

Mitigation of ammonia emissions by acidification of organic fertilizers

# „Baltic Slurry Acidification“

## First results of field trials in Germany



**Blunk**

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# Background of the Interreg project Baltic Slurry Acidification

## Baltic Slurry Acidification

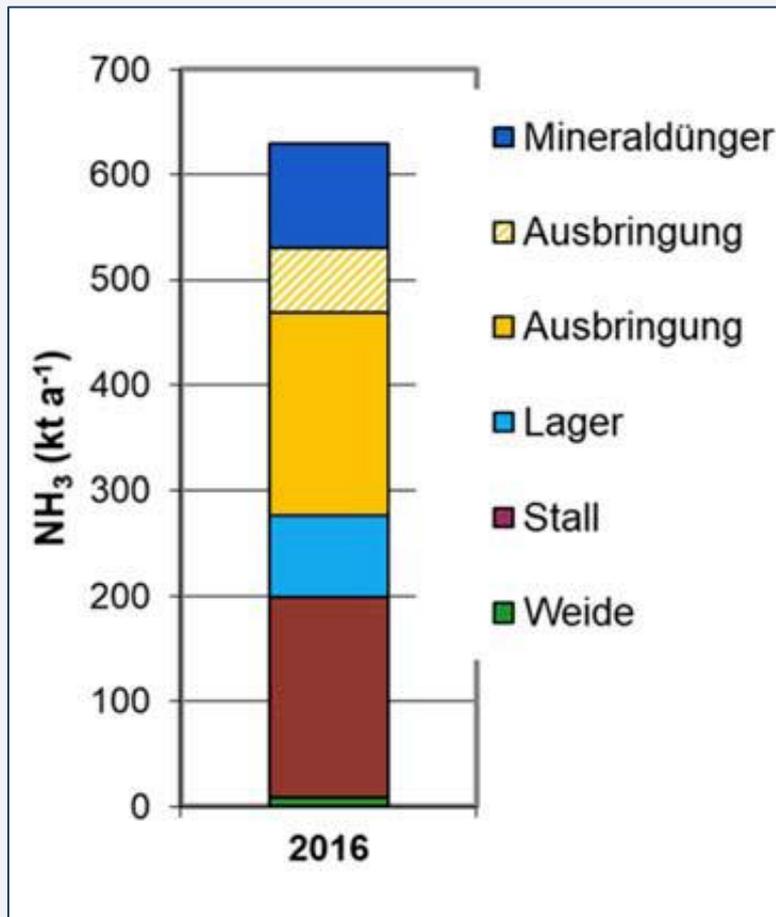
- 95 % of ammonia emissions originate from agricultural sector in Germany (Haenel et al., 2016)
- Europe: up to 80 % of total emissions (Petersen et al., 2012)

		<b>Ammonia</b>
Emission ceilings of NEC Directive (2001/81/EG)	starting 2010 in kt/a	550
<b>Reduction commitment of the new NEC Directive (2016/2284/EU)</b>	<b>starting 2020 in % to 2005</b> <b>starting 2030 in % to 2005</b>	<b>- 5</b> <b>- 29</b>
Reported emissions in 2015 (UBA data) in kt		759
Emissions to determine NEC compliance in 2015 (UBA data) in kt		696
Compliance with the emission ceilings of the NEC Directive (2001/81 / EC) in 2015		<b>no</b>

Source: modified according to UBA, 2016

# Background of the Interreg project Baltic Slurry Acidification

## Baltic Slurry Acidification



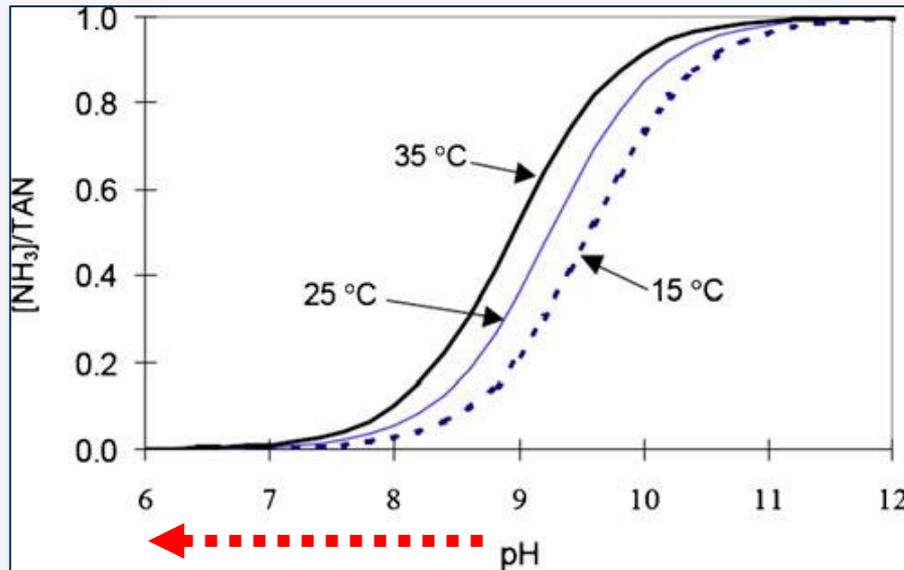
- About 40% of the total ammonia emission of the agriculture sector originate from the spreading of organic manure.

Source: Nationaler NH<sub>3</sub>-Emissionsbericht, 2018

# Background of slurry acidification

## Baltic Slurry Acidification

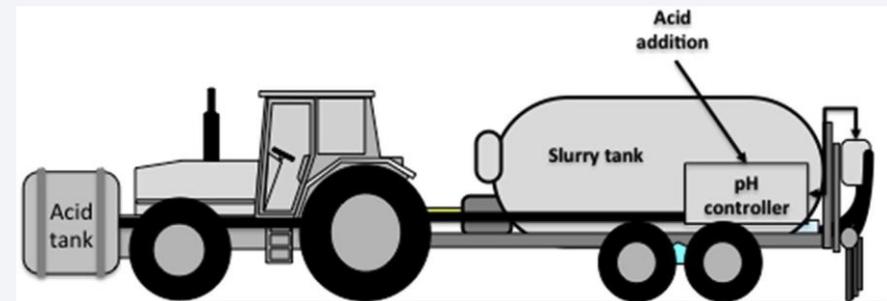
- Dissociation equilibrium between  $\text{NH}_4^+$  und  $\text{NH}_3$



Effect of pH and temperature on equilibrium between  $\text{NH}_4^+$  and  $\text{NH}_3$  in aqueous solutions. Behera, et al. 2013

- pH-target value: 4.5 – 6.8 (Fangueiro *et al*, 2015)

- Acidification became a full-scale commercial operation in Denmark in 2003 (Fangueiro *et al.*, 2015)



Fangueiro *et al.*, 2015

- ADR license required
  - Addition of acid immediately before application
  - Acid demand: Slurry: ~ 1-3 l/m<sup>3</sup>
- Reduction of ammonia emissions compared to trailing hose application without acidification by 49 %, pH reduction to 6.4 (VERA, 2010)

## Sulfuric acid ( $H_2SO_4$ )

- For efficient acidification only sulfuric acid comes into question
- Density  $H_2SO_4$  (98%): 1.8 kg/l

### Advantages:

- Cheap
- Strong acid ( $pK_s$  – Value: -3.0)
- Low corrosivity at high concentration
  
- Positive effect of sulfur fertilization
  - Acidification with 3 l  $H_2SO_4$  (98%) per  $m^3$  slurry/digestate
  - For example 20  $m^3/ha$ 
    - 35.3 kg S/ha
    - Savings on mineral sulfur fertilization



[www.eqjooki.de](http://www.eqjooki.de)



Photo: M. Zacharias

### Denmark

- 20 % of applied slurry is acidified (Birgmoose und Vestergaard, 2013; Jacobsen, 2015)
- Best Available Technology (BAT)

# In-field acidification

## Baltic Slurry Acidification

- Large scale field trials in cooperation with the agricultural contractor Blunk GmbH in grassland, wheat, triticale and maize



Photo: E. Schmidt-Holländer

# In-field acidification

- Trials on micro plot scale in grassland and winter wheat



Photos: Dr. Frank Steinmann, LLUR

## Material and Methods

Trial site 2017: Grönwohld

- Grassland (0.44 ha) und Wheat (0.2 ha)
- Randomized Block experiment

### Measuring program:

- Yield sampling by hand
  - Grassland: 5 silage cuts
- NH<sub>3</sub>-Emissions (daily, several times a day after fertilization up to 7 days)
  - Passive samplers und Dräger-Tube Method (Pacholski, 2006)
- N<sub>2</sub>O-Emissions (weekly 365 d, daily after fertilization):
  - „closed-chamber“ (Hutchinson und Moirier, 1981)



## Material and Methods

Grassland	Wheat
Digestate	Digestate
Digestate H <sub>2</sub> SO <sub>4</sub>	Digestate H <sub>2</sub> SO <sub>4</sub>
CAN	CAN
Urea	Control
Urea stabilized	
Control	



- Mineral-N based
- Digestates (pH-value: 8,7)
- Acidification immediately before application to pH 5,5 – 6 with H<sub>2</sub>SO<sub>4</sub>
- „trailing hose application“ with watering cans
- Additional **PKS**-fertilization after each N-fertilization

## Material and Methods

- Grassland:

	Fertilizations
360 kg N/ha	120/100/100/40
240 kg N/ha	90/60/60/30
120 kg N/ha	60/40/20/0

← NH<sub>3</sub> measurements

- Wheat:

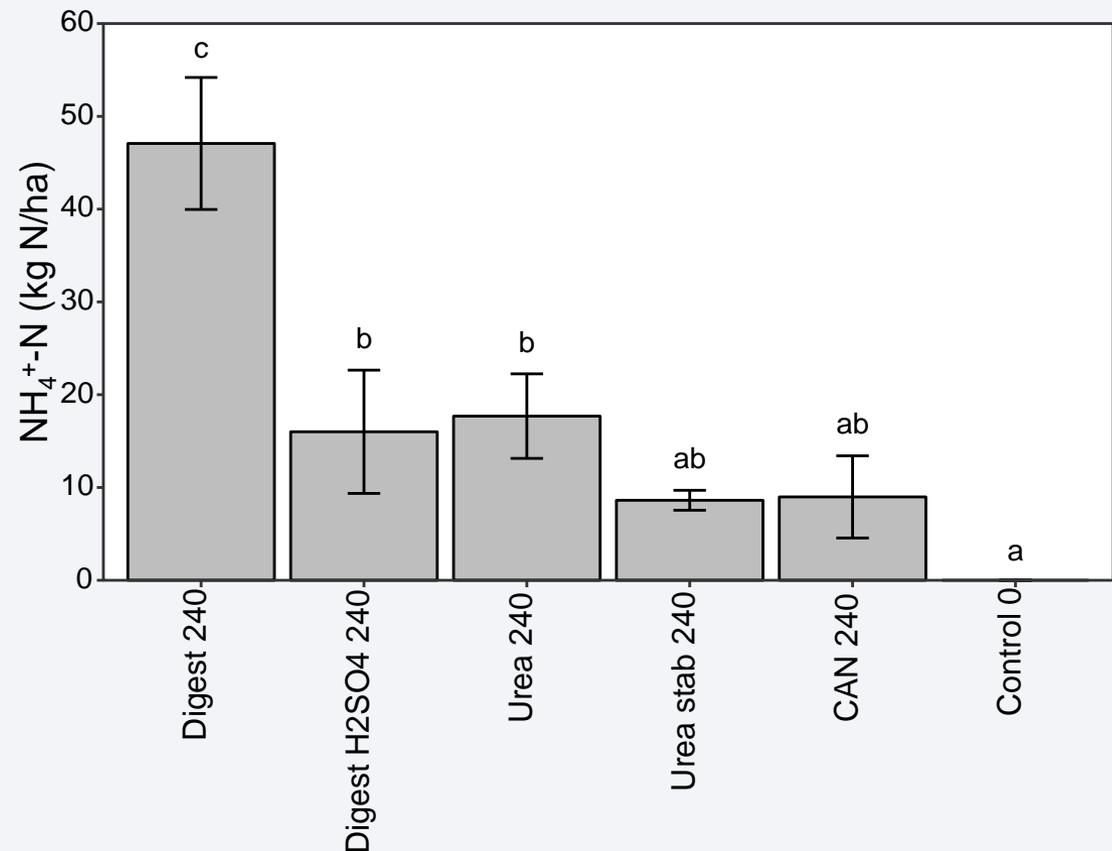
	Fertilizations
300 kg N/ha	100/100/100
200 kg N/ha	100/50/50
100 kg N/ha	50/50/0

← NH<sub>3</sub> measurements



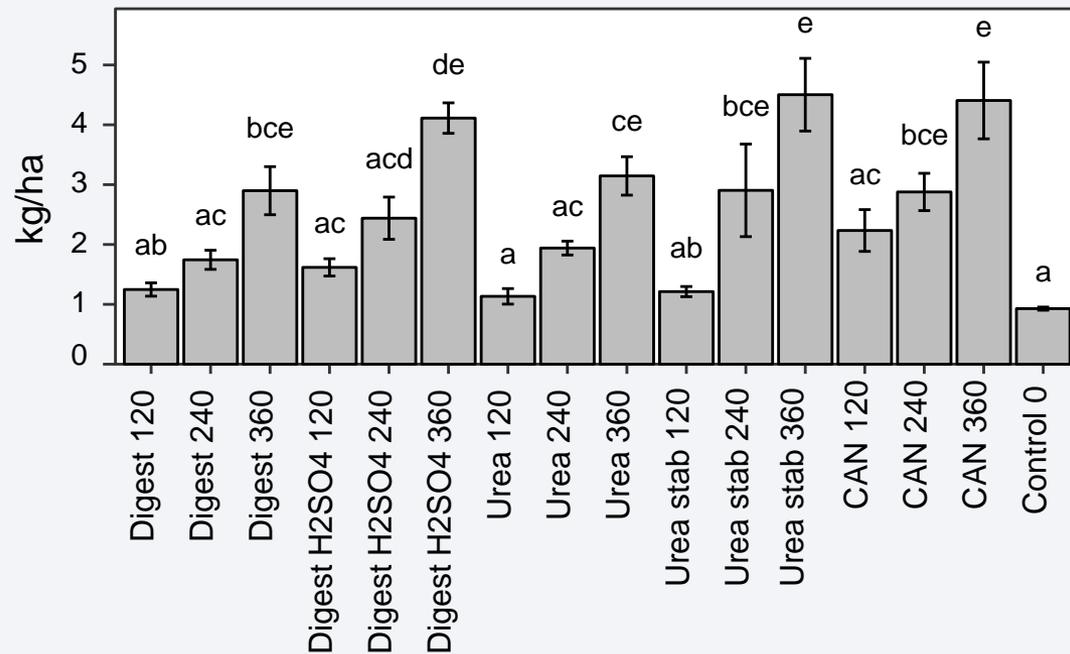
## Ammonia emissions

- Cumulated by passive samplers (minus CT)
- 4 fertilizations
  
- Reduction potential due to acidification approximately 66%
  
- Reduced emissions of stabilized Urea in comparison to the non stabilized treatment



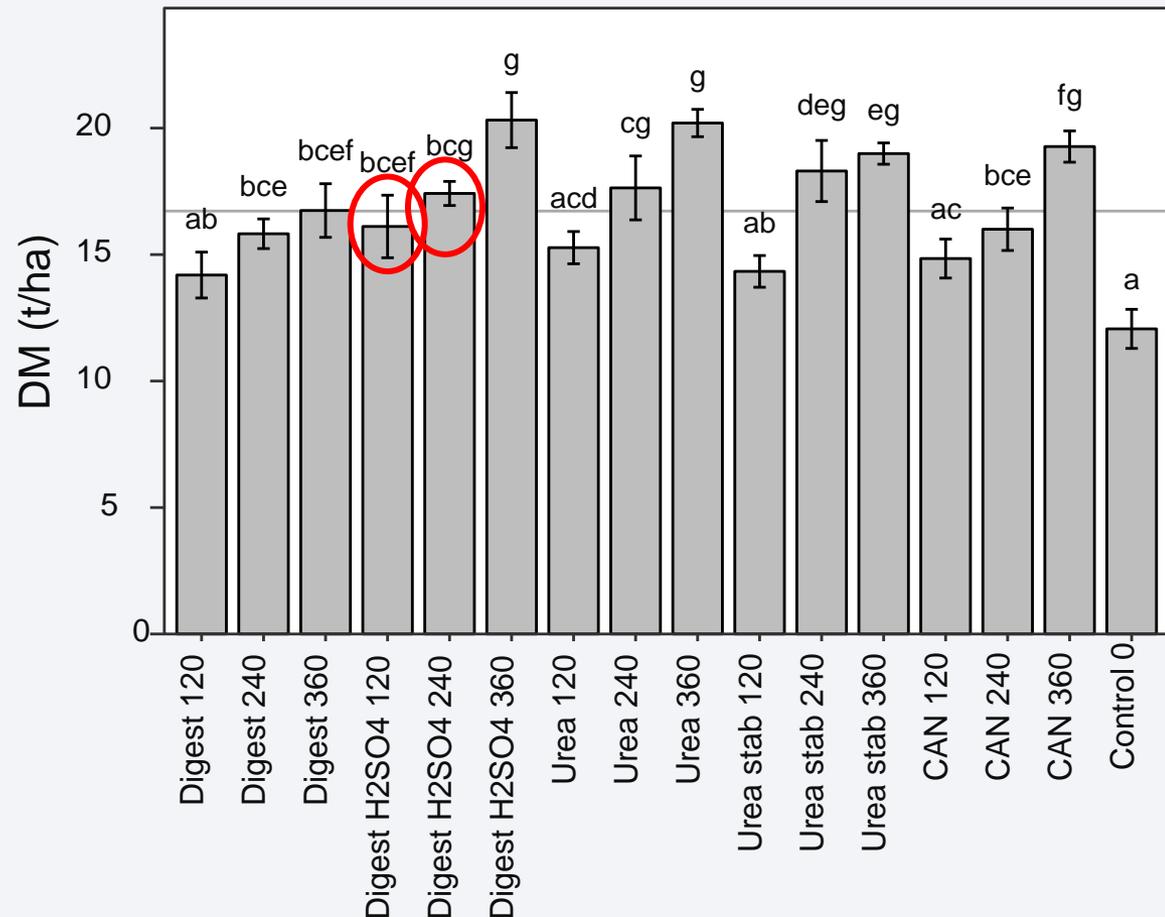
## Nitrous oxide

- 01.03.2017-31.01.2018
- Increasing emissions with increasing N fertilization
- Higher emissions in acidified treatments in comparison to the non acidified digestates at all N-levels
- Tendencies for higher emissions of Urea stabilized than Urea
  - Indications for higher amounts of available nitrogen in the soil due to acidification and stabilization



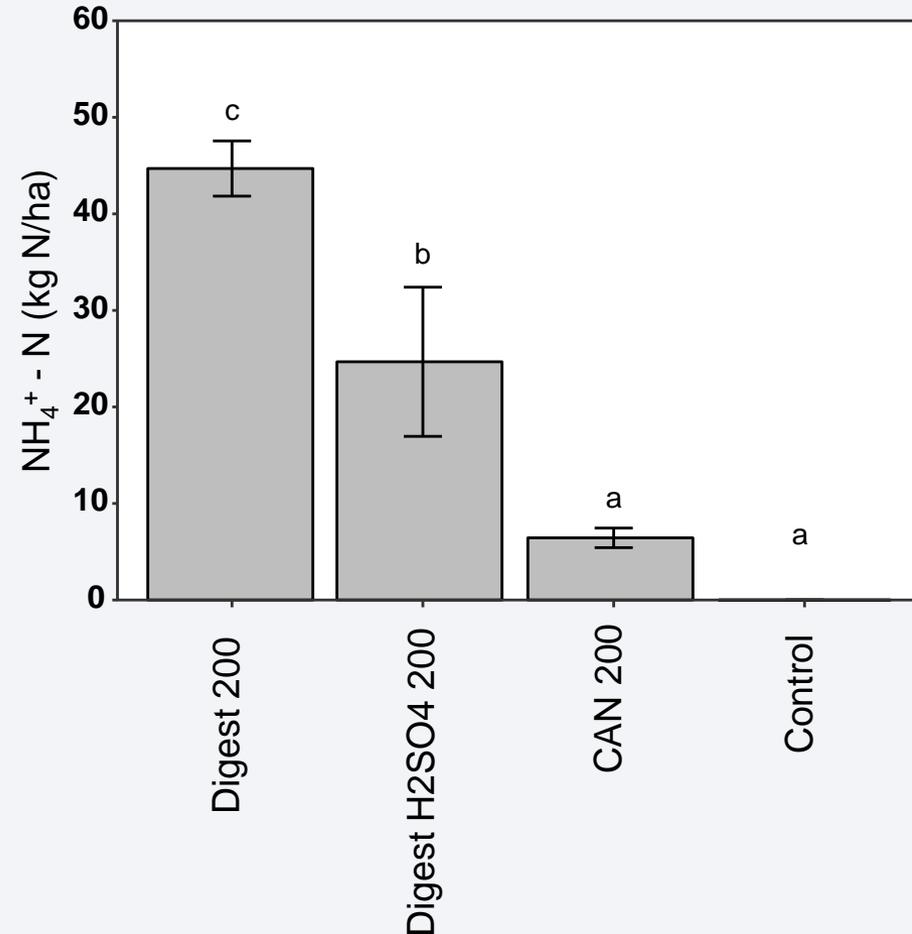
## DM (t/ha) cumulated, 5 silage cuts

- The acidified treatment with 120 kg N/ha reached the highest yields of all treatments at lowest N level
- Acidified digestate 240 kg N/ha reached comparable yields than the non acidified treatment 360 kg N/ha
- Indications for higher amounts of plant available nitrogen due to acidification

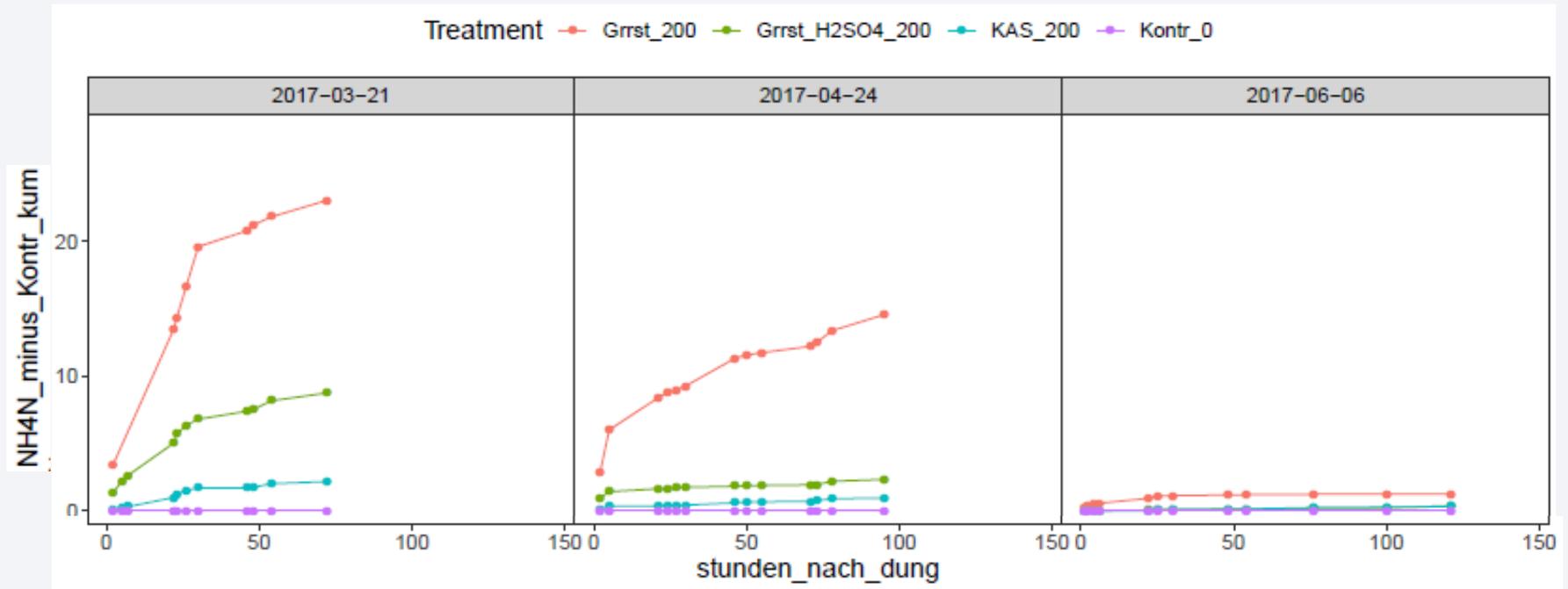


## Ammonia emissions

- Cumulated by passive samplers
- 3 fertilizations
- Reduction potential due to acidification approximately 44 %

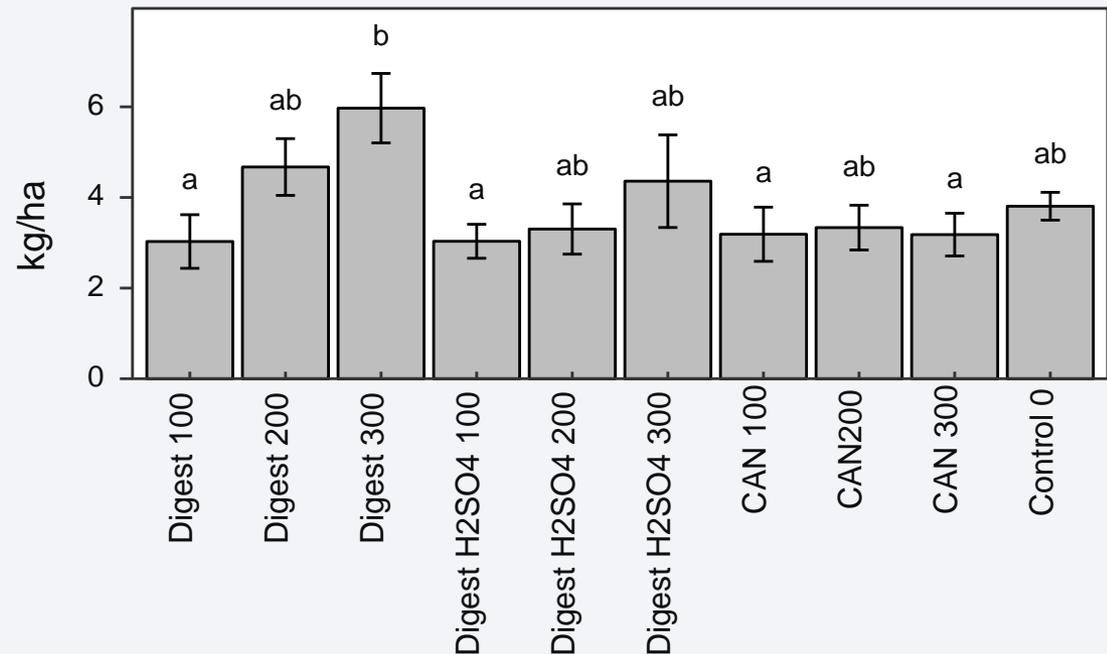


# Preliminary results winter wheat 2017



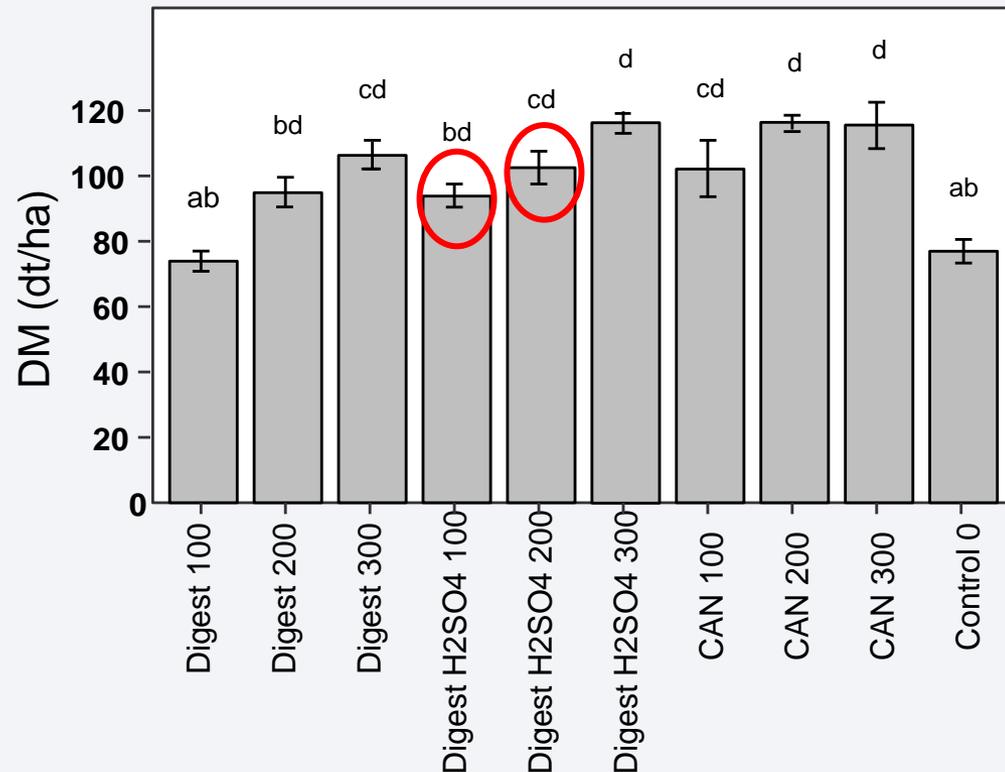
## Nitrous oxide

- 01.03.2017-31.01.2018
- Higher emissions in the non acidified treatments in comparison with emissions of treatments with acidification
- No rise in emissions with increasing N level could be observed in CAN treatments
- High emissions in the control



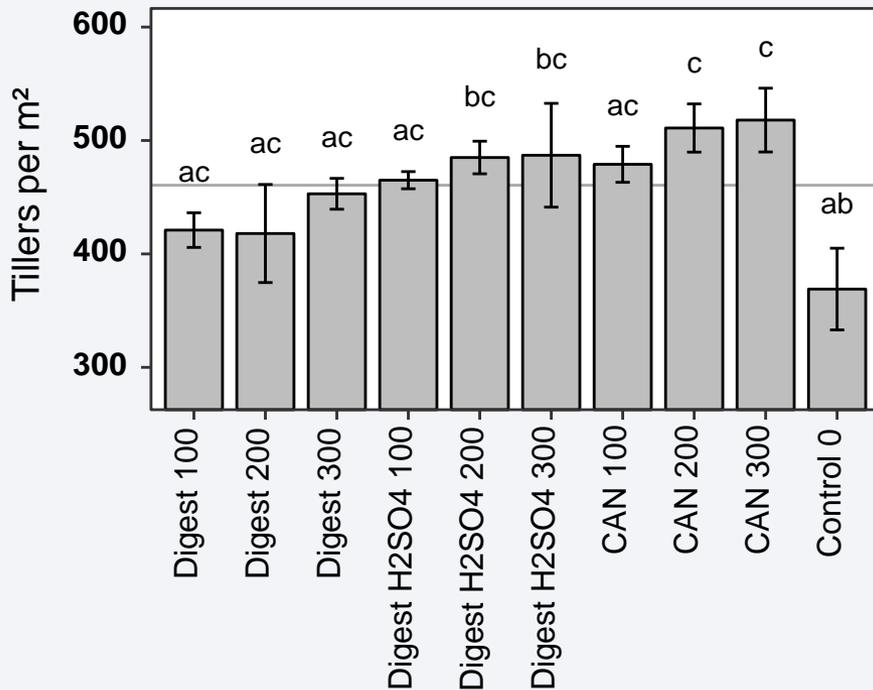
## Kernel DM yield (dt/ha)

- Acidified treatment 100 kg N/ha reached comparable results to 200 kg N/ha without acidification
- Acidified digestate 200 kg N/ha reached comparable yields like non acidified digestate 300 kg N/ha
- Lower increases in yield with increasing N fertilization in CAN treatments
- Indications for higher amounts of plant available nitrogen due to acidification

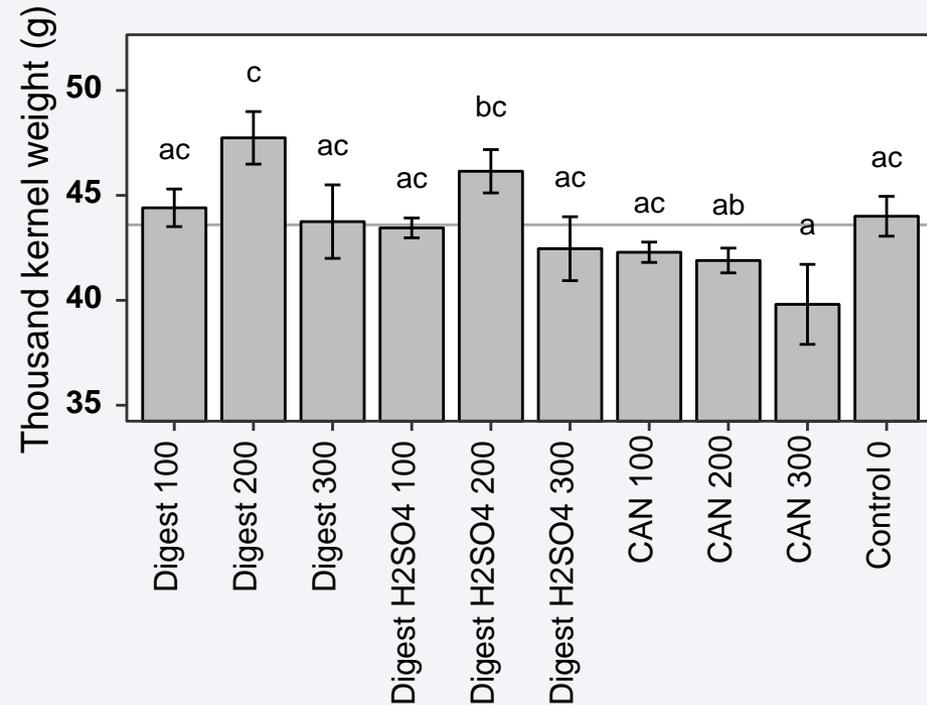


# Preliminary results winter wheat 2017

### Ears/tillers per m<sup>2</sup>



### Thousand kernel weight



- Tendency towards higher tiller densities and lower kernel weights at an increased N fertilization and N availability



## Work Package 3: Pilot Farms 5 trial locations in Schleswig Holstein 2017

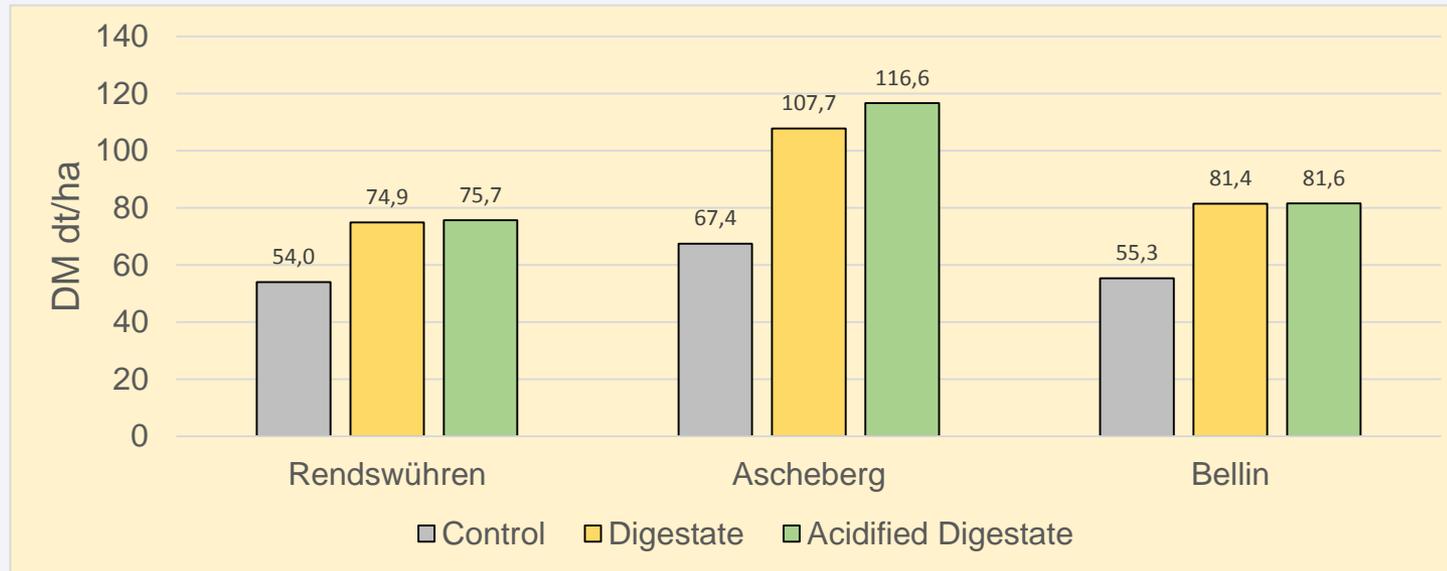
Location	Crops	
Rendswühren	Triticale	Grassland
Bredeneek	Grassland	
Ascheberg	Wheat	Grassland
Bellin	Wheat	
Selent	Maize	

- Acidification of digestates to the first fertilization with  $4 \text{ l H}_2\text{SO}_4/\text{m}^3$
- Mineral supplementation to following fertilizations
- Yield sampling, ears/ $\text{m}^2$ , thousand kernel weight
  - Track: ~ 180 m , ~ 60 m per treatment
  - 3 samplings ( $0,5 \text{ m}^2$ ) per treatment by hand



# Preliminary results– pilot farms

## Pilot Farms: Kernel DM Yield (dt/ha)



Location	N total (kg/ha)	07.04.17
Rendswühren (Triticale)	180 (90/90)	90 kg NH4-N/ha (Nmin included) 27 m <sup>3</sup> /ha digestates
Ascheberg (Wheat)	180 (110/70)	110 kg NH4-N/ha (Nmin included) 29 m <sup>3</sup> /ha digestates
Bellin (Wheat)	190 (100/50/40)	100 kg NH4-N/ha (Nmin included) 38 m <sup>3</sup> /ha digestates

## First conclusions

### Field trials:

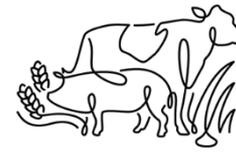
- Lowering the pH to 5,5-6 significantly reduced ammonia emissions.
- Comparable low absolute  $\text{NH}_3$  losses in 2017
- Acidification resulted in higher or similar yields compared to fertilization with non-acidified substrate, especially at low N level.
  - Additional plant available nitrogen especially increased yield at lower N level.
- Results from large scale field trials confirm these results.
- On grassland, nitrous oxide emissions of the acidified treatments were slightly higher in comparison with the non-acidified treatments.
- In winter wheat the acidified treatments showed slightly lower  $\text{N}_2\text{O}$  emissions.



- Urgent need to reduce ammonia emissions (NEC, etc.)
- Experience from Denmark shows that acidification of manure is an effective tool for reducing ammonia emissions.

➤ Acidification, in addition to other best practice application techniques, is another tool for the efficient application of slurry and digestates.





## Baltic Slurry Acidification

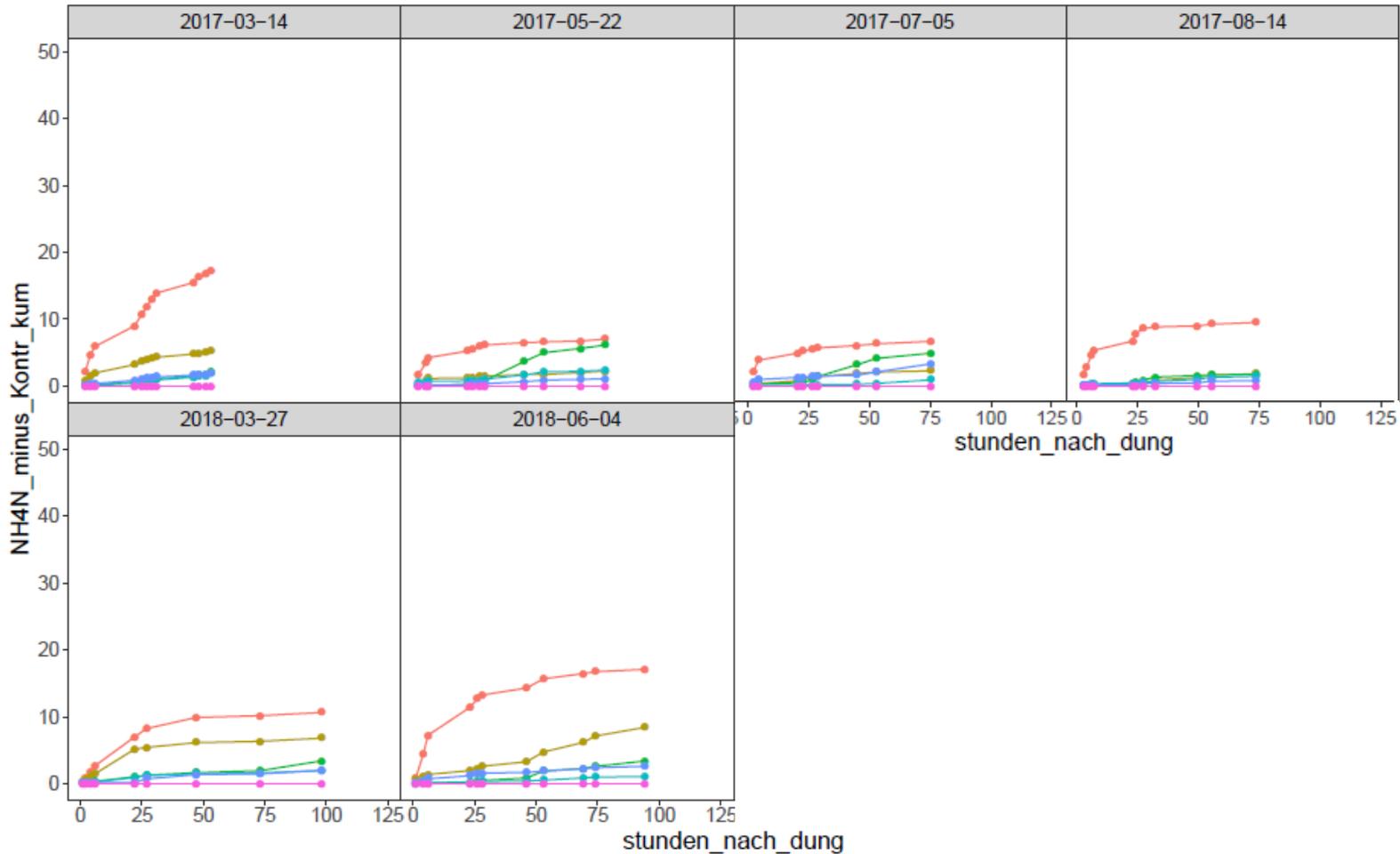
# Thank you for your attention!



01.06.18

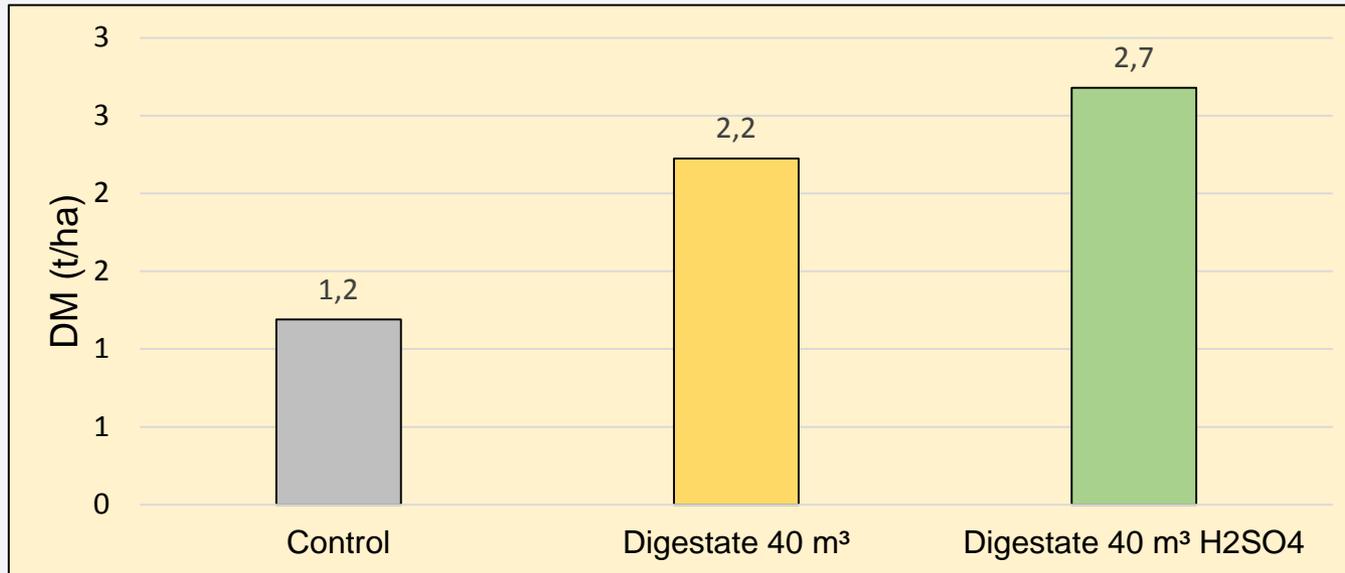
# Preliminary results permanent grassland 2017

Treatment    Grrst\_240    Hstoff\_240    KAS\_240  
                  Grrst\_H2SO4\_240    Hstoff\_stab\_240    Kontr\_0



# Preliminary results– pilot farms 2018

## Field Grass, Ascheberg (15.05.18)



- Fertilization: 21.04.18, 40 m³ digestate
- Silage cut: 15.05.18

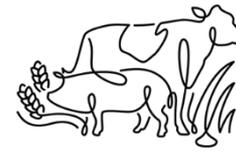


# Field trials on Grassland and Wheat

## Material and Methods

- **NH<sub>3</sub>-Emissions** (daily, several times a day after fertilization up to 7 days)
  - Calibrated passive sampling
    - Dräger-tube-method (DTM)
    - Passive-sampler
  - Principle idea: to link a simple semi-quantitative measuring method for the measurement on many plots, with a quantitative method by simultaneous measurements with both methods on a few plots (Pacholski, 2016).
  - Passive samplers as semi-quantitative measurement method
  - DTM is employed to obtain a transfer coefficient, converts the semi-quantitative losses of the passive sampler to quantitative losses (kg N ha<sup>-1</sup>)





## Baltic Slurry Acidification

Tabelle 1: Potenziale der  $\text{NH}_3$ -Emissionsminderung (in %) gegenüber oberflächlicher Breitverteilung von Gülle ohne Einarbeitung (verändert aus Flessa et al. 2012)

Applikationstechnik	Webb et al. (2009) <sup>1</sup>	NIR (2010) <sup>2</sup>
Sofortige Einarbeitung innerhalb einer Stunde auf unbewachsener Fläche	Pflug: 89-98 Scheibenegge: 25-75 Egge: 25-30	Rindergülle: 80 Schweinegülle: 82
Einarbeitung auf unbewachsener Fläche mit Güllegrubber		Rindergülle: 90 Schweinegülle: 88
Ausbringung mit Schleppschauch, Acker	Rindergülle: 22 Schweinegülle: 29	<sup>3</sup> Rindergülle: 30 <sup>3</sup> Schweinegülle: 48
Ausbringung mit Schleppschauch, Grünland	Rindergülle: 34 Rindergülle: 48	Rindergülle: 10 Schweinegülle: 30
Ausbringung mit Schleppschuh, Acker mit Aufwuchs	Rindergülle: 45 Schweinegülle: 78	Rindergülle: 28 Schweinegülle: 52
Ausbringung mit Schleppschuh, Grünland	Rindergülle: 60 Schweinegülle: 66	Rindergülle: 40 Schweinegülle: 60
Gülleschlitztechnik, Injektion (open slot injection), Acker	Rindergülle: 79 Schweinegülle: 97	Rindergülle: 52 Schweinegülle: 76
Gülleschlitztechnik, Injektion (open slot injection), Grünland	Rindergülle: 21	Rindergülle: 60 Schweinegülle: 80
Injektion (closed slot injection), Acker	Rindergülle: 82-86	
Injektion (closed slot injection), Grünland	Rindergülle: 81 Schweinegülle: 89	

<sup>1</sup> Die Angaben aus der Referenz Webb et al. (2009) beziehen sich auf durchschnittliche Emissionsminderungen

<sup>2</sup> Bewertung der Verfahren im Rahmen der nationalen Emissionsberichterstattung

<sup>3</sup> Bei Schleppschauchanwendung im stehenden Bestand