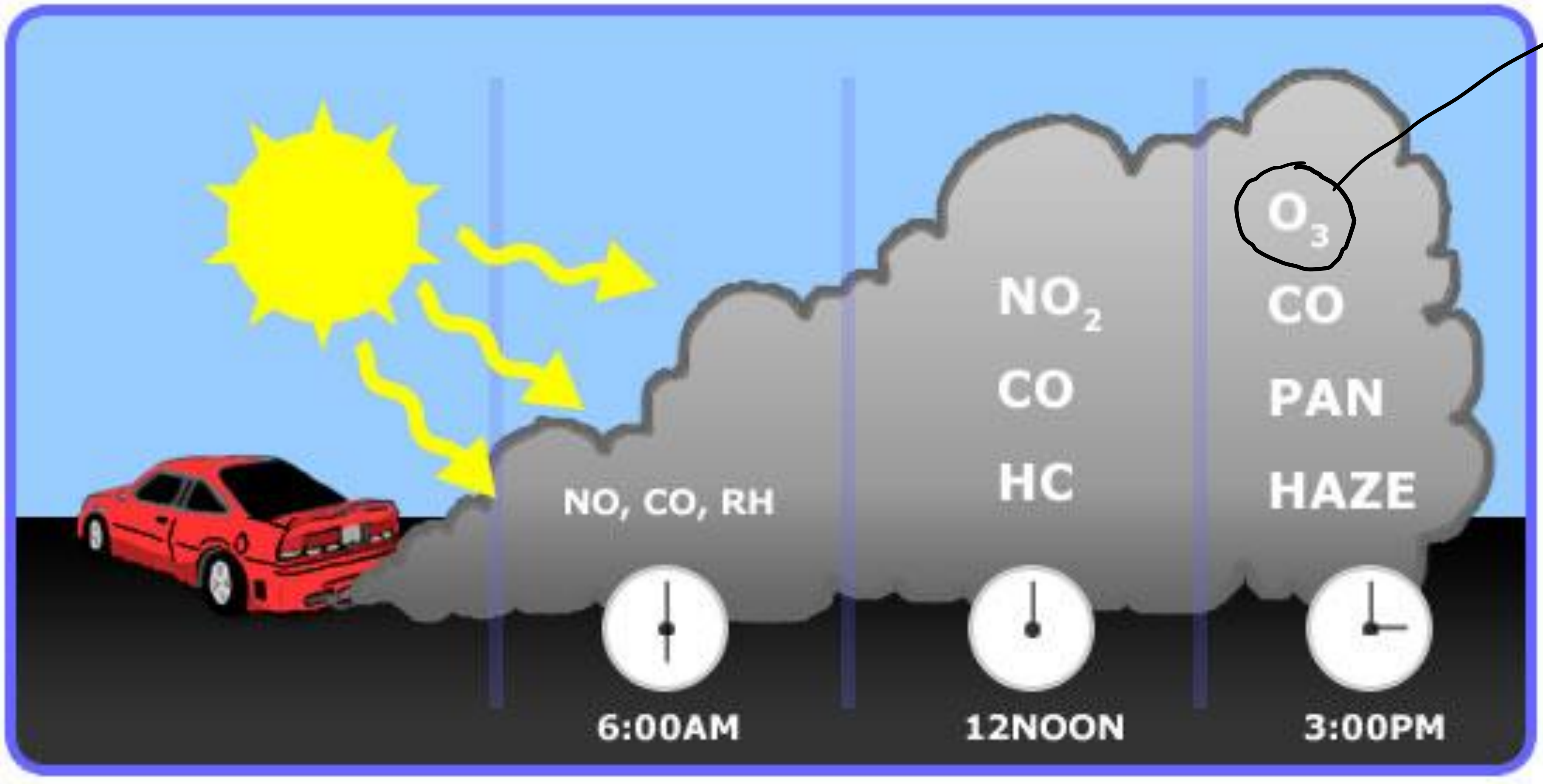
AARHUS
UNIVERSITY
DEPARTMENT OF ENGINEERING

*sasha.hafner@eng.au.dk

Volatile organic compounds (VOC) from silage

1. The problem with VOC emission
2. Organic compounds and sources
3. Emission processes
4. Measurement and estimation of VOC emission
5. Reducing VOC emission
6. Conclusions and recommendations

VOC emission contributes to poor air quality through the formation of secondary pollutants



O_3 is the biggest problem. Strong oxidizer

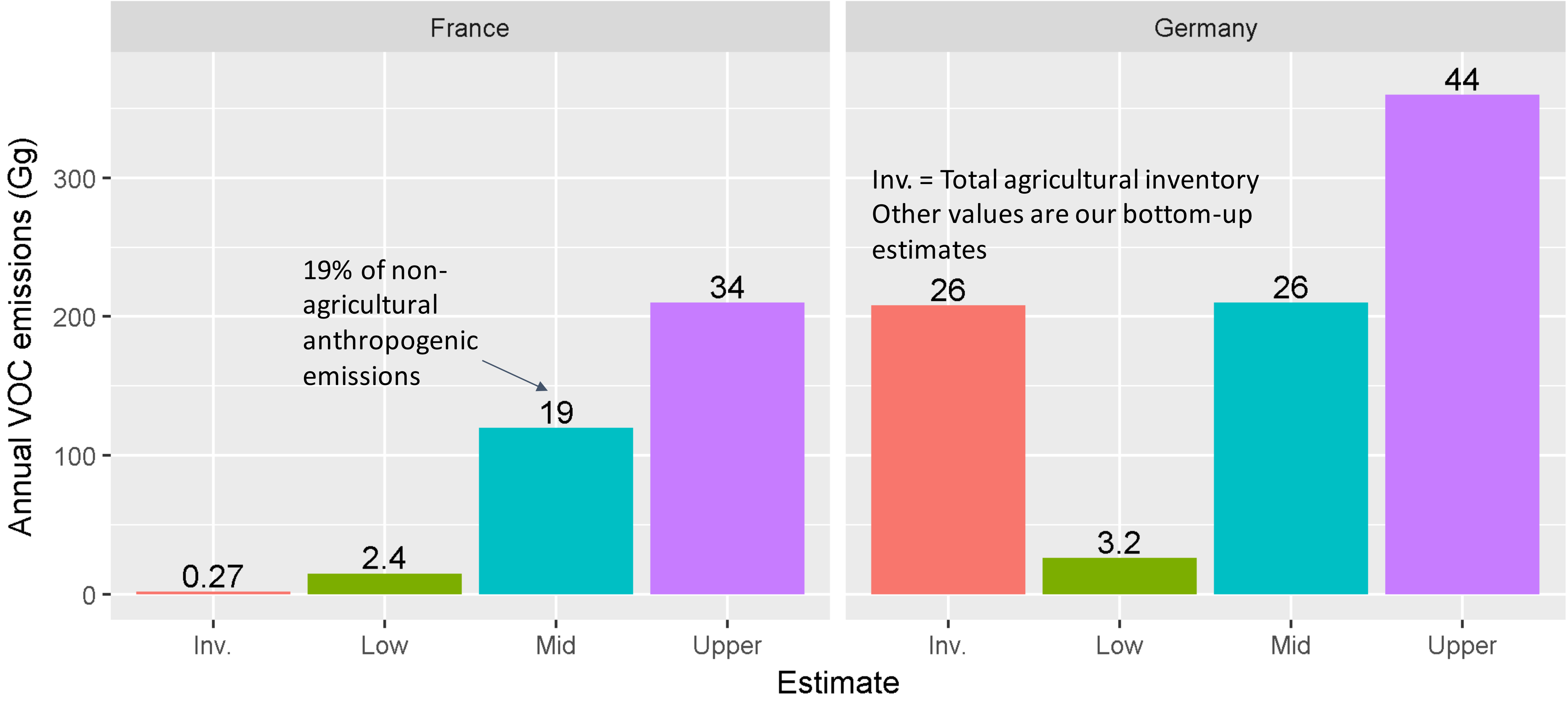
Source: Dr. Sarma Pisupati, PSU, https://www.e-education.psu.edu/egee102/node/1975

Ozone and other secondary pollutants impact human and ecosystem health

- Total mortality due to tropospheric ozone probably > 1 million deaths per year
  - Highest mortality in India and Asia: ca. 300 000 – 400 000 yr^{-1}
  - Africa, Europe, and North America: each ca. 50 000 yr^{-1}
- Ozone reduces productivity of agricultural and natural ecosystems
- Ozone increases susceptibility of plants to drought and disease

See doi: 10.1289/EHP1390 for mortality, doi: 10.1016/j.scitotenv.2016.02.187 for forest effects

Silage is almost certainly a significant source of anthropogenic VOC emissions

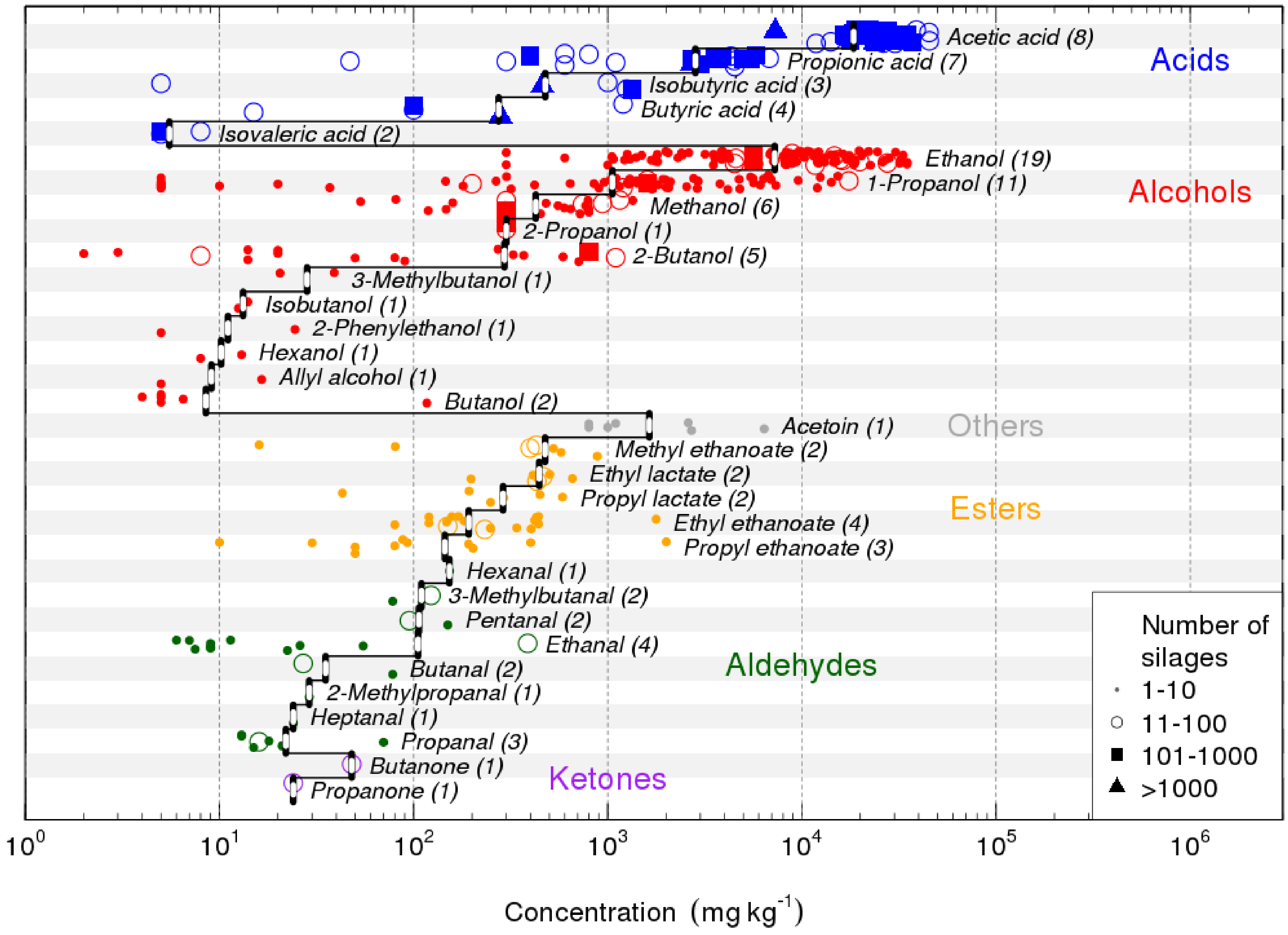


At least 40 VOC are present in silage, but impacts vary

- Effects of VOC on air quality depend on **emission** and **reactivity**
- Emission depends on **production** within silage and **volatility**
- Low emission during fermentation and storage means post-storage silage samples provide an estimate of VOC production
- Reactivity is usually quantified as quantity of ozone produced under particular conditions (g O_3 per g VOC)
  - MIR = maximum incremental reactivity
  - EBIR = equal benefit incremental reactivity

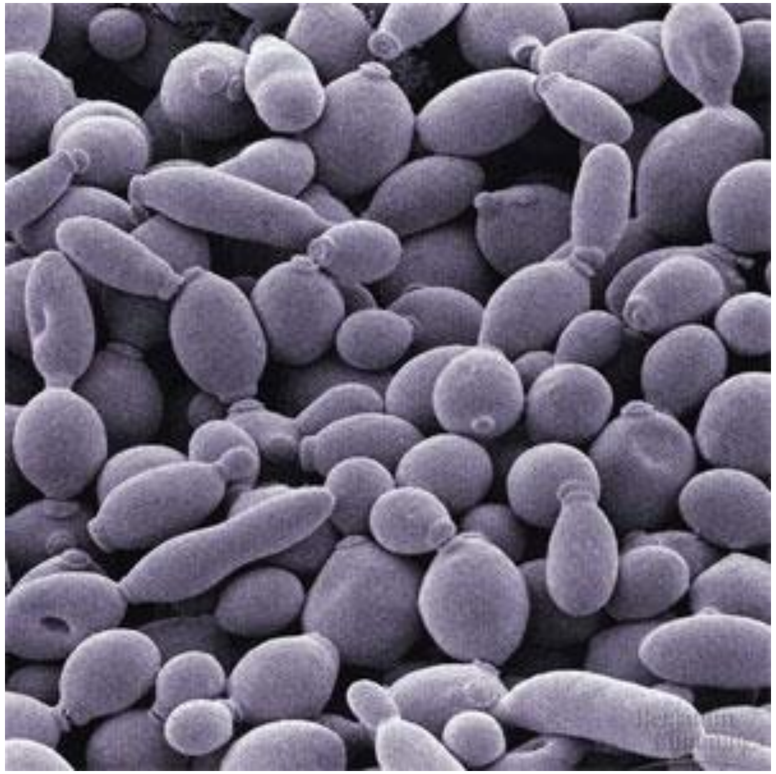
A small number of silage VOC contribute the most to air pollution

- Alcohols are important
  - Mean silage concentration ca. 10 g kg^{-1} (DM basis)
  - By contribution to air pollution, alcohols probably dominate, especially ethanol, although 1-propanol can also be significant
- Aldehydes are less concentrated (600 mg kg^{-1}) but more reactive and more volatile
- Esters (2 g kg^{-1}) are volatile but probably less important
- Acids are produced in a large amount (22 g kg^{-1}) but have lower volatility and are probably less important than alcohols
- Production varies by orders of magnitude

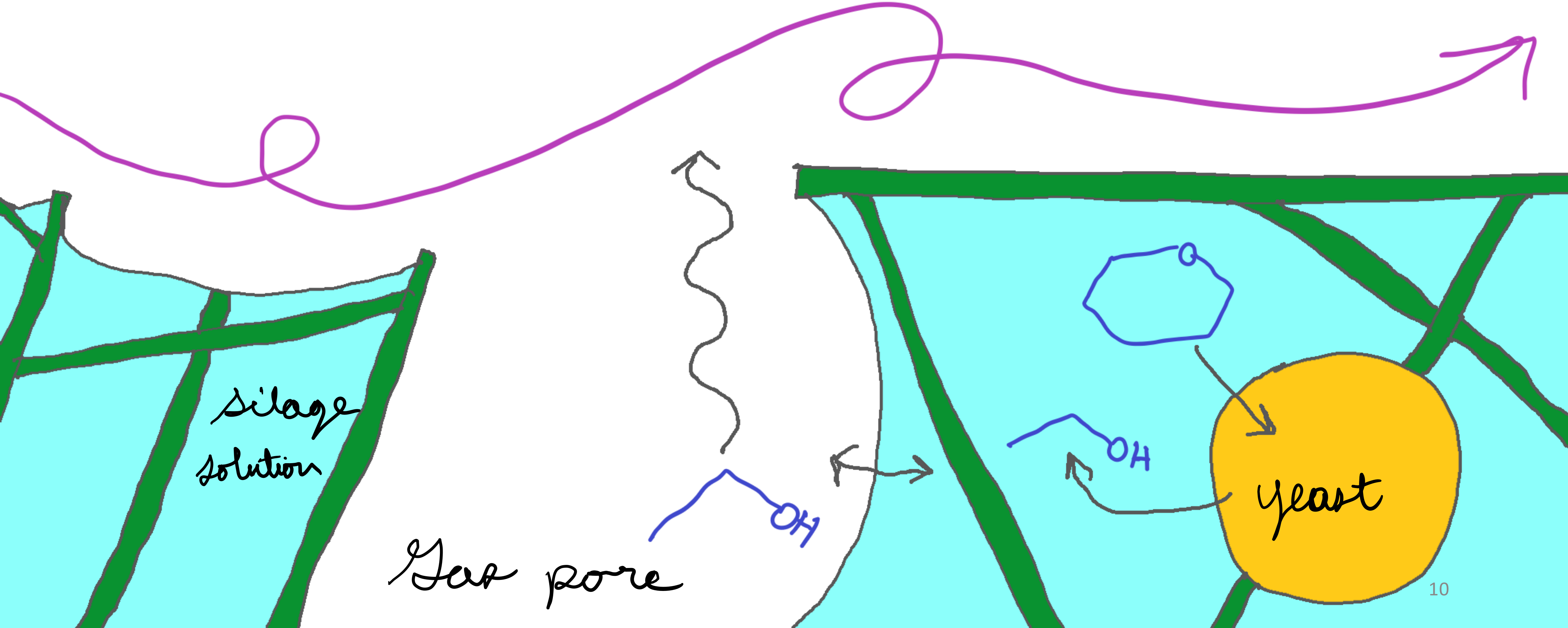

Acetic acid (8)
Propionic acid (7)
Isobutyric acid (3)
Butyric acid (4)
Isovaleric acid (2)
Acids
Ethanol (19)
1-Propanol (11)
Methanol (6)
2-Propanol (1)
2-Butanol (5)
3-Methylbutanol (1)
Isobutanol (1)
2-Phenylethanol (1)
Hexanol (1)
Allyl alcohol (1)
Butanol (2)
Alcohols
Acetoin (1)
Others
Methyl ethanoate (2)
Ethyl lactate (2)
Propyl lactate (2)
Ethyl ethanoate (4)
Propyl ethanoate (3)
Esters
Hexanal (1)
3-Methylbutanal (2)
Pentanal (2)
Ethanal (4)
Butanal (2)
2-Methylpropanal (1)
Heptanal (1)
Propanal (3)
Aldehydes
Butanone (1)
Propanone (1)
Ketones
Number of silages
1-10
11-100
101-1000
>1000
10^0
10^1
10^2
10^3
10^4
10^5
10^6
Concentration (mg kg^{-1})

Silage VOC are primarily produced by microorganisms

- Ethanol: primarily produced by yeasts through alcoholic fermentation, also enteric bacteria through mixed acid fermentation
- Acids: lactic acid bacteria are usually the main source
- Esters: directly by yeasts or indirectly through esterification reactions
- Aldehydes: directly by microorganisms or indirectly by acid/alcohol oxidation



VOC emission is the end result of production, storage, partitioning, and transport



Gas-aqueous partitioning is key to understanding VOC emission

- Partitioning affects both the rate of volatilization from an exposed surface and the rate of transport through silage
- High solubility (lower volatility) means low emission
  - Quantified by Henry's law constant *H* (volumetric concentration ratio, aq:g)
- Soluble VOC such as acids (log *H* ca. 5) tend to stay in solution, and transport through gas pores is relatively slow
- Highly volatile VOC such as aldehydes (log *H* ca. 2.5) are more readily lost
- Alcohols are intermediate (log *H* ca. 3.5)

Transport is directly affected by partitioning

Bulk diffusivity

$$D_\mathrm{b} = \frac{k_\mathrm{sg}}{H\rho_\mathrm{w} w + \phi} + \frac{D_\mathrm{ss}\rho_{\mathrm{H_2O}}}{\rho_\mathrm{w} w + \frac{\phi}{H}}$$

Gas phase

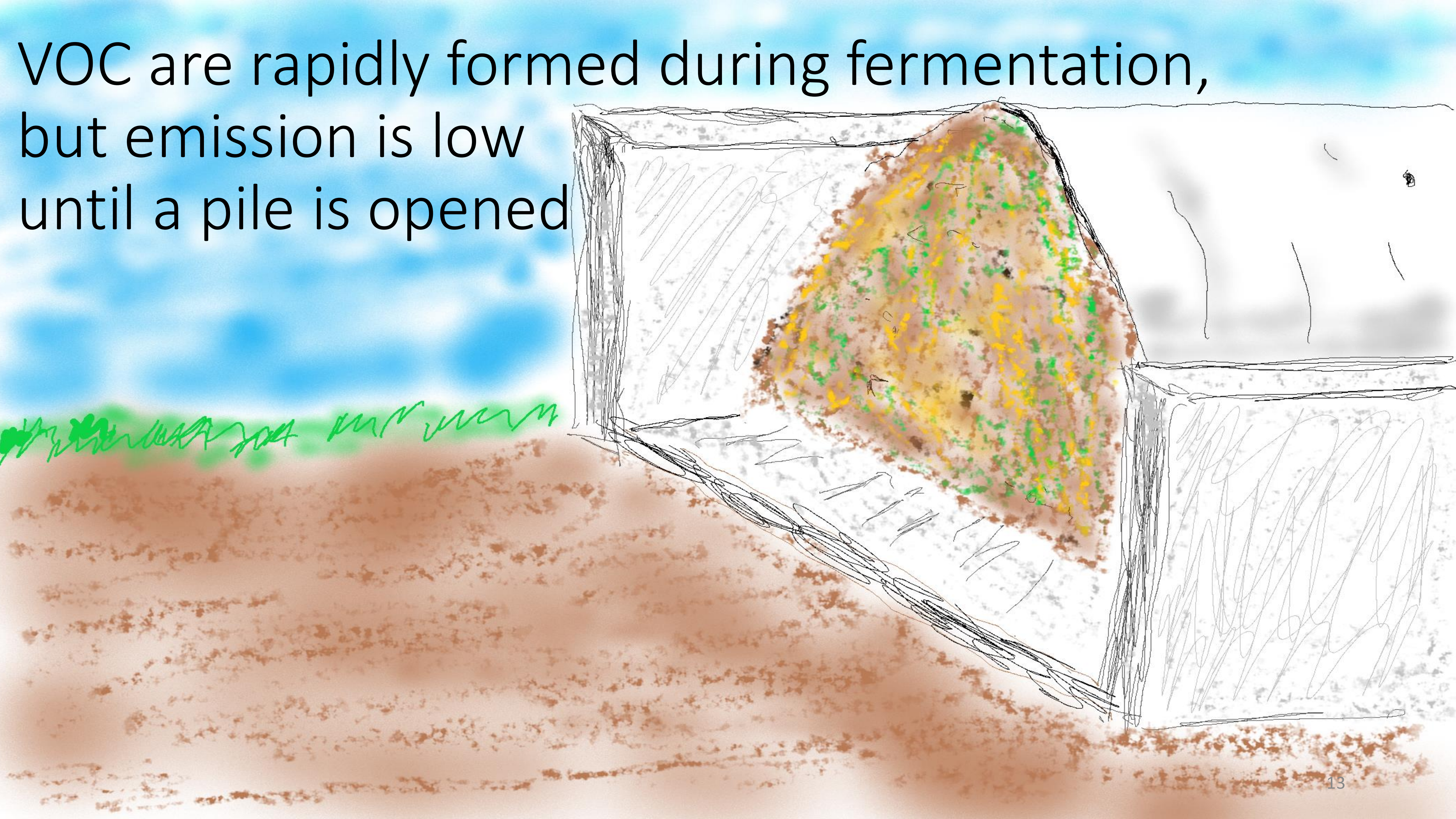
Solution phase

Bulk mass transfer coefficient

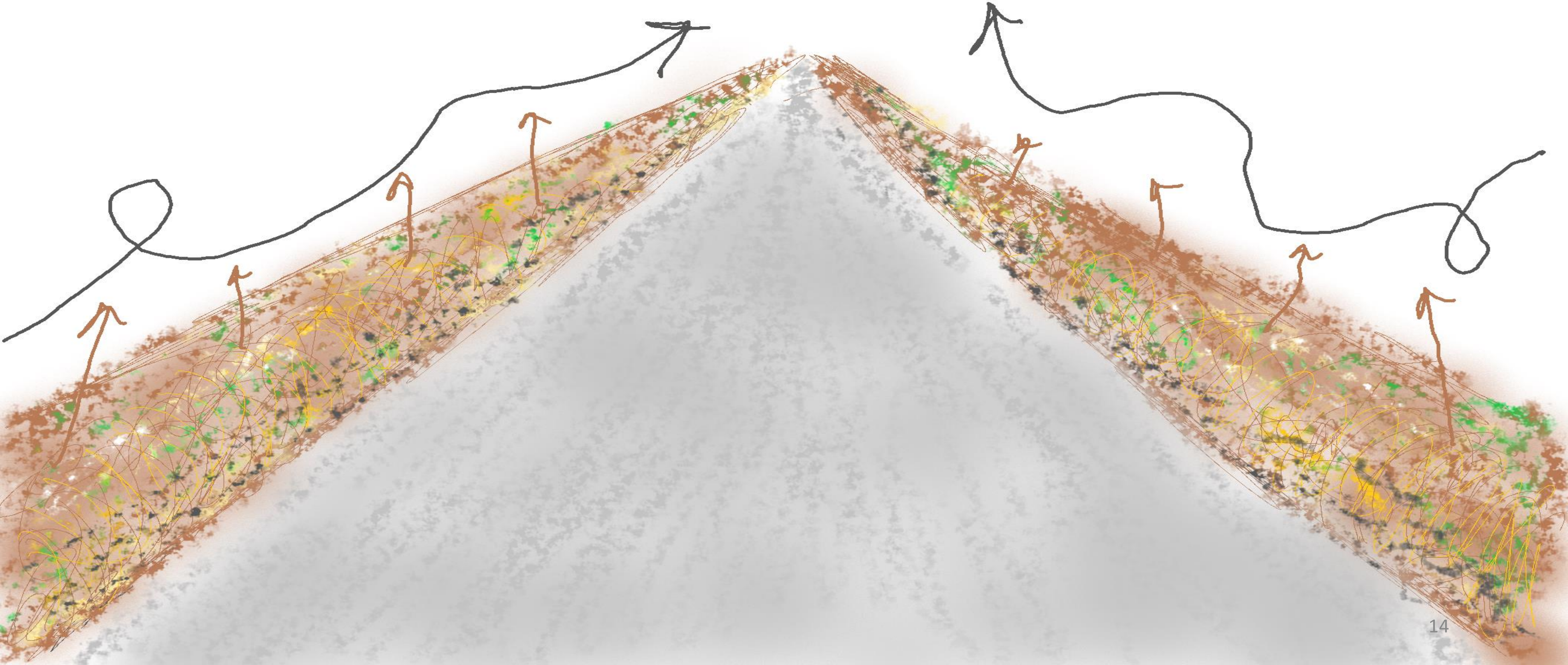
$$\alpha = \frac{h_m}{H\rho_\mathrm{w} w + \phi}$$

Partitioning

VOC are rapidly formed during fermentation, but emission is low until a pile is opened



During feed mixing and transport emission increases, and it probably peaks during feeding

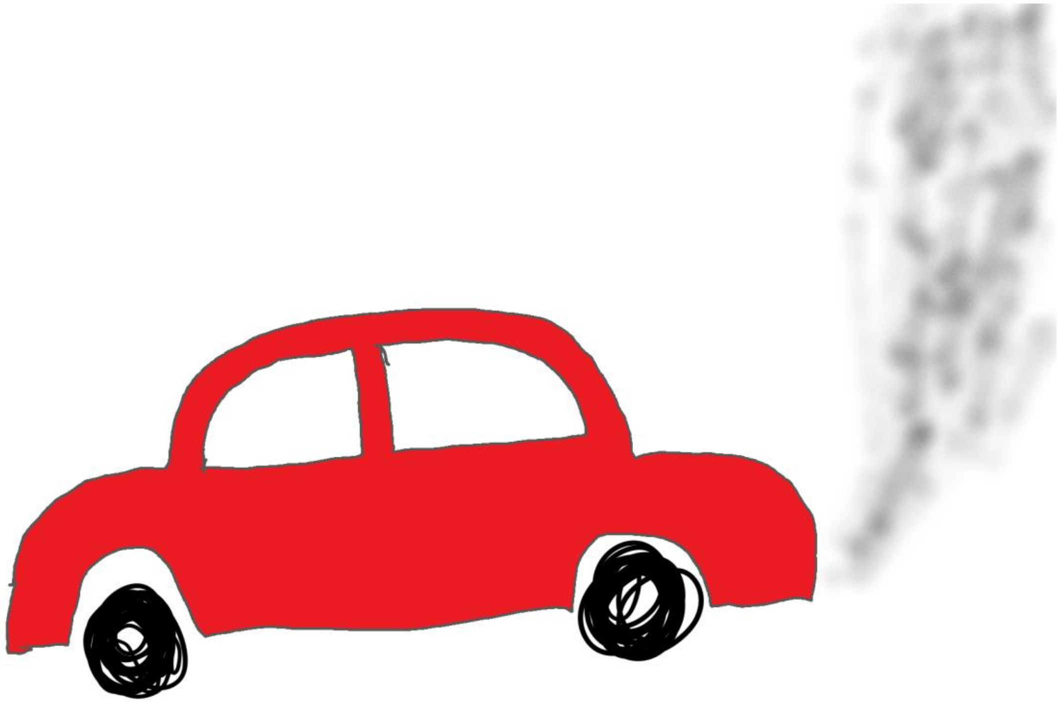


Silage VOC emission effectively ends with feed consumption

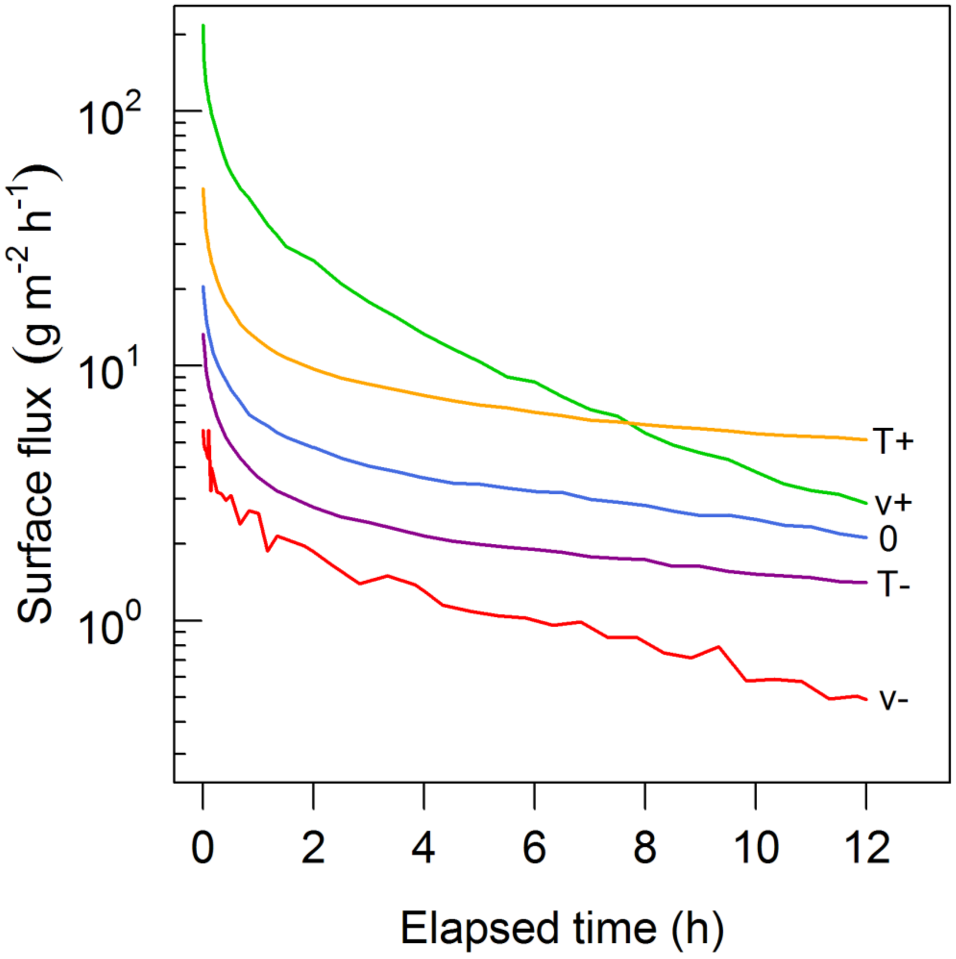
Several options exist for measuring VOC emission rates, and most are inaccurate

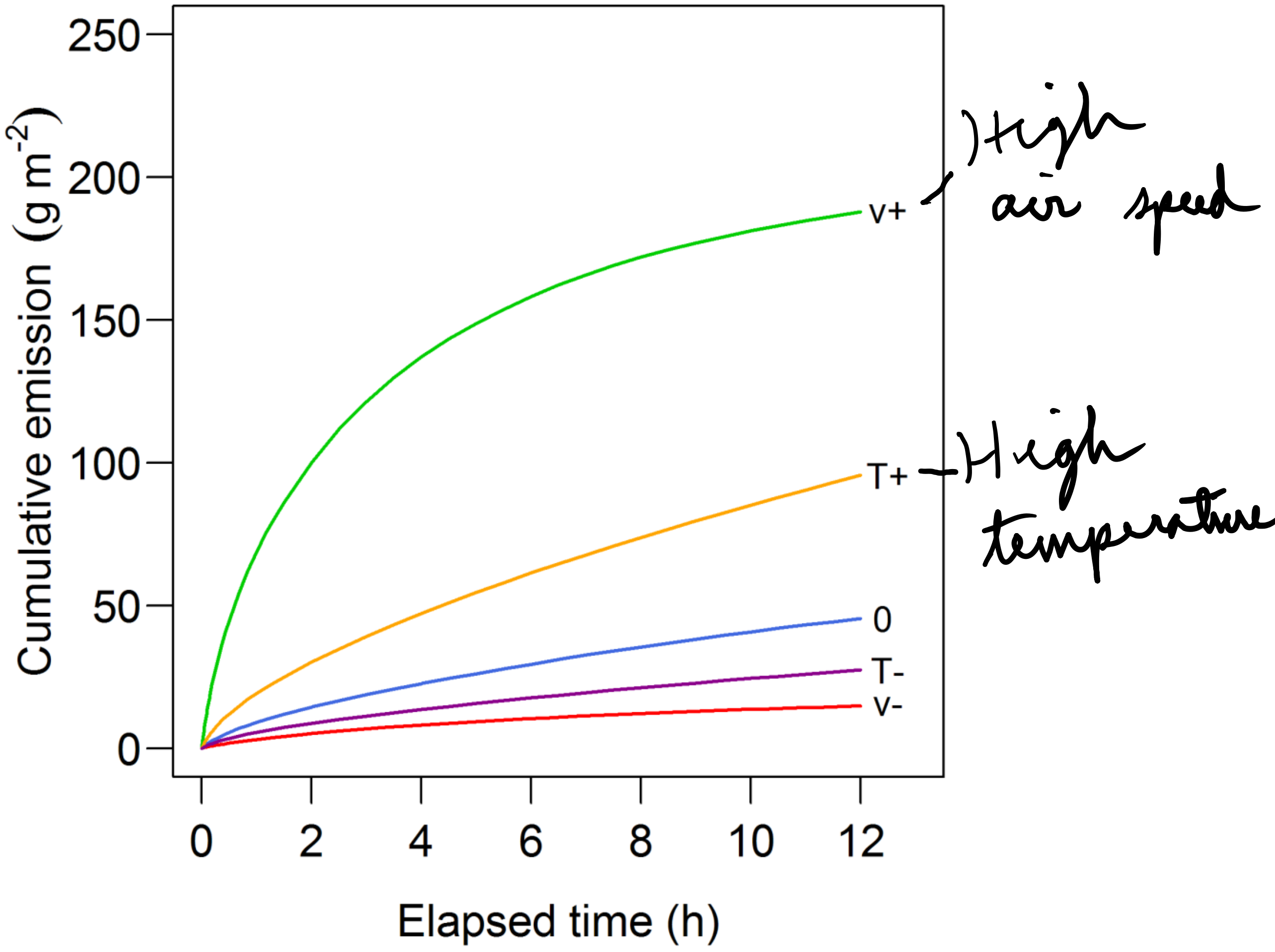
- Measurements and models show that newly fed silage contains a large pool of VOC, and emission is strongly affected by the environment
- Measurement methods that affect the environment do not provide an accurate measurement of emission
  - Bad choice: low air flow flux chamber
  - May be better: wind tunnel
- New methods are needed
  - Mass balance (emission = initial mass – final mass – oxidation loss) shows promise
  - Backwards Lagrangian stoichastic (bLS) modeling and other micrometeorological methods may be the best

VOC emission rate is not production-limited!

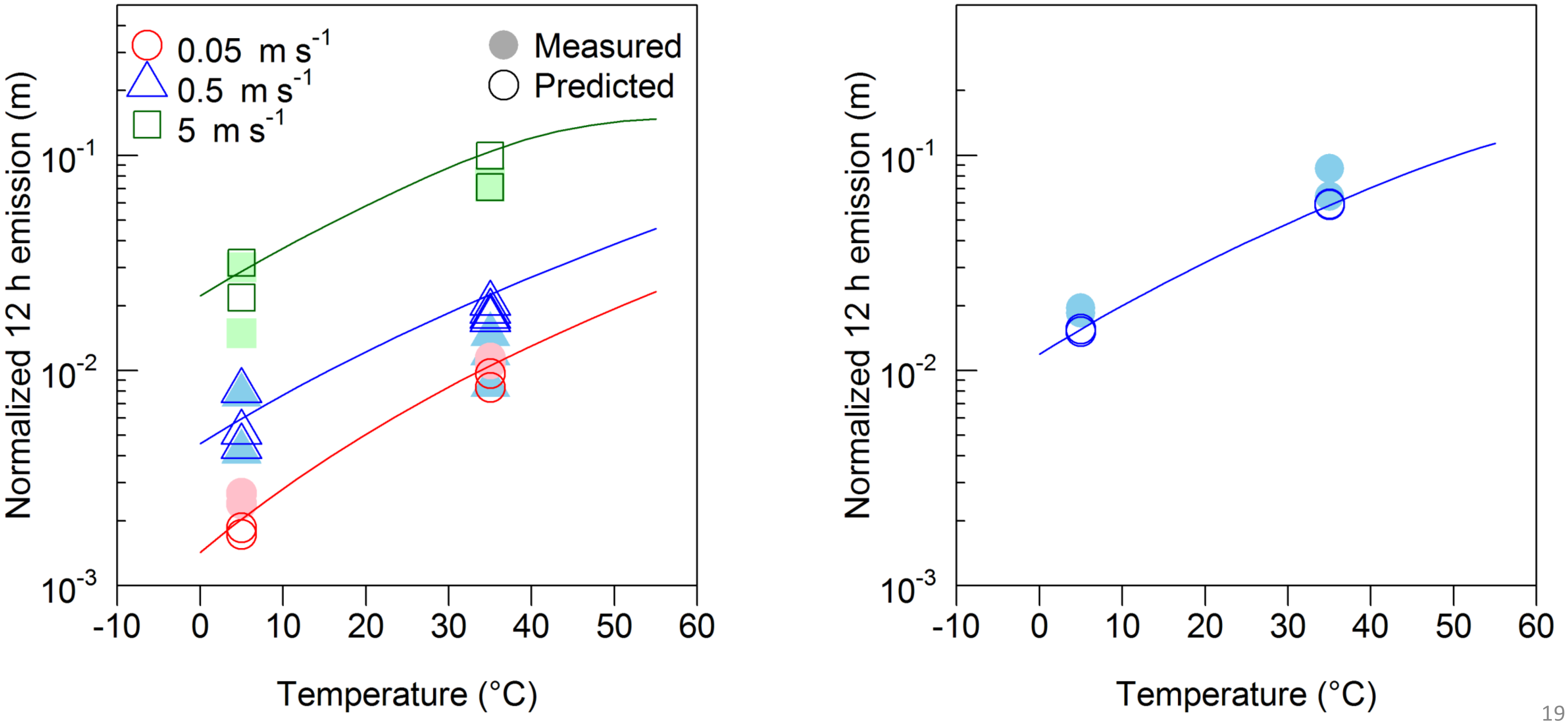


Wind tunnel results show emission is transient and depends on air speed and temperature

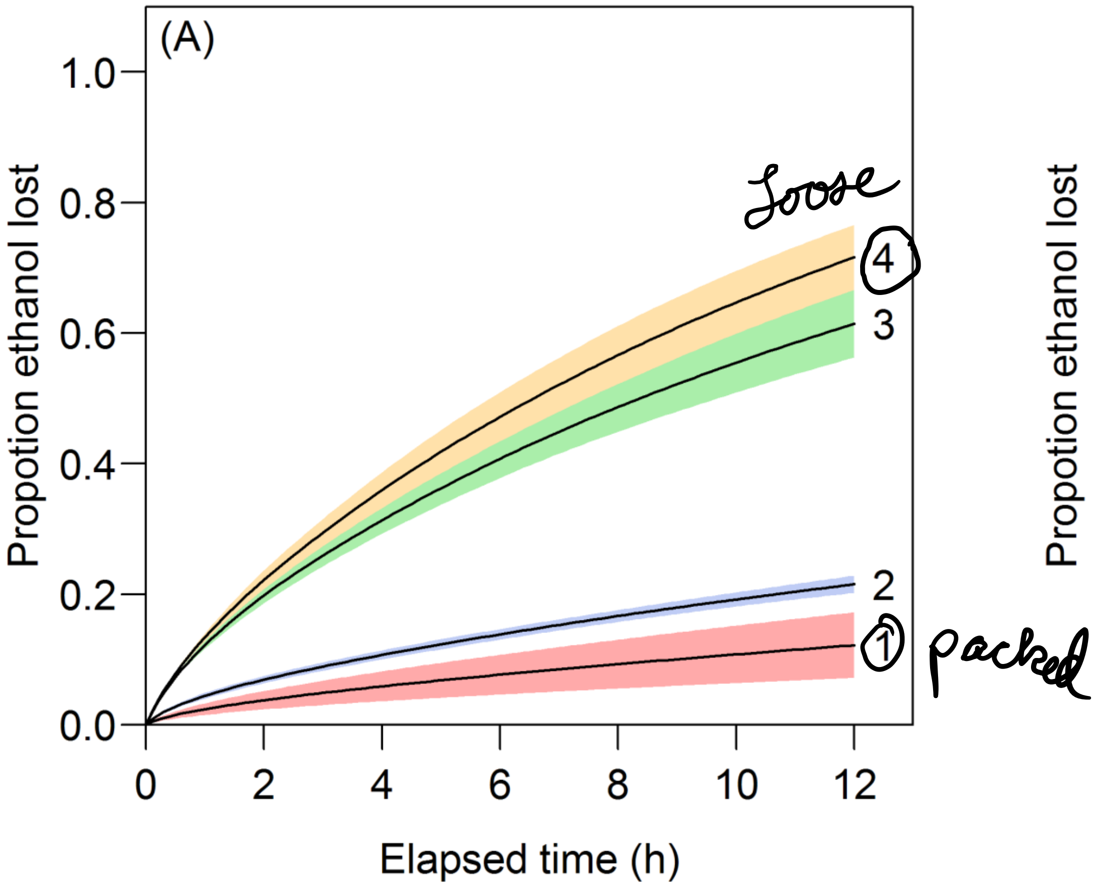


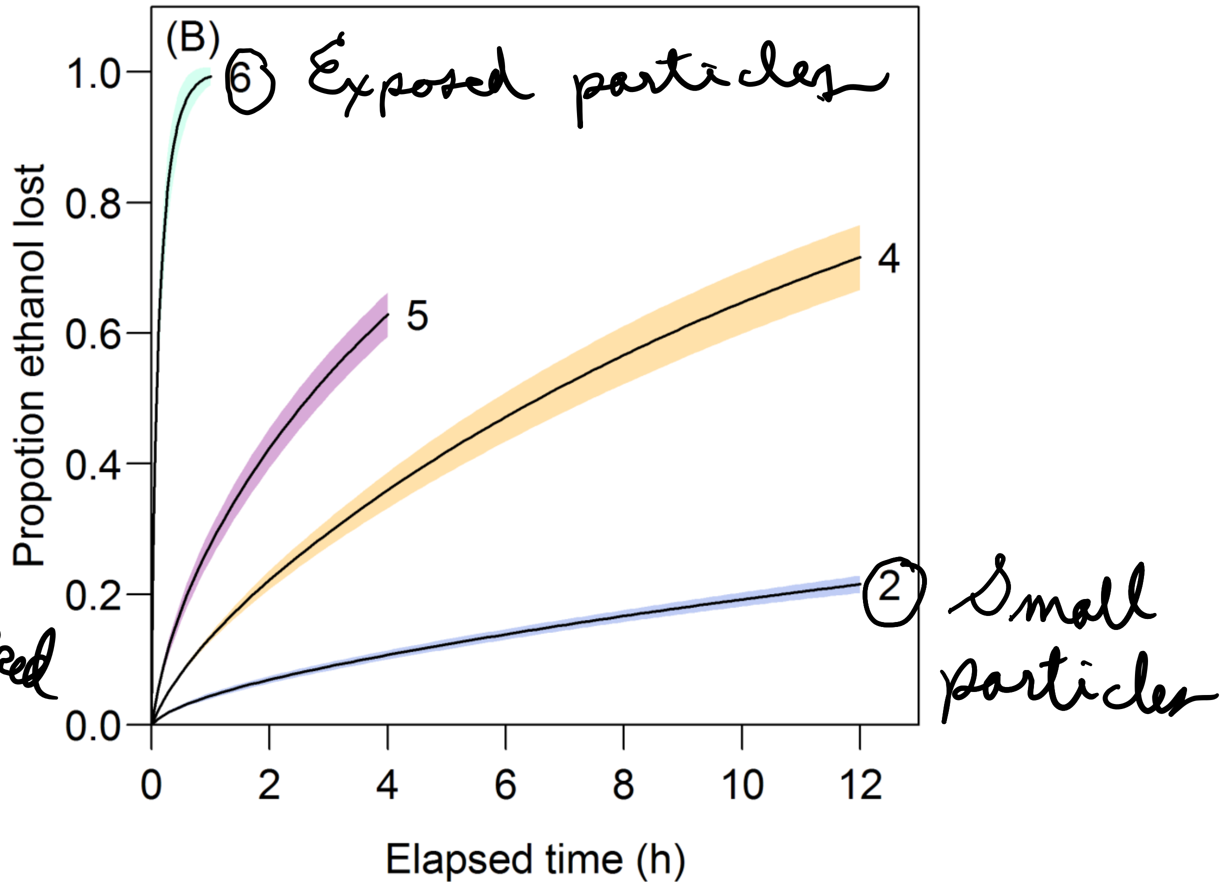


Observed response to temperature follow partitioning predictions



Porosity (density), particle size, and exposure also affect emission





Emission measurements are scarce, so how can we make emissions estimates?

- Theory and measurement show emission is proportional to initial concentration
- Calculations suggest fermentation and **storage losses** are low for alcohols (**<2%**) but possibly high for esters and aldehydes
- Wind tunnel measurements from **packed silage** show about **10% loss of ethanol** (20°C, 0.5 m s^{-1}, 12 h)
- Mass balance results for **loose silage** in barn show about **50% loss of alcohols** and **90% loss of acetaldehye** (25°C, 0.6 m s^{-1}, 6 h)

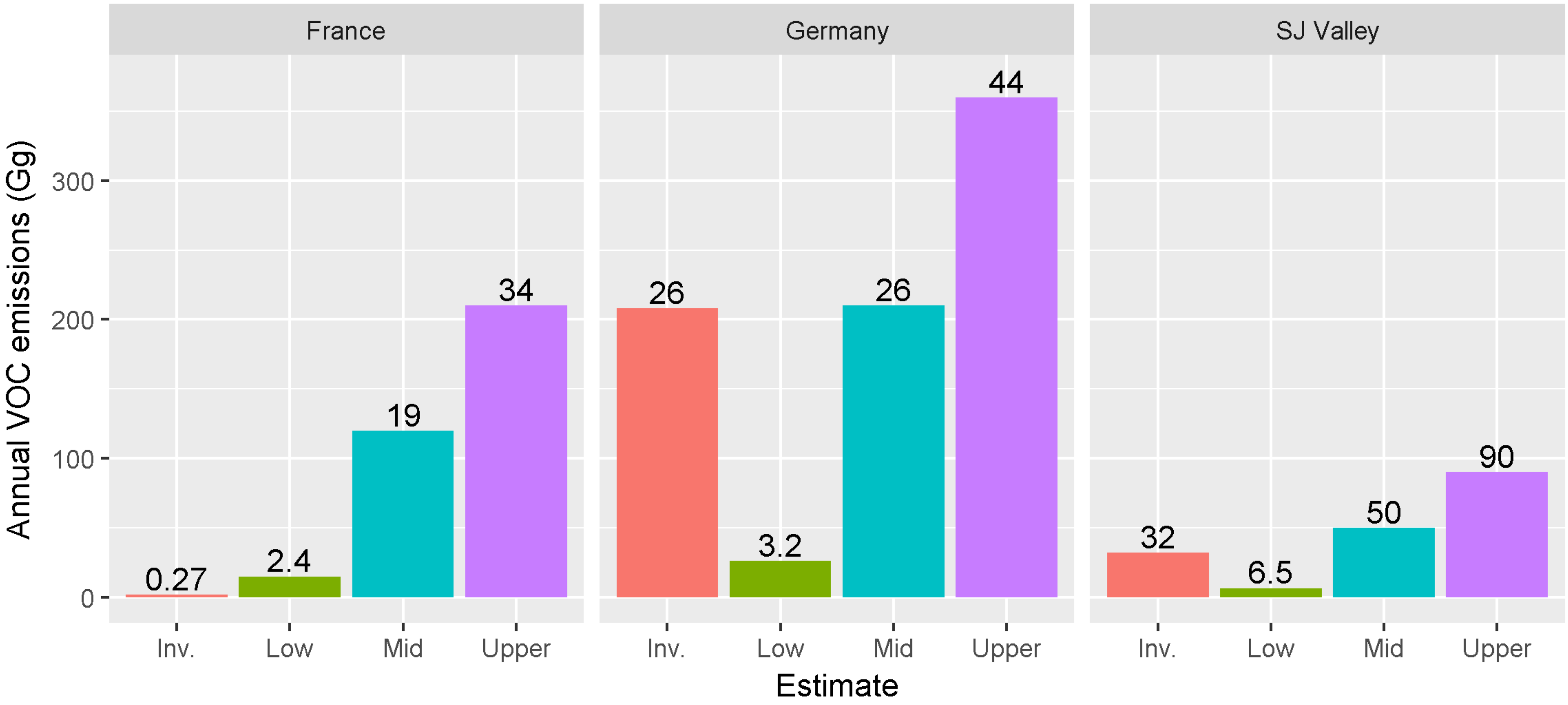
VOC emissions can be estimated from mean production and emission factors

A. VOC production based on post-storage VOC concentrations
B. Fractional emission losses based on measurements and guesswork
C. Silage maize harvest (corrected for dry matter loss)

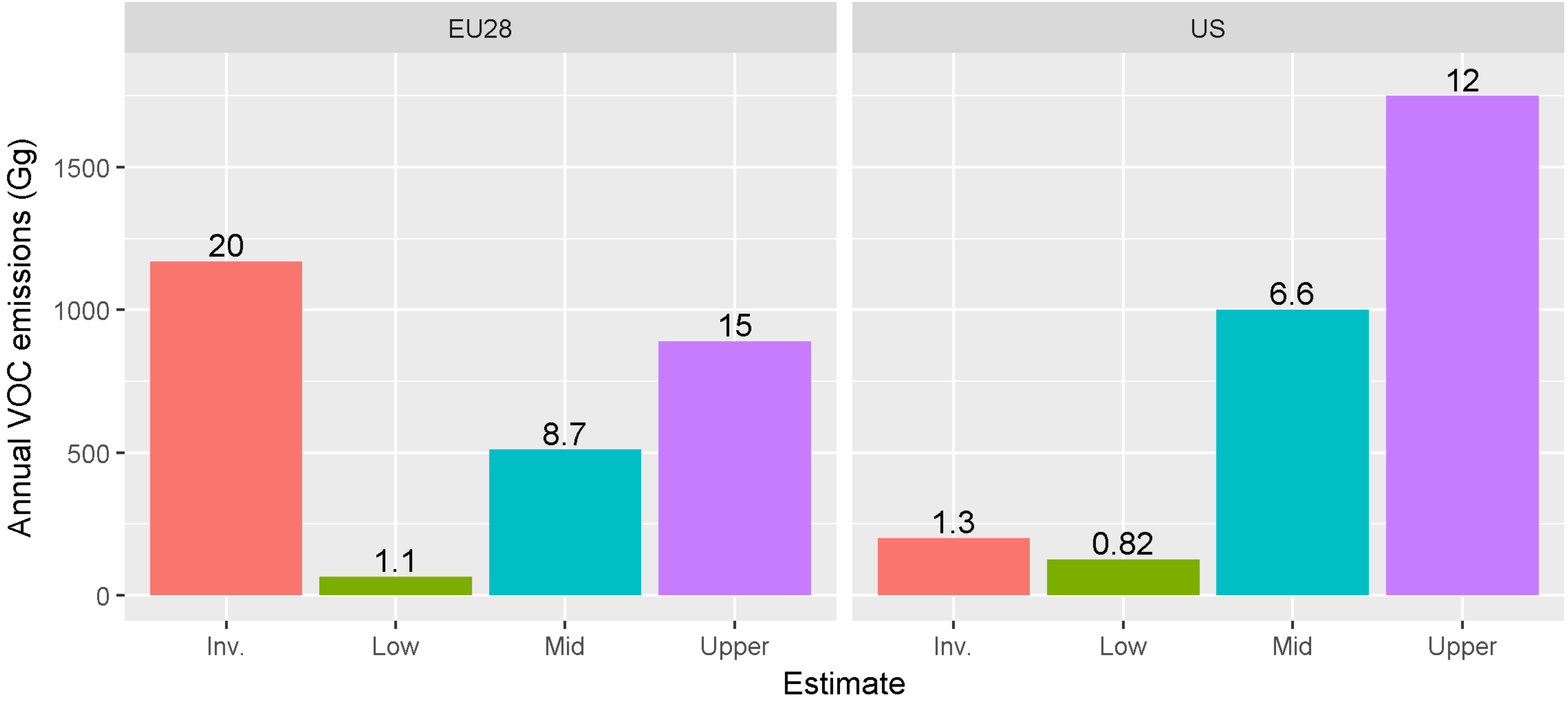
VOC group	Mean maize silage concentration (A) (mg kg^{-1})	Emission loss (B) (fraction)	Emission (A x B) (mg kg^{-1})
Acids	22.1	10% (1%, 20%)	2.21 (0.20, 4.4)
Alcohols	9.7 (5.0)	40% (10%, 70%)	3.88 (0.50, 6.8)
Esters	1.9	70% (20%, 100%)	1.33 (0.38, 1.9)
Aldehydes	0.6	70% (20%, 100%)	0.42 (0.12, 0.6)
Total	34.3		**8 (1, 14)**

Best estimate < 1% DM

Estimates from this approach show that some inventory values are probably too low



Silage probably makes a similar relative contribution to VOC emission in US and EU



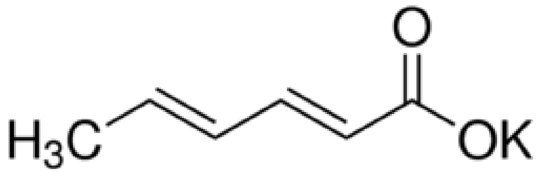
There are at least two general approaches available for reducing VOC emission

1. Control VOC production
    - Emission is proportional to VOC concentration
    - Reduction in VOC production provides a proportional reduction in emission
    - Potential is easy to determine, and most mitigation research has focused on this
2. Control VOC volatilization rate
    - In theory, emission could be reduced to null through management of feed properties or environment (but at what cost?)
    - Some practical steps could possibly reduce emission


DANGER
STAND CLEAR
FRONTIER

Silage additives can reduce VOC production, but not all additives are effective

- Chemical antifungal additives, **sorbic** or **benzoic acid** (1-2 g kg^{-1} as K or Na salts) reduced ethanol production by 45 to 80% compared to untreated silage in 10 studies by 4 different groups
  - When measured, ethyl esters generally showed similar or smaller reductions
  - In some cases, other VOC were reduced also



- Microbial additives (lactic acid bacteria) have inconsistent effects
  - In some cases, VOC production has *increased*

Summary of state of knowledge

1. Silage is a significant and likely underestimated source of anthropogenic VOC emissions, but the magnitude of emissions is not precisely known
2. The single most important compound for air quality is ethanol, but other alcohols, as well as aldehydes, esters, and acids also contribute
3. VOC are produced by bacteria but production by yeasts (primarily ethanol) is more important
4. Emission is affected by VOC production and partitioning, as well as silage properties and environment (exposure, air flow, temperature)
5. Chemical antifungal additives can reduce VOC production

Summary of research needs

1. Development and testing of new, more accurate, methods for measuring VOC emission from silage or whole farms
2. Accurate measurements of VOC emission on farms under a range of conditions
3. Quantitative assessments of the contribution of silage VOC emission to secondary air pollution based on a combination of emission and atmospheric chemistry models
4. Identification and quantification of VOC production pathways through application of molecular biology tools
5. Evaluation of VOC-reducing silage additives from multiple perspectives (VOC, animal health and milk yield, economy)
6. Assessment of management practices other than use of silage additives on VOC emission

Acknowledgements

Institutes

- Aarhus University
- Bern University of Applied Sciences
- California Department of Food and Agriculture
- California Air Resources Board
- The Pennsylvania State University
- University of Wisconsin-Madison
- United States Department of Agriculture, Agricultural Research Service
- Humboldt Universität zu Berlin

Funding, advice, help

- National Milk Producers Federation
- California Air Resources Board
- Frank Mitlohner, Peter Green, Curtis Dell, Walter Mulbry, Jack Meisinger, Travis Edwards, Nadine Houck, Jonathan Leith

Thank you for your attention! Questions?

sasha.hafner@eng.au.dk