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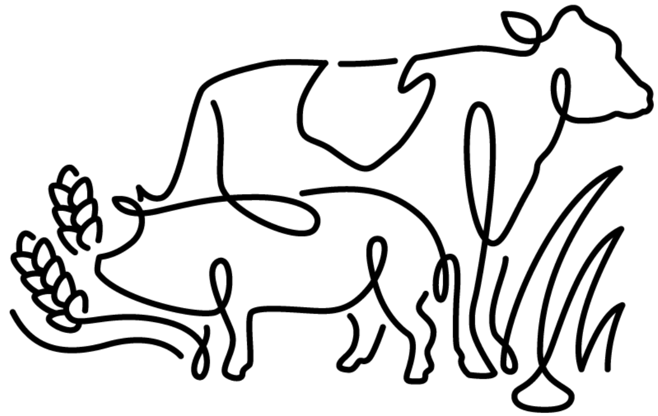

WP 2: Feasibility studies

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Baltic Slurry Acidification

Aim of WP2

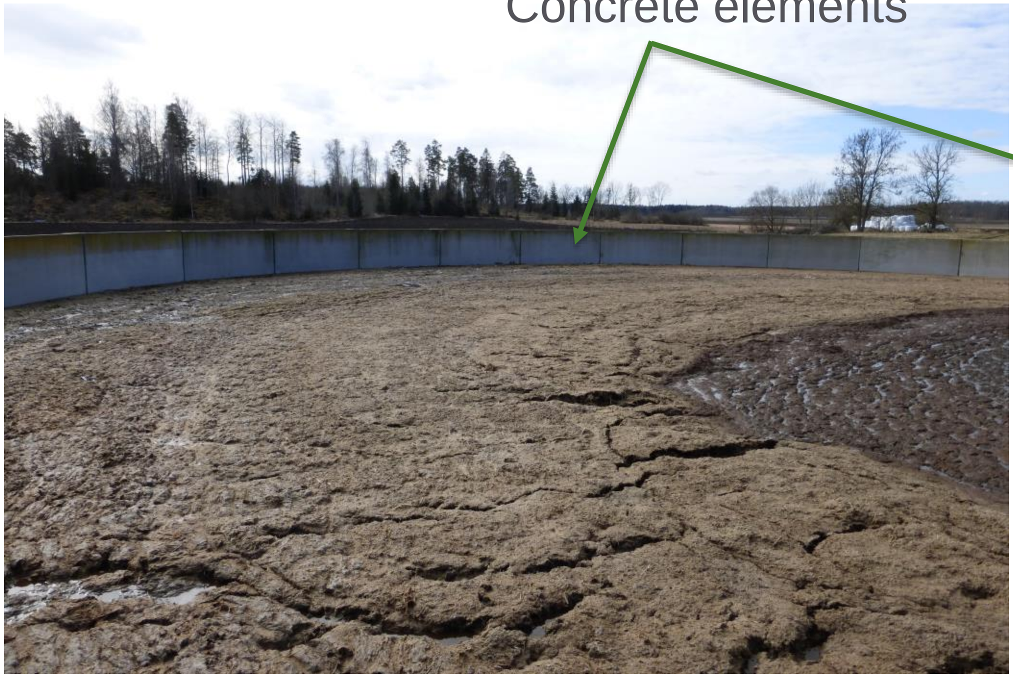
- WP2 aimed to identify technical issues, bottlenecks and other barriers that may hinder the implementation of slurry acidification techniques (SATs), originally developed in Denmark, to other countries in the BSR.

Content

1. Equipment quality evaluations
2. Acid consumptions, slurry buffering capacity
3. Working environment and safety
4. Ammonia emissions from acidified slurry
5. Slurry acidification effects on soils

Equipment quality evaluations, chemical corrosive effect on concrete (pH changed from appr. 7 to 5.5)

Concrete elements



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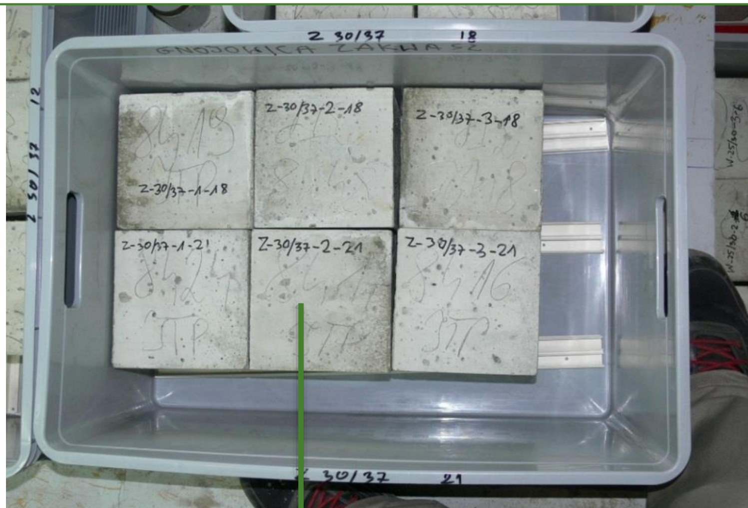
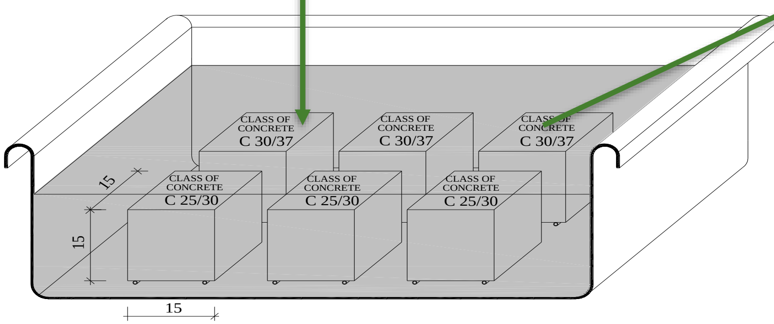
Baltic Slurry Acidification

Compressive strength of concrete ITP, Poland

1. Exposure of two different concrete qualities in water, slurry and acidified slurry (C25/30 and C30/37)

2. Testing of compressive strength after up to 21 month of exposure
Also, testing bending strengths and macroscopic of steel rod





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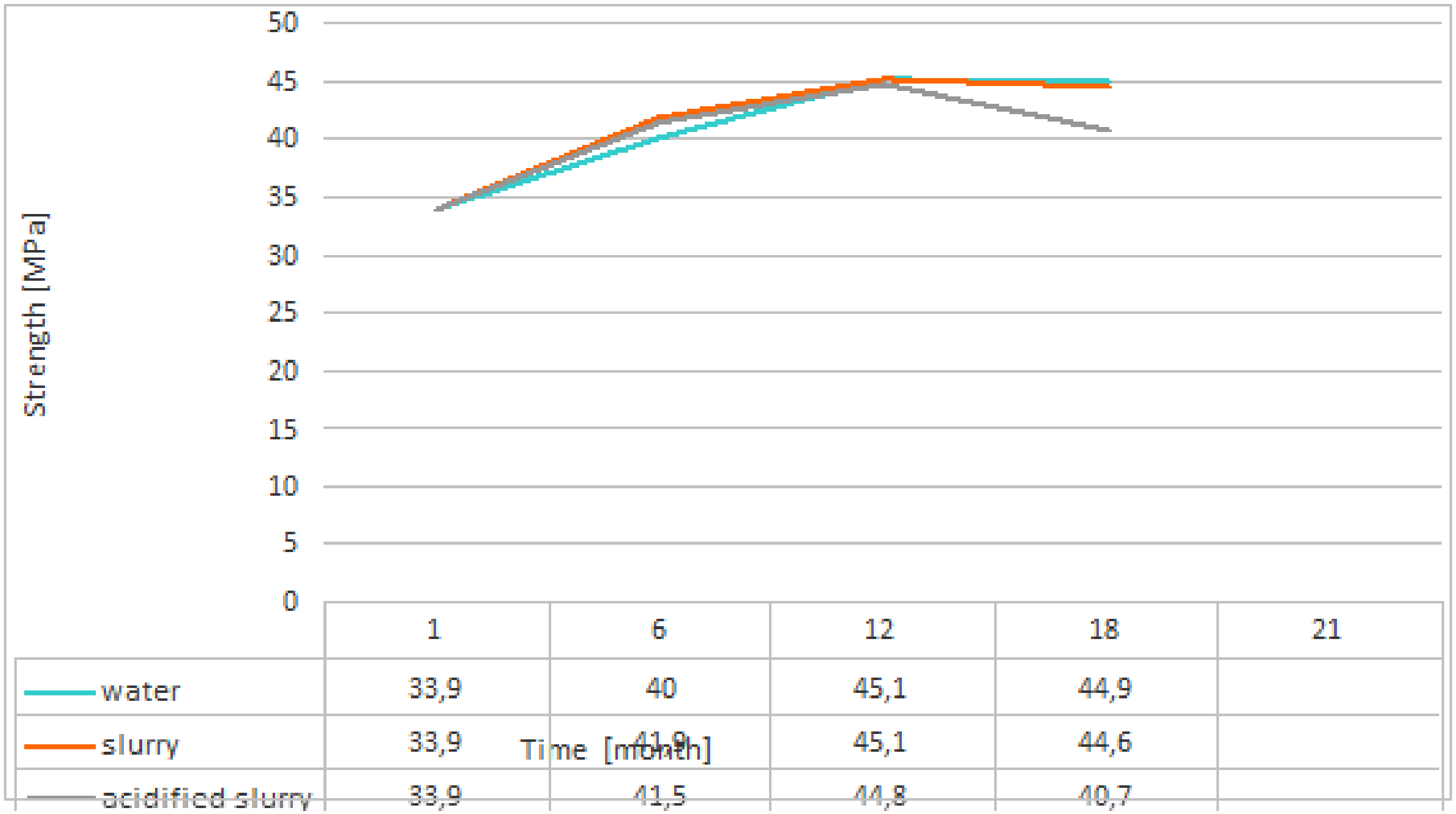
Compression strengths after 1, 6, 12 and 18 months (C25/30)



	1	6	12	18	21
water	33,9	40	45,1	44,9	
slurry	33,9	41,9	45,1	44,6	
acidified slurry	33,9	41,5	44,8	40,7	

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Micro-structural analysis of concrete after exposure in acidified slurry, RISE, Sweden

Experiment started in Dec 2016 till end of Nov 2018

pH measurements

- Cattle slurry, with and without acid (pH 5.5) DM-content 6.5%
- <u>Three concrete qualities:</u>
- - 1) ground,
  - 2) wall element,
  - 3) ”better quality”
  2 years exposure

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Structure analysis, 3 concrete qualities, non-acidified (S) and acidified slurry (AS)

Slurry and concrete quality	Depth of carbonatisation of the cement paste, mm	Depth of increase in the capillary porosity (leaching of the cement paste), mm	Depth of discoloration of the cement paste, mm
S_1	2.5	2.5	0
AS_1	2.5	6.5	0.3
S_2	1.5	1.5	0
AS_2	1	3.5	0.3
S_3	0.1	0	0
AS_3	1	1	0.3

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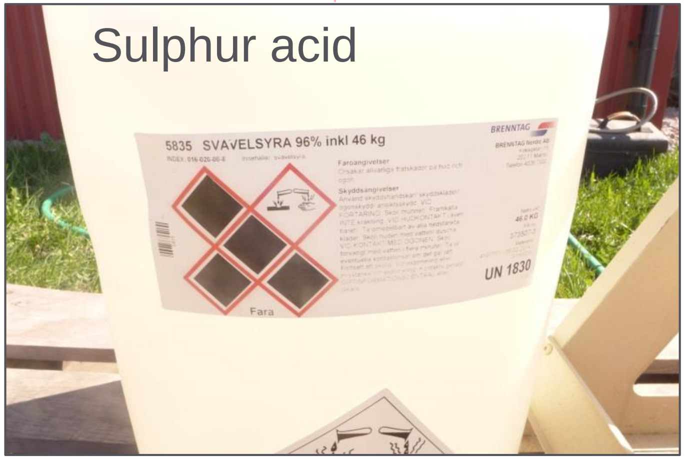
Conclusions: Quality of concrete

- The results from PL showed that acidified slurry couses changes in strenght and concrete structure.
- The results from SE show that the acidified slurry is more chemically aggressive for the cement paste in all the analysed concrete mixes.
- However, to assess the exact risk of negative impact of acidified slurry for concrete used for the construction of slurry channels and slurry tanks, it would be necessary to continue tests for many years in the future.

Working environment and safety



Sulphur acid

EU legalisations

Chemicals
CLP regulation Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 Decem 2008 on classification, labelling and packaging of substances and mixtures, amending a repealing. Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) 1907/2006.CLP.
Work regulations
Council directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)
Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004on the protection of workers from the risks related to exposure to carcinogens or mutagens at work (S individual Directive within the meaning of Article 16(1) of Council Directive 89/391/EEC)
Council directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC).
Environment protection
Directive 2004/35/CE of the European parliament and of the council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage.
Waste
Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.
Commission decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.
Transport
Directive 2008/68/EC of the European parliament and of the council of 24 September 2008 on t inland transport of dangerous goods.
European Agreement concerning the International Carriage of Dangerous Goods by Road. ADI applicable as from 1 January 2013. UNECE.

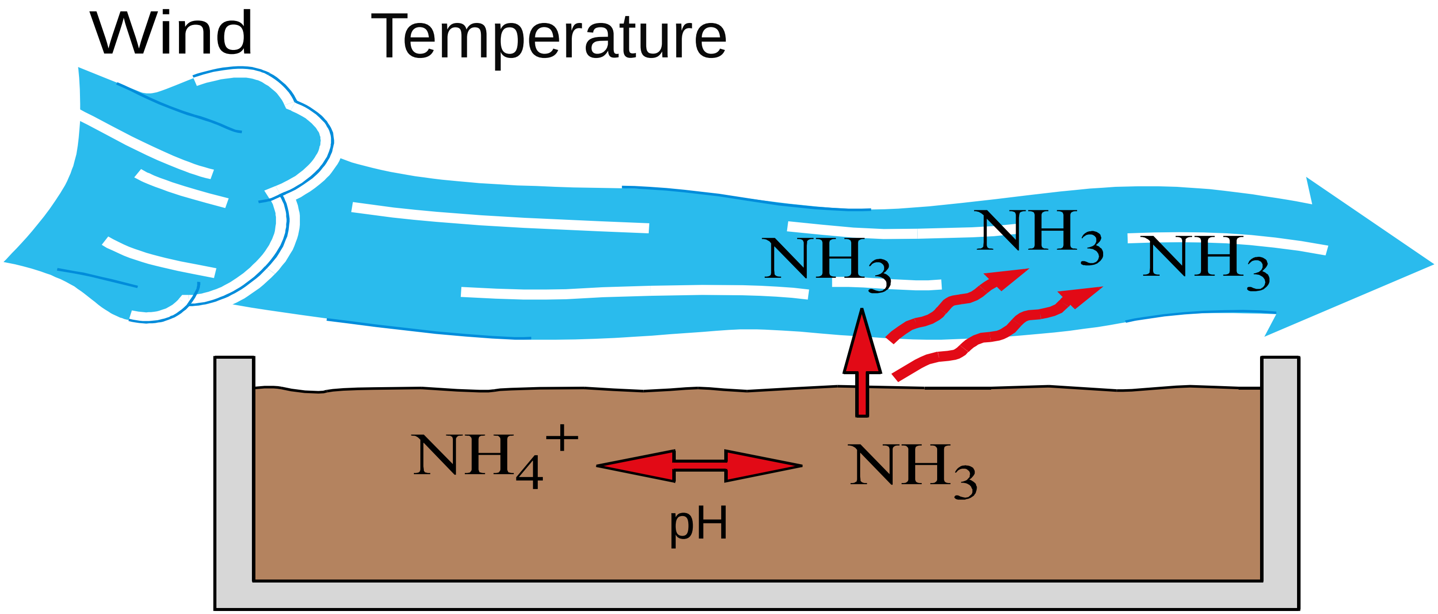
Checklists for:
Working environment, storage of acid, handling, protective equipment and transport of acid

Check item	*YES*	*NO*	*Comments/action*
Working environment			
Acid is not handled by anyone under 18			
Risk assessment is completed			
Risk assessment has recorded: 1. Type of hazard 2. Locations of storage and use 3. Any occupational exposure limit values 4. Other special regulations that may apply			
All serious accidents and serious incidents are reported to the Swedish Work Environment Authority.			
Storage of acid			
Acid storage containers are made of a resistant material			
Acid storage is bunded			
Impact protection is provided where there is a risk of collision			
Storage location is chosen with regard to the distance to drinking water supply, nearby watercourses or other risk objects			
Acid is listed in the company's chemical inventory			
Acid is stored under supervision, or under lock and key and inaccessible to children or other unauthorized persons			
Equipment for neutralizing and collecting spillages is easily accessible			
Handling			
Safety data sheets are easily accessible wherever acid is handled			
Equipment for neutralizing and collecting spillages is easily accessible			
People and animals are kept well away from sulphuric acid during its handling by trained personnel			
Sulphuric acid is **not** stored/handled above eye level.			
Personnel are fully aware of how sulphuric acid reacts with manure and water, for example the acid-into-water (AIW) rule and violent foaming.			
Knowledge of first aid and where the farm's protective equipment is kept is essential.			
Accidents or major spillages are reported to the municipal environmental and health protection administration and, if necessary, the emergency services.			
Protective equipment			
Protective equipment to be available when handling the acid: 1. Emergency shower, 2. Eye wash shower, 3. Respiratory protection, 4. Protective eyewear 5. Protective gloves in, for example, fluorocarbon rubber or butyl rubber, 6. Fully covering protective suit in, for example, butyl rubber or neoprene (may be disposable) 7. Acid-resistant safety boots/shoe			
Transport			
ADR training for transport (excluding transport of IBCs by tractor for agricultural use).			
1.3 training for transport of max. 333 litres (applicable to personnel that for example pack, load or unload dangerous goods, and to others whose tasks relate to the transport of dangerous goods).			
For the transport of value-calculated quantities, the following ADR-S provisions apply: • Personnel, including the driver, have undergone 1.3 training • Packaging, IBCs and bulk packages carry prescribed marking and labelling • Goods declaration is prepared for dangerous goods, with the addition of the value-calculated quantity • Packaging, IBCs and bulk packages are type-approved • Vehicle equipped with at least one fire extinguisher with a minimum capacity of 2 kg dry powder • Goods are grouped in accordance with the provisions of Chapter 7.5 in Part 7. • Load security and loading, unloading and handling are in accordance with the provisions in Part 7.			
Transport training is documented			
Employer retains a detailed description of the training for five years.			

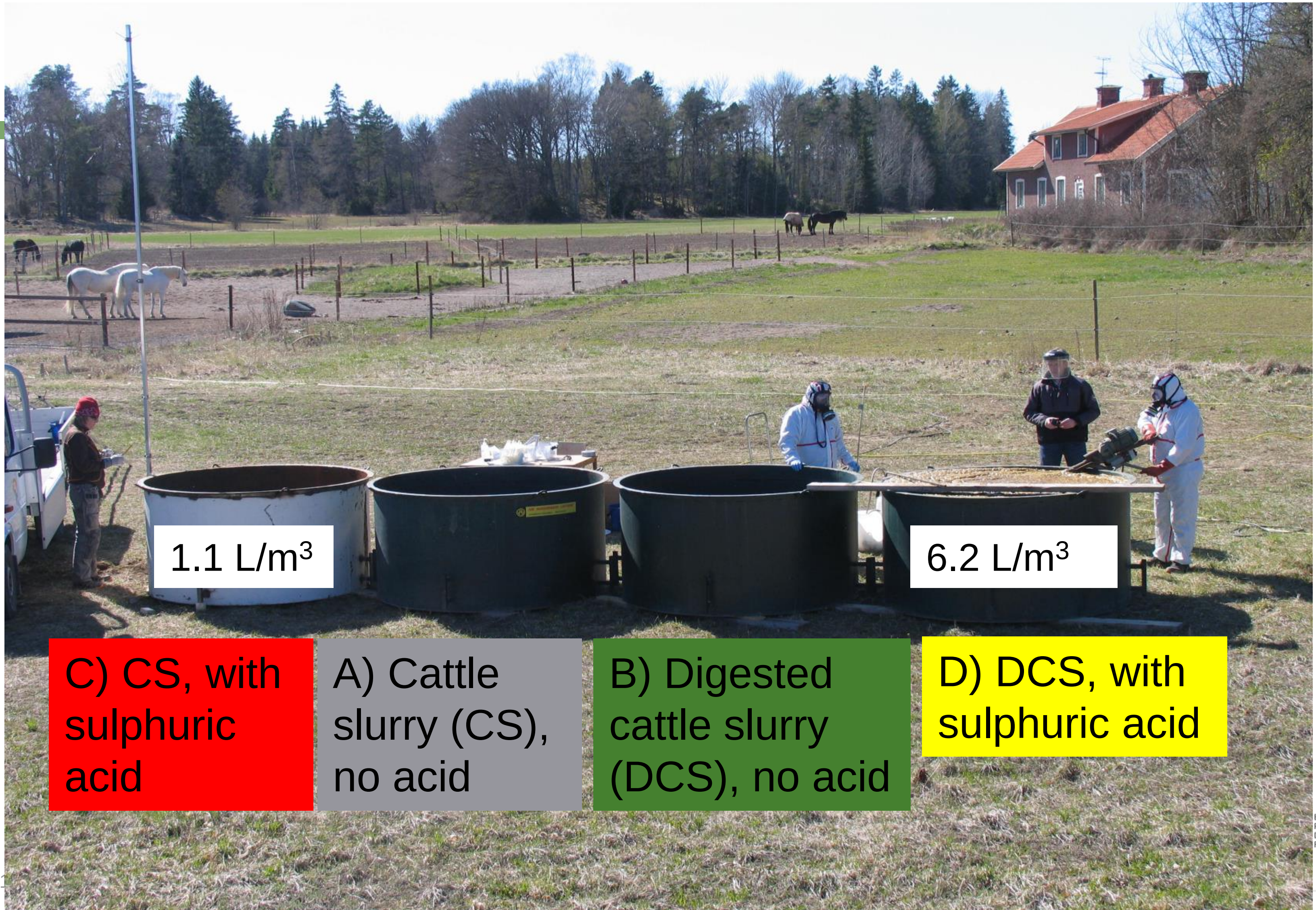
Guidelines and recommendations

- Find a safety advisor
- Make a risk analysis
- Chose the safest technology (no or little risk of contact acid handling)
- Get training
- Follow maintainance program from supplier
- Use protection equipment
- Be prepared for acidents and know what to do

Ammonia emissions from acidified slurry, storage



Storage experiment set up



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Is it possible to predict acid consumption in laboratory scale?

Acid consumption experiment in laboratory scale

C) CS, with sulphuric acid: 2.5 L/m^3

D) DCS, with sulphuric acid: 9.0 L/m^3

- Titrations were done in the laboratory
- Samples were acidified with 1N H_2SO_4
- Constant stirring
- 200 ml slurry in 400 ml containers

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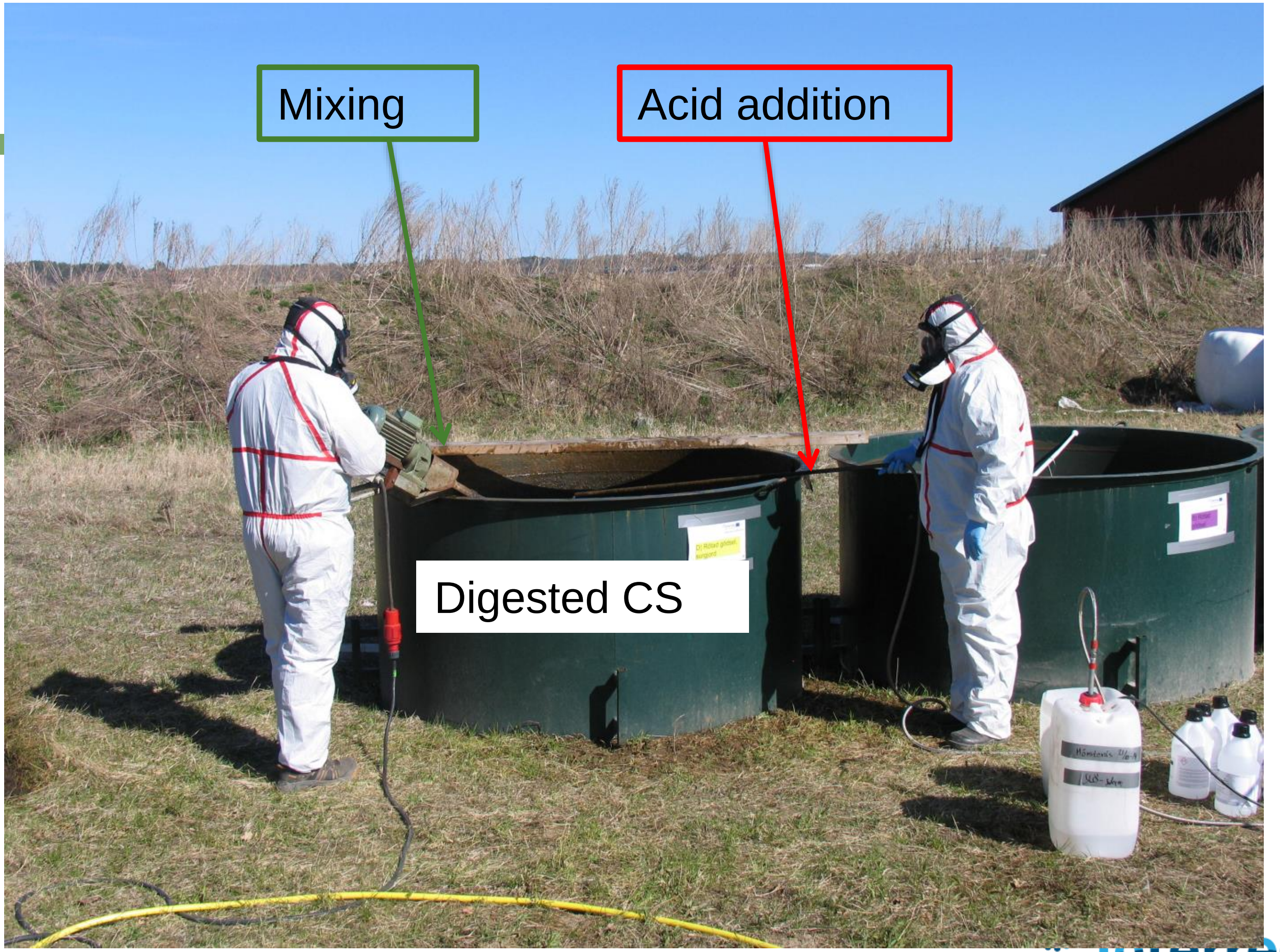
Is it possible to predict acid amounts in laboratory scale?

- In lab scale you could see differences between slurry types, but the rations in acid need, could be different to pilot scale.
- Large variation in acid amounts needed for different slurry types (pH 6.4 varied about 40 times between the lowest and the highest requirement; pH 6.0 about 15 times and pH 5.5 about 9 times).
- Buffering less in pilot scale compared to lab scale (warmer, frequent mixing, small volumes, diluted acid in lab vs. pilot).

Acidifying during mixing, start



Foaming

Baltic Slurry Acidification

Samplers exposed 5 times during 4 months, 1st measurement (5 – 8 May)

Flux samplers

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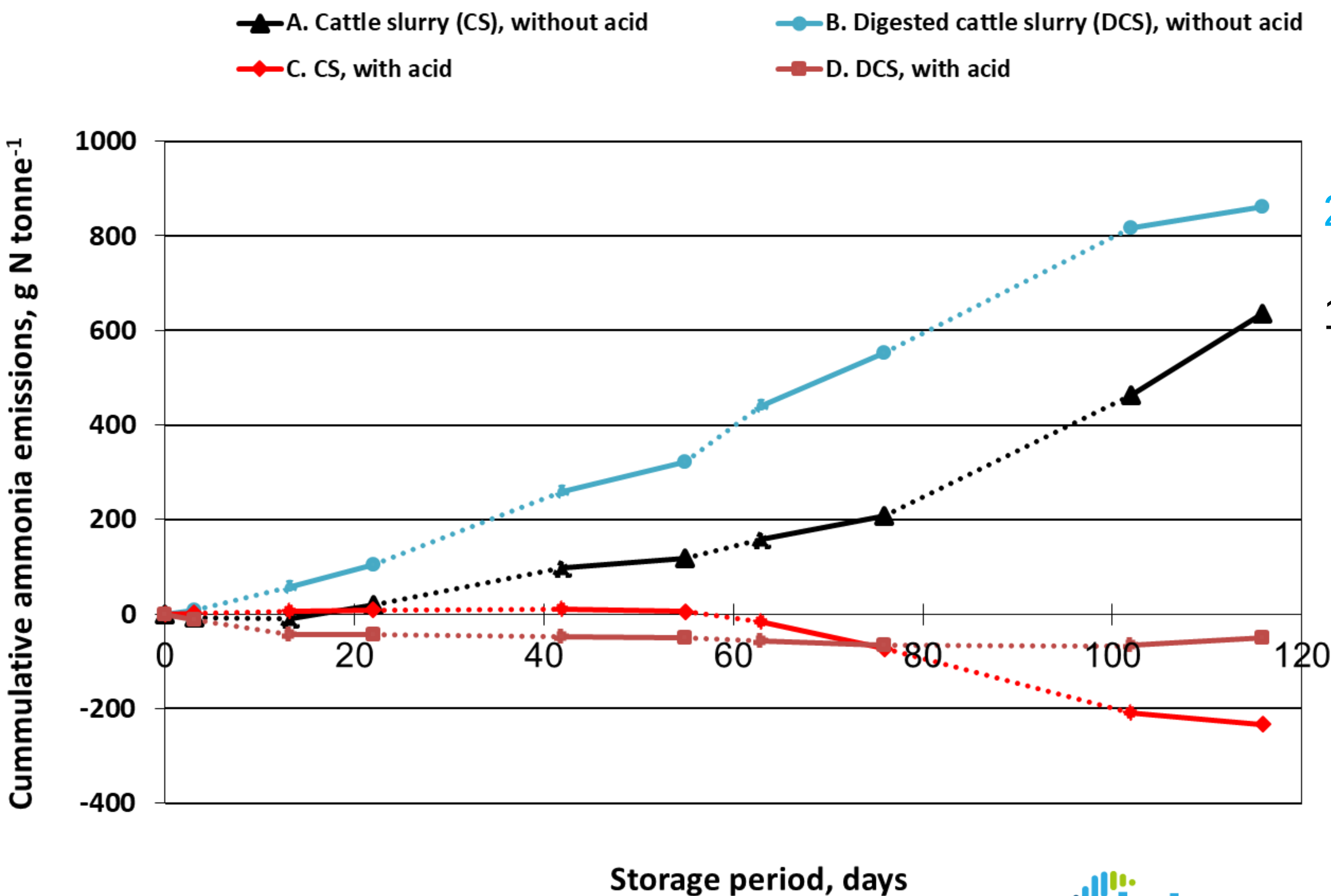
Cumulative ammonia emissions, four months storage



NH_3-N emissions, % of Total-N (% of TAN)

26.1 (57.8)

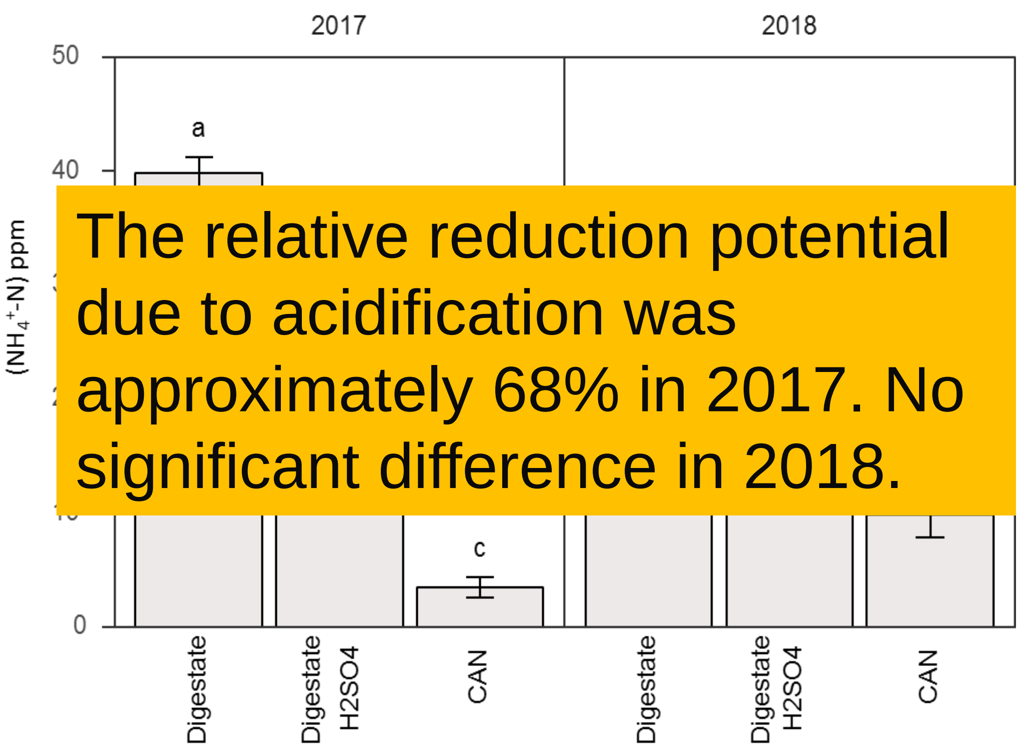
19.3 (53.9)

Ammonia measurements after spreading, LLUR, Germany

Acid trap to capture volatile ammonia on a grassland plot (Source: Sebastian Neumann, LLUR)

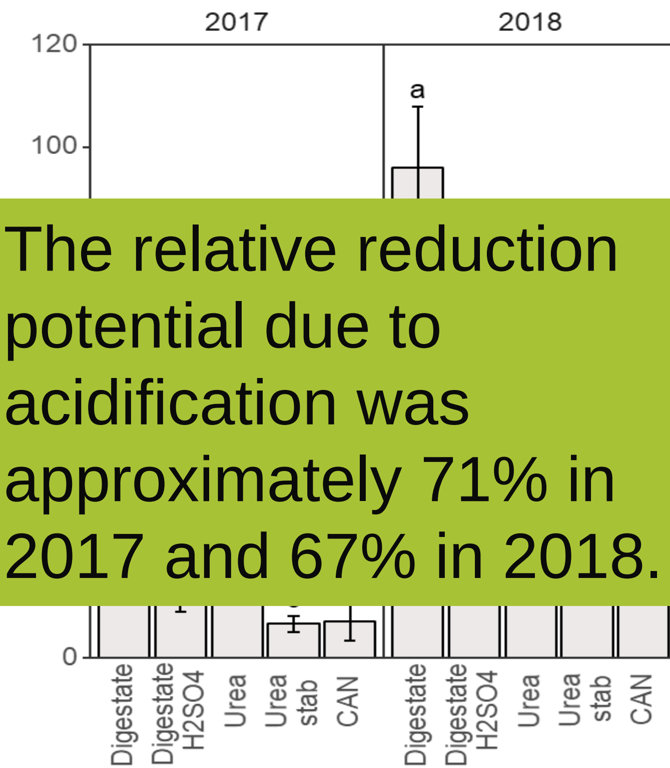
Reduction in ammonia emissions after spreading, Germany

In winterwheat



The relative reduction potential due to acidification was approximately 68% in 2017. No significant difference in 2018.

In grassland



The relative reduction potential due to acidification was approximately 71% in 2017 and 67% in 2018.

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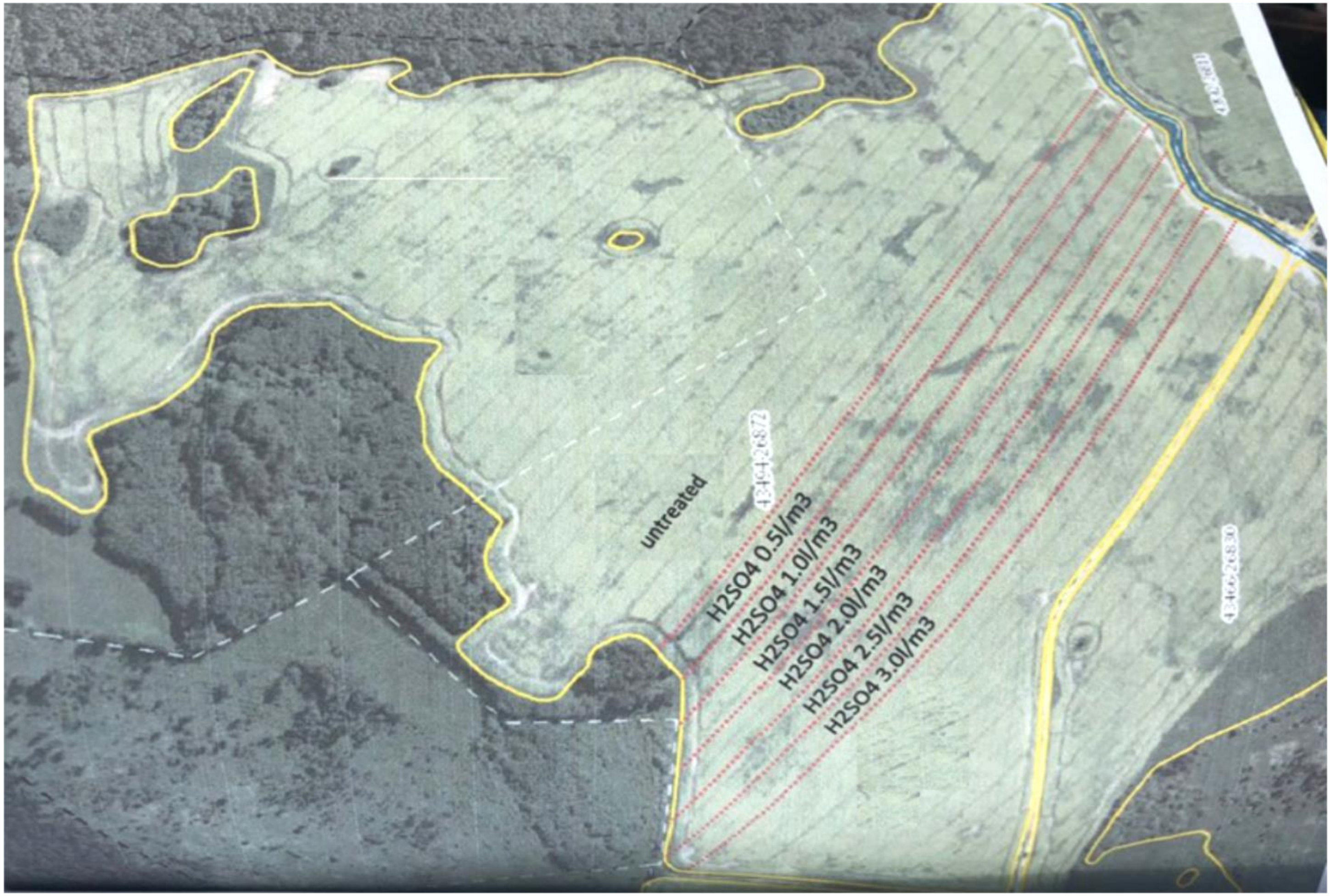
Demo trial on winter wheat in Latvia, 2018



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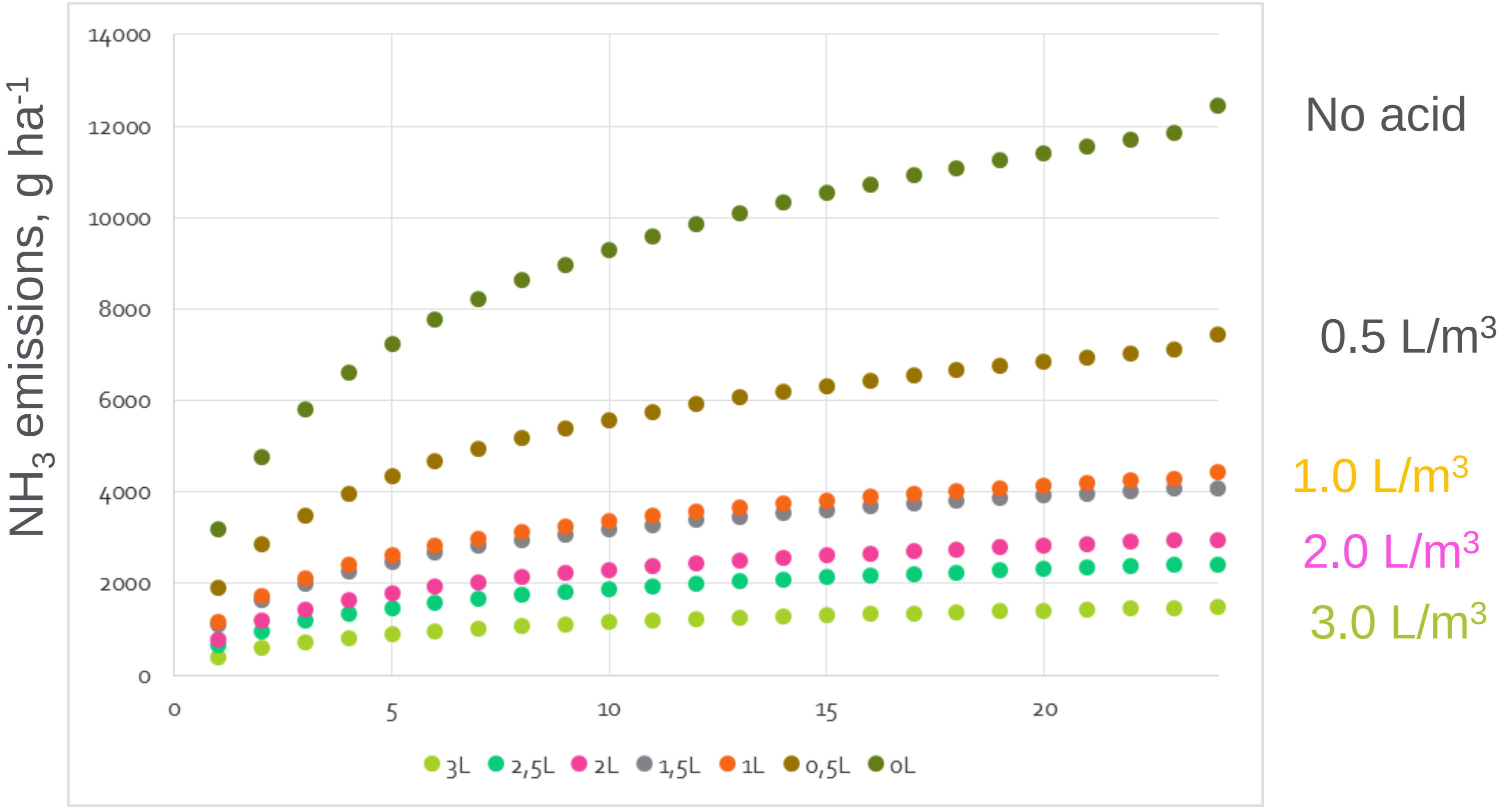
Cumulated ammonia emissions 24 hours after the slurry spread at different amounts of acid added, winterwheat, Latvia



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Summary

- Acidified slurry compared to non-acidified slurry means a negative impact on concrete used for the construction of slurry channels and slurry tanks.
- For safety reasons, choose the technology with little or no risk of contact with acid during handling. Consult a safety advisor, make a risk analysis, complete safety training, use protection equipment and follow maintenance program from supplier. You must be prepared for accidents and know what to do.
- The amounts of acid required to acidify the slurries to a specific pH level varied widely between slurry types.
- Ammonia emissions from slurry are reduced by acidification, both from storage and after field application with sufficient amounts of acid added.

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Slurry acidification effects on soils