



# SyreN Reduced emissions following land application of animal slurry

Test report







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## 2 INTRODUCTION

This test report was made for the verification of SyreN slurry land application system following the AgroTech Test Centre Quality Manual.

## 2.1 Verification protocol reference

This test report was made to meet the requirements defined in the verification protocol for SyreN focussing on land application of animal slurry with reduced ammonia and odour emission.

## 2.2 Name and contact of vendor

SyreN is developed by BioCover A/S, Veerst Skovvej 6, Veerst, DK-6600 Vejen, www.biocover.dk. Contact person of BioCover is Morten Toft. Email: <u>mt@biocover.dk</u>. Phone: +45 2963 4936.

## 2.3 Name of center/verification responsible

The test was performed by DANETV Verification Centre AgroTech, Agro Food Park 15, DK-8200 Aarhus N, Denmark in collaboration with the Aarhus University, Faculty of Science and Technology, Blichers Allé 20, PO Box 50, 8830 Tjele, Denmark.

Aarhus University was responsible for test activities related to the effect of SyreN system on ammonia emission. AgroTech was responsible for test activities related to the effect of the SyreN system on odour emission. Test responsible: Martin Nørregaard Hansen, AgroTech, Agro Food Park 15, DK-8200 Aarhus N, Denmark. Phone: +45 8743 8429, e-mail: mno@agrotech.dk.

## 2.4 Expert group

The technical experts assigned to this test and responsible for review of test plan and test report included:

Internal expert: Torkild Birkmose, Knowledge Centre for Agriculture, Department of Plant Production, Agro Food Park 15, DK-8200 Aarhus N. Since August 2011 Torkild Birmose has been employed by AgroTech, Agro Food Park 15, DK-8200 Aarhus N, phone: +45 3092 1707, e-mail: <u>tsb@agrotech.dk</u>.

External expert for review of results related to the effect of the SyreN system on odour emission: Tavs Nyord, Aarhus University, Faculty of Science and Technology, Blichers Allé 20, PO Box 50, 8830 Tjele, Denmark. Phone +4587157637. E-mail: <u>tavs.nyord@agrsci.dk.</u> Review of the SyreN system's effect on ammonia emission has been done by the National Technical Advisory Committee under the VERA scheme (verification of environmental technologies for agricultural production).





## 3 TEST DESIGN

The SyreN slurry application system was tested in full-scale on fields under normal operational conditions. The test was designed so that it was possible to determine odour intensity following the use of the SyreN system compared to a reference slurry application system.

## 3.1 Test site

### 3.1.1 Characterization of the test site

The SyreN slurry application system was tested at the fields of Research Centre Foulum. The SyreN system was tested using cattle slurry applied to a grass field. The test involved measurements from four slurry application scenarios, see Table 1. In addition the ammonia effect of the SyreN system was tested using pig slurry applied to winter wheat.

Table 1.	Four slurrv	application	scenarios	was tested.
10010 11	i oui oiuiry	application	0001101100	mao tootoa.

Scenario	Description
no.	
1	Application of un-treated cattle slurry using trailing hoses (reference scenario).
2	Open slot injection of un-treated cattle slurry.
3	Addition of sulphuric acid to cattle slurry and land application using trailing hoses.
4	Addition of iron (III) sulphate to cattle slurry and land application using trailing hoses.

### 3.1.2 Addresses

The test was undertaken at Aarhus University, Faculty of Agricultural Sciences, Research Centre Foulum, Blichers Allé 20, 8830 Tjele, Denmark.

### 3.1.3 Description of SyreN slurry application system

The basic idea of the SyreN system is to add sulphuric acid and/or iron sulphate (Fe<sup>3+</sup>) to animal slurry during land application of slurry.







Figure 1. The SyreN-system includes three tanks installed on the front of the tractor. 1: Tank for iron sulphate. 2: Here the tank for sulphuric acid shall be placed. 3: Tank for water.

Table 2 contains technical data on the SyreN system.

Table 2. Technical data of SyreN.

System part	Purpose
Front tanks	Storage system for sulphuric acid and Fe <sup>3+</sup> during land application
Terminal software	Regulation of dosage of sulphuric acid and Fe <sup>3+</sup> to slurry tanker
Pumps	Addition of sulphuric acid and Fe <sup>3+</sup> to slurry tanker
Slurry tanker	Transport and land application of acidified animal slurry

## 3.2 Tests

#### 3.2.1 Test methods

#### Ammonia emission

The emission of ammonia from the animal slurry applied to agricultural land by the SyreN technology was quantified by a test design based on the micrometeorological mass balance technique. The technique is described in detail by Denmead (1983), Ry-den et al. (1984), Leuning *et al.* (1985); Sherlock *et al.* (1989), Huijsmans et al. (2001), but will be described briefly below.

The micrometeorological mass balance technique involves a measuring mast situated centrally in each experimental plot, and a background measuring mast located outside the plots for measurement of the background NH<sub>3</sub> levels. The theoretical profile shape ( $Z_{inst}$ ) method, described by Wilson *et al.*,1983; Sherlock et al., 1989; Gordon et al., 1988 was used for the measurements which involved that both the both the centrally located mast and the background mast were fitted with two measuring units mounted at a fixed distance above soil surface. The fixed distance (Z) is depending on height and roughness of crop and the size of the experimental plot. The actual Z value was calculated as suggested by Wilson et al. (1983) and Sherlock et al. (1983).





#### **Odour nuisance**

The effect of the technology on the odour nuisance from land applied animal slurry was quantified by olfactometric analyses of air samples sampled by a static flux chamber technique. This odour measuring system is described in detail by Hansen et al. (2006) but will be briefly described below.

The odour effect of the technology investigated was estimated by measuring the odour concentration of air samples sampled above untreated and SyreN treated cattle slurry following land application to grass land. The odour concentration was measured by olfactometric analyses. To avoid heterogeneity of wind disturbance during sampling and to pre-concentrate odour samples the slurry treated surface were covered by a static flux chamber system before air sampling.

#### Composition and dosage of animal slurry

Samples of the animal slurry used in the experiments were taken while the slurry was land applied. The slurry application rate was calculated by weighing the amount of animal slurry applied to the experimental plots and by measuring the area of the experimental plots onto which the slurry was applied. The amount of slurry applied was measured by weighing the manure application device before and after manure application on each plot. The area of land applied manure was calculated by measuring the area of land applied animal slurry.

#### Meteorological data

The ammonia emission from land applied slurry is highly depending on the meteorological conditions during and following land application. Hourly data for wind speed, temperature, incident solar radiation, atmospheric humidity and precipitation were therefore continually measured during the measurement period by a meteorological station situated less than 1 km from the experiment site.

The experimental plots were situated at least 100 m apart, and more than 300 m away from ammonia emitting sources like animal houses and manure storage facilities. As a free wind-profile is required the experimental plots were situated as far away from wind breaks like houses and trees as possible, and no closer than 10 times the height of the wind break.

#### 3.2.2 Test staff

The test staffs involved in the odour test of SyreN were:

Martin Nørregaard Hansen, AgroTech, Agro Food Park 15, DK-8200 Aarhus N, Denmark. Phone: +45 8743 8429, e-mail: <u>mno@agrotech.dk</u>.

Merete Mahn, AgroTech, Agro Food Park 15, DK-8200 Arhus N, Denmark. Phone: +45 8743 8632, e-mail: mma@agrotech.dk.

The ammonia reduction effect and the odour effects of the SyreN system were tested simultaneously. The ammonia measurements were performed by the Faculty of Science and Technology at Aarhus University. The following was responsible for planning, measuring, and quantification of ammonia emission: Tavs Nyord, Aarhus University, Faculty of Science and Technology, Blichers Allé 20, PO Box 50, 8830 Tjele, Denmark. Phone +45 87157637. E-mail: tavs.nyord@agrsci.dk





### 3.2.3 Test schedule

The test was scheduled as described in table 3 below.

Task	Deadline
Contract with Bio Cover signed	01.05.2010
Test plan prepared and practical planning	01.05.2010
Sampling day 1	04.05.2010
Sampling day 2	18.05.2010
Sampling day 3	02.06.2010
Sampling day 4	15.06.2010
Analyses ready from laboratory	15.10.2010
Test report draft	01.02.2011
Test report final version	23.12.2011

### 3.2.4 Test equipment

#### Ammonia sampling systems

Passive flux samplers were used as ammonia traps (See picture in Figure 2). By this system the ammonia holding air passively passes through the internal of the passive flux samplers. The internal of the passive flux samplers was coated before the sampler were attached to the measuring masts by an acid solution (Leuning *et al.*, 1985). The passive flux samplers consists of an outer cylinder fitted with mounting pivots and fins to keep the device aligned with the wind and a detachable venturi shield which holds a thin orifice plate (see Figure 2). When passive flux samplers are used for trapping of ammonia, the determination of a wind profile is not required.



Figure 2. Picture of a passive flux sampler fitted with mounting pivots and fins to keep the device aligned with the wind.

The flux of ammonia was measured continuously 96 hours following manure application.

#### Odour sampling system

A flux chamber system was used for measurements of the odour effect of the technology investigated. The flux chamber system consisted of three equal static flux chambers (Figure 3). Each flux chamber covered 2.6 m<sup>2</sup> of slurry-applied soil surface and was equipped with an oscillating internal ventilator to allow for simulation of internal wind speed and for mixing of internal air.







Figure 3. The static flux chambers. The left picture shows the three identical passive flux chambers used for sampling of air above the land applied slurry. The right picture shows the internal of the chambers and the internal ventilators.

The external surface of the chambers was covered by aluminium foil to restrict unequal solar heating of the chambers during sampling. The manure-treated surface was covered by the static flux chamber immediately after manure application.

### 3.2.5 Type and number of samples

Description of number of treatments and number of samples.

#### Experimental operation for ammonia measurements

The animal slurry was each experimental test day uniformly applied to two experimental plots (36m x 36m) situated more than 100 m apart. One of the plots was applied ca. 30 tonnes of untreated animal slurry per ha, while the other plot was applied ca. 30 tonnes of acidified slurry per ha. The plots were created by applying the slurry to premarked experimental plots. The application was done by three parallel passes of the 12 m wide land applicator system. Slurry applied outside the experimental plots were incorporated into the soil as soon as possible to stop emission of ammonia.

As soon as possible after the slurry was applied to the first half of the plot – which usually was within two minutes after the start of the application, the central mast attached measuring units was placed in the centre of the experimental plot. After placement of the central mast the ammonia measurements were initiated at both background and central masts, halfway through the manure application.

The ammonia emission from the experimental plots were continuously measured for 144 hours (6 days) after manure application. During the first twelve hours – when the rate of  $NH_3$  volatilization was highest – the ammonia traps were replaced three times to avoid oversaturation of the ammonia sampling system. Further replacement took place every morning for the following 3 days and after six days. The amount of ammonia volatilized during each interval was calculated by the amount of ammonia trapped by the ammonia traps

#### Experimental operation for odour measurements

The animal slurry was each experimental test day uniformly applied to experimental plots (6m x 36m). One of the plots was applied ca. 30 tonnes of untreated animal slurry per ha, one was applied ca. 30 tonnes of acidified slurry per ha, and one was applied ca. 30 tonnes of animal slurry added 0,5 l of Fe<sup>3+</sup> per ton of slurry. The plots were created by applying the slurry to pre-marked experimental plots.





As soon as possible after the slurry application three identical static flux chambers were placed on the each experimental plot applied untreated or treated animal slurry. Eight minutes after the placement of the chambers 30 L of internal air was sucked from the internal of the chambers into 30-L nalophan bags by vacuum boxes. The odour concentration in the nalophan bags was determined by dynamic dilution olfactometric analyses within 24 h (CEN, 2003). All air samples and odour analyses were replicated in triplicate.

### 3.2.6 Operation conditions

The ammonia reduction effect of the SyreN system is depending on the quantity of sulphuric acid added to the animal slurry. The amount of acid added to the animal and its effect on slurry pH was measured each experimental day. Used amounts can be seen in table 4.

Table 4. Day of expe	riment, type of ani	imal slurry and am	nount of sulphuric acid	used by the SyreN system
in the ammonia study	Ι.			

Day of experi-	Type of slurry	Type of crop	Supplied acid	pH of slurry	
ment			I t <sup>-1</sup> slurry	Untreated	Acidified
04.05.2010	Pig slurry	Winter wheat	2.0	7.2	6.1
18.05.2010	Pig slurry	Winter wheat	2.2	7.9	6.7
02.06.2010	Cattle slurry	Grass	2.3	7.4	6.1
15.06.2010	Cattle slurry	Grass	2.9	7.8	6.5

The odour effect of the SyreN application system is depending on the amount of sulphuric acid and  $Fe^{3+}$  added to the slurry before land application. The amount of acid and  $Fe^{3+}$  added to the animal and its effect on slurry pH was measured each experimental day. Used amounts can be seen in table 5.

Table 5. Day of experiment, type of animal slurry and amounts of sulphuric acid and iron sulfate (Fe	<sup>3+</sup> )
added to the cattle slurry by the SyreN system in the odour study.	

Day of experi- ment	Type of slur- ry	Type of crop	Supplied acid or Fe <sup>3+</sup> I t <sup>-1</sup> slurry		pH of slurry	
			Acid	Fe <sup>3+</sup>	Untreated	Treated
02.06.2010	Cattle slurry	Grass	2.3	0	7.4	6.4
15.06.2010	Cattle slurry	Grass	2.9	0	7.8	6.4
15.06.2010	Cattle slurry	Grass	0	0.5	7.8	7.8

The measured meteorological data during the ammonia emission study can be seen in table 6.

Table 6. Mean temperature, wind speed and precipitation during the measurement of ammonia emission.

Period of exper-	Temperature	nperature Precipitation		Wind speed	
iment Celsius		mm of rain	%	M sek <sup>-1</sup>	
4-10 of May	7.8	0	76	3.9	
18-24 of May	11.2	14	79	5.0	
2-8 of June	16.2	18	82	3.8	
15-21 of June	15.2	29	84	4.5	





#### 3.2.7 **Operation measurements**

No other parameters than ammonia and odour were measured as part of the test.

#### 3.2.8 Product maintenance

The need for product maintenance was not evaluated as part of this test.

#### 3.2.9 Health, safety and wastes

Issues related to health, safety and wastes were not evaluated in this test.

#### **REFERENCE ANALYSIS** 4

#### 4.1 Analytical laboratory

Air and slurry samples were analysed by Eurofins Steins laboratory, Smedeskovvej 38 8464 Galten. Website: www.eurofins.dk. E-mail: agro@eurofins.dk.

#### 4.2 Analytical parameters

In table 7 the analytical parameters included in the test are presented.

Parameter Method used Ammonia The micrometeorological mass balance method Odour Dynamic olfactometric analyses

Table 7. Analytical parameters included in the test.

#### 4.3 Analytical methods

In table 8 the analytical methods of the analytical parameters are presented.

Table 8. Analytical parameters and corresponding analytical methods.

Parameter	Unit	Measured by	Analytical method
Ammonia	Mg NH₃ ha⁻¹	The micrometeorlogical	The integrated horizontal flux
		mass balance method	method
Odour	Odour units <sub>E</sub>	Static flux chamber	Dynamic olfactometric analyses
	m⁻³ air	method	

#### 4.4 Analytical performance requirements

A maximum allowed uncertainties of data was not included in any of the used analytic methods.





## 4.5 Preservation and storage of samples

The ammonia sampling units were transported to the analytic laboratory and analysed for absorbed ammonia within two hours after used in the study. The odour samples were stored in closed transporting cardboard boxes during transport and until they were analyses in the odour laboratory. The transport and storage time was less than 24 hours after sampling.

## 5 DATA MANAGEMENT

Data management including filing and archiving procedures are described in the Agro-Tech Test Centre Quality Manual.

## 5.1 Data storage, transfer and control

Some data are collected and written down during the test at the test site. Appendix 6 includes data recording sheets that were used for registration of data at the test site.

Results from external laboratories were sent to AgroTech test staff electronically by email or in paper version by mail.

Data type	Data media	Data recorder	Data record timing	Data storage
Test plan and test	Protected pdf-files.	Test responsible	When approved	Files and archives
report				at AgroTech
Data manually recorded at test site	Data recording forms	Test staff at test site	During collection	Files and archives at AgroTech
Calculations	Excel files	Test responsible, AgroTech	During calculation	Files and archives at AgroTech
Analytical reports	Paper / pdf-files	Test responsible, AgroTech	When received	Files and archives at AgroTech

Table 9. Data compilation and storage summary.

## 6 QUALITY ASSURANCE

The test followed the AgroTech Test Centre Quality Manual, which is ISO 9001 compliant, but not certified.

## 6.1 Test plan review

The test plan was subject to internal review by the verification responsible from Agro-Tech Test Centre.

External review of the test plan was done by the technical expert assigned to this verification task.





## 6.2 *Performance control – reference analysis*

Due the setup of the study a performance control was not included.

## 6.3 Test system control

The stability of the test equipment was controlled continuously by supervision and recording of data. Procedures for ensuring that test facilities and equipment are calibrated and fit for the purposes are described in the Quality Manual for the Laboratories of AgroTech. These procedures are subject to internal audits from the AgroTech Management.

## 6.4 Data integrity check procedures

All transfers of data from printed media to digital form and between digital media have been checked by spot check undertaken by test responsible. If errors are found in a spot check, all data transfers from the specific data collection are checked.

## 6.5 Test system audits

Internal audits from AgroTech are done following the procedure described in the Agro-Tech Test Centre Quality Manual.

## 6.6 Test report review

The test report was subject to internal review by the verification responsible from Agro-Tech Test Centre.

External review of the test report was done by the technical expert assigned to this verification task as part of the review of the verification report. The verification report includes the full test report as an appendix.

## 7 TEST REPORT

The test report follows the template of the AgroTech Test Centre Quality Manual and will be included as an appendix in the verification report.

## 7.1 Test site report

No specific test site report has been made since it is not judged relevant to make as part of this test. At the test site data were collected and registered on data reporting forms found in Appendix 6 of the test plan.

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## 7.2 Test data report

No specific test data report was made since it was not judged relevant to make this as part of this test. All data recorded during the test including results from external analytical laboratories have been gathered and archived according to the AgroTech Test Centre Quality Manual.

## 7.3 Amendment report

In this test report there is a section (section 8.4) on amendments to and deviations from the test plan. This section compiles all changes of the test plan that occurred <u>before</u> testing with justification of deviations and evaluation of any consequences for the test data quality.

## 7.4 Deviations report

In this test report there is a section (section 8.4) on amendments to and deviations from the test plan. This section compiles all changes of the test plan that occurred <u>during</u> testing with justification of deviations and evaluation of any consequences for the test data quality.

## 8 TEST RESULTS

## 8.1 Test performance summary

The test summaries the ammonia and odour emission effects following land application of animal slurry by the SyreN system. The SyreN system is a land application system for animal slurry which is able to acidify animal slurry to a preset pH level during the land application process.

The ammonia emission effect of the SyreN system was tested in four comparative studies of ammonia emission following trailing hose application of animal slurry (reference), and trailing hose application of animal slurry added between 1.9 and 2.9 I of sulphuric acid (96 %) per 1000 I of applied slurry (SyreN). The ammonia emission from land applied animal slurry was on average found to be reduced by 42 per cent when the pH of the slurry was reduced by addition of between 1.9 and 2.9 I of sulphuric acid per 1000 I of animal slurry by the SyreN application system.

The odour effect of the SyreN system was tested in two comparative studies of the odour concentration in air sampled above trailing hose applied cattle slurry (reference), and trailing hose applied cattle slurry added between 2.3 and 2.9 I of sulphuric acid (96%) per 1000 I of applied slurry (SyreN), and one comparative study of the odour effect of addition of 0.5I of Fe<sup>3+</sup> sulfate (42%) per 1000 I of cattle slurry. It was found that the odour concentration right after land application was unaffected by the addition of sulphuric acids, while the odour concentration was lower in air sampled above land applied cattle slurry. The long term odour effect of addition of sulphuric acids and Fe<sup>3+</sup> to animal slurry, and the odour effect of both addition of sulphuric acid and Fe<sup>3+</sup> to animal slurry were not studied.





### 8.2 Test measurement summary

The emission of ammonia was measured both for pig slurry land applied to winter wheat and for cattle slurry land applied to grass land. The emission from animal slurry applied by the SyreN system was compared to the emission of untreated slurry applied by trailing hoses and by shallow injection.

Trailing hose application of slurry was found to give the highest emission of ammonia, while shallow injection of animal slurry was found to give the lowest emission (Table 10). The ammonia emission from trailing hose applied animal slurry added between 1.9 and 2.9 I of sulphuric acid by the SyreN system was found to be 42 per cent lower on average than the ammonia emission from trailing hose applied untreated animal slurry.

Table 10. Average ammonia (NH<sub>3</sub>) emission from pig and cattle slurry following land application by trailing hoses, shallow injection and the SyreN system. The SyreN system was trailing hose application of animal slurry added between 1.9 and 2.9 l of sulphuric acid per 1000 l of slurry.

Turpo of olympic	Cron	NH <sub>3</sub> -N loss, % of applied NH <sub>4</sub> -N					
Type of slurry	Сгор	Trailing hoses	Shallow injected	SyreN			
Pig slurry	Winter wheat	23	11	15			
Cattle slurry	Grass land	41	18	21			
Average		30	13	18			

The odour nuisance of animal slurry following land application was measured by olfactometric analyses. The effect of the SyreN application system was only tested for application of cattle slurry to grass land. The odour effect of both addition of sulphuric acid (acid) and iron sulfate ( $Fe^{3+}$ ) was tested, but not together. The odour effect was compared to trailing hose application, and shallow injection of untreated cattle slurry. As the test of  $Fe^{3+}$  failed the first measuring day, this test was repeated twice the second measuring day (table 11).

Table 11. Average odour concentration measured in air sampled above cattle slurry land applied by trailing hoses, shallow injection and by the SyreN system with addition of sulphuric acid or iron sulphate ( $Fe^{3+}$ ). The SyreN system was trailing hose application of animal slurry added between 1.9 and 2.9 I of sulphuric acid per 1000 I of slurry or 0.5 I of  $Fe^{3+}$  per 1000 I of animal slurry. Values shown in parentheses are standard error of means.

		Odour concentration, Odour units (OU <sub>E</sub> ) m <sup>-3</sup> air					
Type of slurry	Crop	Trailing	Trailing Shallow injected SyreN ac		SyreN	SyreN	
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	·	hoses	-		Fe <sup>3+</sup> a	Fe <sup>3+</sup> b	
Cattle slurry	Grass land	903 (225)	320 (60)	853 (132)	-	-	
Cattle slurry	Grass land	627 (90)	310 (32)	737 (203)	363 (67)	320 (51)	

It was found that the odour concentration right after trailing hose application was unaffected or slightly increased by addition of sulphuric acids to the slurry by the SyreN system, while the odour concentration was lower in air sampled above land applied cattle slurry added  $Fe^{3+}$  than in air sampled above trailing hose applied untreated cattle slurry (Figure 4). Higher concentrations of odour were found above trailing hose applied slurry added sulphuric acid than in air sampled above shallow injected slurry. The long term odour effect of addition of sulphuric acids and  $Fe^{3+}$  to animal slurry, and the odour effect of both addition of sulphuric acid and  $Fe^{3+}$  to animal slurry were not studied in this test.







Figure 4. Odour concentration in air sampled above land applied cattle slurry. The cattle slurry was applied to grassland by trailing hoses, shallow injection, or by addition of sulphuric acid (SyreN-acid), or addition of iron sulfate (Fe<sup>3+</sup>) by use of the SyreN system (SyreN-Fe<sup>3+</sup>). The top diagram (a) shows the results obtained following land application the 2. of June, and the diagram b shows the results obtained the 15. of June. All data were sampled seven minutes after land application. Error bars show the standard error of means.

## 8.3 Test quality assurance

The ammonia emission effect of the SyreN system was tested in minimum three independent tests following land application of pig slurry and minimum three independent test following land application of cattle slurry. The odour effects of the SyreN land application system were tested in two independent test following land application of cattle slurry to grassland. All samplings and analyses in these tests were triplicated.

## 8.4 Amendments to and deviations from the test plan

It was part of the test plan to include measurements of the effect on odour emission from addition of both sulphuric acid and iron sulphate in order to evaluate the effect from this combination. Due to technical problems related to the SyreN system this report includes results from addition of iron sulphate without addition of sulphuric acid at the same time. Another deviation was that the addition of Fe<sup>3+</sup> to the slurry failed during the test on the first measuring day (02.06.2010). Consequently, there are no odour concentration results from this first measuring day. Instead this test was done twice on the second measuring day (15.06.2010).





Terms and definitions used in the test plan





Word	DANETV
Analytical labo- ratory	Independent analytical laboratory used to analyse test samples
Application	The use of a product specified with respect to matrix, target, effect and limitations
DANETV	Danish center for verification of environmental technologies
(DANETV) test center	Preliminary name for the verification bodies in DANETV with a verification and a test sub-body
Effect	The way the target is affected
(Environmental) product	Ready to market or prototype stage product, process, system or service based upon an environmental technology
Environmental technology	The practical application of knowledge in the environmental area
Evaluation	Evaluation of test data for a technology product for performance and data quality
Experts	Independent persons qualified on a technology in verification
Matrix	The type of material that the product is intended for
Method	Generic document that provides rules, guidelines or characteristics for tests or analysis
Performance claim	The effects foreseen by the vendor on the target (s) in the matrix of in- tended use
Performance parameters	Parameters that can be documented quantitatively in tests and that pro- vide the relevant information on the performance of an environmental technology product
Procedure	Detailed description of the use of a standard or a method within one body
Producer	The party producing the product
Slurry	Faeces and urine produced by housed livestock, usually mixed with some bedding material and some water during management to give a liquid manure with a dry matter content in the range from about $1 - 10\%$ . A slurry is a mixture of liquid and solid materials, where typically the solid materials are not dissolved in the liquid phase, and will precipitate out of the slurry under a prolonged period of storage.
Slurry additive	Manufactured or naturally occurring products or substances that are add- ed to manures to modify their biological, chemical or physical properties. Many additives are commercially available but most have not been sub-





Word	DANETV
	jected to independent testing so their effectiveness has not been as- sessed.
Standard	Generic document established by consensus and approved by a recog- nized standardization body that provides rules, guidelines or characteris- tics for tests or analysis
Target	The property that is affected by the product
Test center, test sub-body	Sub-body of the test centre that plans and performs test
Test center, verification sub- body	Sub-body of the test center that plans and performs the verification
Test/testing	Determination of the performance of a product for parameters defined for the application
Vendor	The party delivering the product to the customer
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance





References





- [1] AgroTech (2009): AgroTech Test Centre Quality Manual. Not published.
- [2] VERA (2009): Test Protocol for Measurement of Gaseus Emissions from Land Applied Manure. Published by the Secretariat for Verification of Environmental Technologies for Agricultural Production (VERA). Available from www.veracert.dk. 28 pp.
- [3] CEN (2003): Air Quality Determination of Odour Concentration by Dynamic Ofactometry. EN 13725:2003. Published by European Committee for Standardization, Brussels, Belgium.
- [4] Nyord, T., Adamsen, A.P., Liu, D., Petersen, S.O. og Hansen, M.N. (udateret): Emission af ammoniak, lugt og lattergas ved udbringning af gylle med slæbeslanger, nedfældning og forsuring med SyreN- og Infarmsystemer. Notat om SyreN-projekt. Not published. 18 pp.





**References methods** 





The reference methods are presented in section 4 Reference methods.





In-house test methods





The in-house test methods used in the test are described in the section 3.2.5.

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In-house analytical methods





All air samples for the odour test were analysed by certified external laboratories.

The analyses of ammonia concentration were performed by the following in-house analytic methods (in Danish).

#### Metodebeskrivelse til koncentrationsbestemmelse af NH<sub>4</sub>-N på ELISA mikrotiterlæser

#### Apparatur:

Elisa, EL800 Universal Microplate Reader, Bio-Tek Instruments, Inc. Mikrotiterplade, Buch og Holm Art nr. 1957116 med låg, Buch og Holm Art nr. 1957122. 8 kanalspipette: Thermo Finnpipette Digital 5-50µl, med spidser Finntip 250. 8 kanalspipette: Thermo Finnpipette Focus Plus 30-300, med spidser Finntip 300. Reagenskar Rystebord, gerhardt

Til fortynding:

Reagensglas. Div. Pipetter Wortex mikser

#### Reagenser:

Der skal fremstilles to farvereagenser:

Farvereagens 1: Opløs 65g ± 1g natriumsalicylat og 65g ± 1g trinatriumcitrat ( $C_6H_5O_7Na_3H_2O$ ) i en 500ml kolbe i ca. 400ml seradestvand. Dette omrøres til det er helt opløst.

Derefter tilsætte 0,485g  $\pm$  0,005g natriumprusside ((Fe(CN)<sub>5</sub>NO)Na<sub>2</sub>2H<sub>2</sub>O), dette opløses og kolben fyldes op med seradestvand.

Farvereagens 2: Opløs 16g ± 1g natriumhydroxid (NaOH) i en 500ml kolbe i ca. 400ml seradestvand. Dette omrøres til det er helt opløst. Opløsningen kan blive varm. Derefter tilsætte 1,00g ± 0,02g natriumdiklorisocyanurate (C<sub>3</sub>N<sub>3</sub>O<sub>3</sub>Cl<sub>2</sub>Na2H2O), dette opløses og kolben fyldes op med seradestvand.

Farvereagenserne skal opbevares i køleskab og har en holdbarhed på ca. 3 uger.





#### Standardrække:

Koncentrationen af N-NH<sub>4</sub><sup>+</sup> Bestemmes ved hjælp af spektrofotometri. For at kunne omregne fra den målte absorbans til den ønskede koncentration kalibreres spektrofotometeret.

Der laves en standardrække udfra en stamopløsning af NH<sub>4</sub>Cl.

Det anvendte NH<sub>4</sub>Cl skal inden brug tørres ved 105°C i 2 timer, hvorefter det sættes i en eksikator for at opnå stuetemperatur.

Stamopløsning 1: 1000 mgN/L.

Der afvejes 3.819g  $\pm$  0.004g ad 1000 ml dem. vand.

Beregning:

1 mol NH₄Cl	~	1 mol NH3-N
xg		1000 mg/l
53,49g/mol		14,01g/mol
xg ÷ 53,49g/mol	=	1000 mg/l ÷ 14,01g/mol
х	=	(53,49g/mol · 1000 mg/l) ÷ 14,01g/l
х	=	3817,99mg/l
х	=	3,818g/l

Stamopløsningen opbevares i køleskab.

Ud fra stamopløsningen laves en standardrække i de koncentrationer man ønsker. (se bilag bagerst)

#### Forberedelse:

Fortynding:

Det kan være nødvendigt at fortynde prøverne inden analyse. Hvis koncentrationen af NH<sub>4</sub> i prøven er for stor vil absorbansen ligge udenfor det lineære måleområde.

Hvis prøven efter tilsætning af farvereagens er mørk grøn eller blålig skal prøven fortyndes.

Prøven fortyndes med seradest-vand og 2 ml af fortyndingen udtages til analyse. Prøver fra ammoniakfordampningsforsøg, vil ofte skulle fortyndes 20-50 gange.





Mikrotiterplader:

Hver brønd tilsættes 160µl prøve / standard, 80µl farvereagens 1 og 40µl farvereagens 2, der skal altid foretages 3 dobbelt bestemmelse af de enkelte prøver, derudover er der en fordel at medtage et antal standarder og blindprøver på hver plade.

En plade kunne f.eks. se du som følger:

Plate:	Test 021106
--------	-------------

	1	2	3	4	5	6	7	8	9	10	11	12
		0	0	0	0	0			0	, ,	0	6
Α	Blank	Sam 1	Sam 3	Sam 5	Sam 7	Sam 9	Sam11	Sam 13	Sam 15	Sam 17	Sam 19	Biank
В	Blank	Sam 1	Sam 3	Sam 5	Sam 7	Sam 9	Sam11	Sam 13	Sam 15	Sam 17	Sam 19	Blank
С	Blank	Sam 1	Sam 3	Sam 5	Sam 7	Sam 9	Sam 11	Sam 13	Sam 15	Sam 17	Sam 19	Blank
D	Blank	Std 1	Std 1	Std 1	Std 3	Std 3	Std 3	Blank	Std 5	Std 5	Std 5	Blank
Ε	Blank	Std 2	Std 2	Std 2	Std 4	Std 4	Std 4	Blank	Std 6	Std 6	Std 6	Blank
F	Blank	Sam 2	Sam 4	Sam 6	Sam 8	Sam 10	Sam 12	Sam 14	Sam16	Sam 18	Sam 20	Blank
G	Blank	Sam 2	Sam 4	Sam 6	Sam 8	Sam 10	Sam 12	Sam 14	Sam 16	Sam 18	Sam 20	Blank
н	Blank	Sam 2	Sam 4	Sam 6	Sam 8	Sam 10	Sam 12	Sam 14	Sam1 6	Sam 18	Sam 20	Blank

Mikrotiter plader skal stå min. 2 timer i køleskab efter tilsætning af farvereagens, derefter bestemmes absorbansen ved en bølgelængde på 690nm på Elisa Mikrotiter Readeren.

Analyse: Se Analysevejledning til bestemmelse af NH<sub>4</sub>-N på Elisa.





Test data report





#### Test data report for odour sampling (in Danish language) 02.06.2010 and 15.06.2010

Teknik	Lugt- kam- mer nr.	Pose ID	Udbring- nings- tidspunkt	Tidspunkt, pla- cering kammer (tid 0)	Tidspunkt, start af olfac. sampling (tid 8)	Længde af olfac. må- ling	Tidspunkt, slut af olfac. sam- pling	NH₃ konc. ppm (tid 20)	H2S konc. ppm (tid 15)	K type	Olfactometri results OU <sub>E</sub> m <sup>-3</sup>
Nedfældning	1	Nedf-k-a	11:08	11:09	11:17	00:01	11:18	6	bd	а	200
Nedfældning	2	Nedf-k-b	11:08	11:09	11:17	00:01	11:18	16	bd	а	390
Nedfældning	3	Nedf-k-c	11:08	11:09	11:17	00:01	11:18	10	bd	а	370
Slæbeslanger	1	Ref-k-a	11:56	11:57	12:05	00:01	12:06	12	bd	а	520
Slæbeslanger	2	Ref-k-b	11:56	11:57	12:05	00:01	12:06	32	bd	а	890
Slæbeslanger	3	Ref-k-c	11:56	11:57	12:05	00:01	12:06	42	bd	а	1300
SyreN	1	Syren-k-a	12:43	12:45	12:53	00:01	12:54	4	bd	а	650
SyreN	2	Syren-k-b	12:43	12:45	12:53	00:01	12:54	14	bd	а	1100
SyreN	3	Syren-k-c	12:43	12:45	12:53	00:01	12:54	12	bd	а	810
Syren FeS	1	Syren-FeS-k-a	15:35-15:39	15:41	15:49	00:01	15:50	0	bd	а	*
Syren FeS	2	Syren-FeS-k-b	15:35-15:39	15:41	15:49	00:01	15:50	0	bd	а	*
Syren FeS	3	Syren-FeS-k-c	15:35-15:39	15:41	15:49	00:01	15:50	0,5	bd	а	*

Table A6-1. Data from odour analyses of air samples obtained the 2<sup>nd</sup> of June 2010.

\* Note: Unfortunately the addition of Fe<sup>3+</sup> to the slurry failed during the test on the first measuring day (02.06.2010). Consequently, there are no odour concentration results from this first measuring day. Instead this test was done twice on the second measuring day (15.06.2010).





#### Table A6-2. Data from odour analyses of air samples obtained the 15<sup>nd</sup> of June 2010.

Teknik	Lugt- kam	Pose ID	Ud- bringning	Tidspunkt placering	Tidspunkt, start af	Længde af olfac. må-	Tidspunkt, slut af olfac	Tidspunkt, start af	Tidspunkt, slut af ATD	NH <sub>3</sub> konc. ppm, (tid	H2S konc,	K type	Olfactometri results			
	mer nr.		hh:mm	kammer (tid 0)	olfac sam- pling (tid 7)	ling min	sampling	ATD sam- pling (tid 3)	sampling (tid 13)	10)	ppm, (tid 13)		OU <sub>E</sub> m <sup>-3</sup>	L <sub>E</sub> m <sup>-3</sup>	Usikker- hedsf.	Følsom som- hed
Nedfæld- ning	1	Nedf-k-a	11:45	11:46	11:53	00:01	11:54			10	bd	а	300	360	1,83	0,83
Nedfæld- ning	2	Nedf-k-b	11:45	11:46	11:53	00:01	11:54	11:49	11:59	11	bd	а	260	310	1,83	0,83
Nedfæld- ning	3	Nedf-k-c	11:45	11:46	11:53	00:01	11:54	11:52	12:02	12	bd	а	370	450	1,83	0,83
Slæbes- langer	1	Ref-k-a	13:11	13:12	13:19	00:01	13:20			21	bd	а	470	570	1,83	0,83
Slæbes- langer	2	Ref-k-b	13:11	13:12	13:19	00:01	13:20	13:13	13:23	42	bd	а	780	940	1,83	0,83
Slæbes- langer	3	Ref-k-c	13:11	13:12	13:19	00:01	13:20	13:14	13:24	40	bd	а	630	760	1,83	0,83
SyreN	1	Syren-k-a	13:48	13:49	13:56	00:02	13:58			1	bd	а	1100	1400	1,83	0,83
SyreN	2	Syren-k-b	13:48	13:49	13:56	00:02	13:58	13:51	14:01	4	bd	а	710	850	1,83	0,83
SyreN	3	Syren-k-c	13:48	13:49	13:56	00:02	13:58	13:52	14:02	6	bd	а	400	480	1,83	0,83
SyreN FeS a	1	Syren-FeS-k-a	14:28	14:29	14:36	00:01	14:37			12	bd	а	240	290	1,83	0,83
Syren FeS a	2	Syren-FeS-k-b	14:28	14:29	14:36	00:01	14:37	14:32	14:42	21	bd	а	470	570	1,83	0,83
Syren FeS a	3	Syren-FeS-k-c	14:28	14:29	14:36	00:01	14:37	14:33	14:43	23	bd	а	380	460	1,83	0,83
SyreN FeS b	1	Syren-FeS-k-d	15:06	15:07	15:14	00:01	15:15			17	bd	а	250	300	1,83	0,83
Syren FeS b	2	Syren-FeS-k-e	15:06	15:07	15:14	00:01	15:15	15:10	15:20	24	bd	а	290	350	1,83	0,83
Syren FeS b	3	Syren-FeS-k-f	15:06	15:07	15:14	00:01	15:15	15:11	15:21	21	bd	а	420	510	1,83	0,83





Amendment and deviation reports for test





#### Deviations from the test plan

It was part of the test plan to include measurements on the effect on odour emission from addition of both sulphuric acid and iron sulphate in order to evaluate the effect from this combination. Due to technical problems related to the SyreN system no sulphuric acid was added during the test. Consequently this report includes results from addition of iron sulphate without addition of sulphuric acid at the same time.

Unfortunately the addition of  $Fe^{3+}$  to the slurry failed during the test on the first measuring day (02.06.2010) due to technical problems related to the SyreN system. Consequently, there are no odour concentration results from this first measuring day. Instead this test was done twice on the second measuring day (15.06.2010).

#### Amendments to the test plan

The SyreN system's effect on odour emission was evaluated by olfactometric analyses. However, during the test the olfactometric odour analyses were supplemented by continuously measurements of concentrations of key odour components in air above the slurry surface. These measurements were done by test staff of Aarhus University and the results are not included in this test report. However, the additional measurements are shortly mentioned in the following.

The investigations of key odour components showed a dynamic development in concentrations of specific odour components in air sampled above the slurry treated area.

This indicates that the odour concentration measured by the olfactometric analyses is depending on when the odour samplings were taken – the lag time between slurry application and odour sampling. The time lag chosen between slurry application and odour sampling may therefore influence the odour effect of the tested technology.

The odour test may therefore be improved by supplementation of test of the development of specific odour components and by repeated odour samplings following slurry application.