Thesis report

Reduction of ammonia emission through the combined application of liquid or slurry manure and water with The Green Duo

Author:
C.P Nienhuis

Supervisor:
E.A. Lantinga

Dairy farm:
H.O. & K. Wolters
Winsum (Gr.)

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Student:	Ciska Nienhuis
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Examiner:	Prof. Dr. P.A. Tittonell
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Preface

In the summer of 2011 I asked Egbert Lantinga if he had an interesting MSc thesis topic for me. It was a coincidence that dairy farmer Klaas Wolters had contacted Egbert about his plans to re-develop a liquid manure application technique that combines manure and water. I already had gained interest in the topic because a year before I followed a course with an excursion to The Northern Frisian Woodlands. This is an area where a group of famers have permission to surface spread the manure if they follow certain guidelines. It was even a bigger coincidence that the farm of the family Wolters is situated only 10 kilometers from my home.

I am very grateful to my supervisor Egbert Lantinga, his enthusiasm was contagious and he stimulated me to think beyond borders. He even came to the north of the Netherlands with his wife to help during two experiments, it was a privilege to have such an involved supervisor.
Secondly, I would like to thank Klaas Wolters for his patience during the experiments and his enthusiasm and commitment to lift this research to a higher level. Thereby, also many thanks to his parents Hommo and Tineke and wife Martine Wolters who supported me practically during the research.
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I am deeply grateful for the support of my family and friends (Jacquelien and Anja Nienhuis and Johan Blauwiekel in particular) during the whole process of my MSc thesis!

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Ciska Nienhuis

Summary

Ammonia (NH_3) volatilization is an environmental issue and the agricultural sector contributes most to ammonia emission in the environment. There are several ways to decrease ammonia emissions in agriculture, for example by feeding the cattle less protein and more structure, by preventing or delaying urine and faeces to come together so ammonia will not be formed, by manure additives that lower the potential ammonia emission and by adjusted manure application techniques. A lower ammonia emission can be achieved with manure application strategies that decrease the surface area of the applied manure and by applying water at the same time or right after manure application.

In the early nineties the Dutch government decided to implement the law “Besluit Gebruik Meststoffen” (manure use regulations) to decrease ammonia emission in agriculture. This law obligated farmers to apply the manure in bands on or into the soil and this technique was chosen because it has proven to be effective and easy to control.

Manure application has consequences for the ecological environment. Some researches indicated that broadcast manure application will have less negative impacts on soil fauna, meadow bird population, sward and soil structure and N_2O emissions. There are also indications that mycotoxins and antibiotic resistant genes potentially decrease when manure is broadcast spread.

The combined application of manure and water above ground has advantages that lower the ammonia emission. It dilutes the ammonium in the manure and this will enhance infiltration into the soil, it stimulates ammonia to adsorb onto soil colloids and it lowers the soil surface temperature. In addition it reduces the smell of volatile fatty acids. Farmer Klaas Wolters re-developed the Duospray machine of Jan Treur, this technique applies manure and water vertically at the same time, and is called The Green Duo.

The Green Duo contains standardly 10 m^2 manure and 4 m^2 water and was compared with broadcast manure spreading and shallow injection, and the experiments were repeated three times. Two additional experiments were done with The Green Duo with a manure : water ratio of about 1:1 and one experiment was done with The Green Duo with a manure : water ratio of about 1: 2. Manure composition and weather circumstances differed in particular among the experiments.

Measurements were conducted on field scale using two methods: diffusion samplers installed 20 cm above the surface for a period of 24-72 hours and by using a closed flux chamber connected to a photoacoustic gas monitor called INNOVA. Each experimental plot consisted of five measuring sites in the middle of the longitudinal plot, evenly distributed downwind along a fetch measuring 90-160 meter. Ammonium was collected with the diffusion samplers, and an equation was used to calculate the average ammonia concentration. Because ammonia emission is a diffusion process, the equilibrium concentration of the ammonia just above the surface in a closed flux chamber will be reached quickly. This equilibrium level and the initial slope of the diffusion process were used as a second indicator to compare emissions.

Emissions and differences between treatments were low and there was a big spread in the results. This last aspect could be related with the finding that within a distance of a few decimeters the measured ammonia concentration varied up to factor 4. The results of all experiments done with the diffusion samplers showed that The Green Duo in standard form compared to broadcast reduced NH_3 emission with on average ¼. The experiments where The Green Duo applied more water showed that with a few millimeters of water the ammonia emission can be further reduced substantially. The large variation between the experiments can partially be explained by different manure compositions and weather circumstances.

Besides comparing application techniques, additional experiments were done to measure the NH_3 emission pattern in time and the pattern of NH_3 concentration at increasing distances behind the manured plot. The ammonia flux and amount of ammonium captured were measured in time intervals of approximately one hour for slurry manure applied with the standard Green Duo for this purpose. The obtained time patterns demonstrated that NH_3 emission becomes insignificant after two to six hours. The absolute emission factor (amount of total ammoniacal nitrogen (TAN) emitted in relation to the amount of TAN applied) appeared to be not higher than 1-2 %. However, static flux chambers exclude meteorological conditions like turbulent wind, and from published validation checks it is known that with the INNOVA a time delay occurs when increasing NH_3 concentrations are measured. If these

underestimations and variations based on literature resources are considered, the emission factor for surface-applied slurry manure as derived from the current study was still not higher than several tens of per cent. This is far below the officially used emission factor in The Netherlands.

The micrometeorological mass balance method (MBM), which is commonly used in The Netherlands to estimate NH_3 emission from field-applied manure, is based on the assumption that NH_3 is mainly transported by advection over the manured surface by the wind, rather than upwards through turbulent vertical diffusion. It was observed that at a height of 20 centimeters starting from the edge of the field, a quick increase in NH3 concentrations over the first meters occurred. Thereafter, the average NH3 concentration remained unchanged up till the downwind end of the field. Consequently, by applying the MBM to estimate ammonia fluxes within the field, smaller values will be obtained when the measurements are carried out inside the field instead of at the border, what is the current standard procedure. Measured NH_3 concentrations behind the manured plot decreased exponentially with increasing distance. After 20 meters the concentration was already declined with 50% on average. This also supports the finding that advection of the emitted ammonia is a relatively insignificant process.
It is recommended to carry out additional simple experiments with diffusion samplers at several heights above and distances along the whole fetch of a manured grassland field to further elucidate on the spatial distribution of the emitted NH_3. In this way, together with measured wind profiles, the MBM method can be evaluated in greater detail.

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Introduction

1.1 Ammonia

Ammonia (NH_3) volatilization or emission has a negative impact on the environment because it can lead to eutrophication and acidification. These processes enlarge the possibilities of damage to the ecosystem and loss of biodiversity. Acidification can decrease groundwater quality and damage materials, buildings and agricultural crops (Lükewille & Alewell, 2008). Most of the NH_3 emission finds its source in agriculture (Lükewille & Alewell, 2008; De Haan et al., 2009; http://www.emep.int as cited by Velthof et al., 2011). Ammonia together with sulphur dioxide and nitrogen oxides are the most acidifying compounds (De Haan et al., 1994).

Velthof et al. (2011) calculated with NEMA (National Emission Model Ammonia) a total NH_3 emission from agriculture in the Netherlands of 88.8 Gg NH_3 in 2009; 50% of the emission found its source in housing, 37% in manure application, 9% in mineral N fertilizer, 3% in storage of outside manure and 1% in grazing. Cattle farming contributed with 50% the most to the NH_3 emission in The Netherlands (Velthof et al., 2011).

Cows don't excrete NH_3, but this is formed when urine comes in contact with the urea in the manure, within a few hours the urea is converted (Van Dooren & Smits, 2007). NH_3 emission is the transfer of dissolved NH_3 from the liquid manure surface to the free air (Pinder et al., 2004). NH_3 concentration in the air close to the manure surface is in equilibrium with the NH_3 dissolved in the manure. (Génermont and Cellier, 1997). This process is explained with the following equations given by Van Dooren & Smits (2007) and Freney et al. (1983) (Equation 2):

Equation 1.

$$\text{Protein} \rightarrow \text{urea} \rightarrow NH_4^+{}_{(aq)}$$

Equation 2.

$$NH_4^+{}_{(aq)} \leftrightarrow NH_{3\,(aq)} + H^+ \rightarrow NH_{3\,(g)}$$

Only the NH_4-N in manure is directly susceptible to volatilize as NH_3 or other gasses. This NH_4-N is also called Total Ammonical Nitrogen (TAN). With field application of manure, NH_3 is transported vertically by diffusion and horizontally by advection, as air passes over the manure surface (Sommer & Hutchings, 2001).

1.2 Measures to reduce ammonia emissions in dairy farming

Carbon (C) and Nitrogen (N) cycles are strongly interrelated. When measures to reduce NH_3 emissions are taken, this might increase other losses like nitrous oxide (N_2O) or methane (CH_4). This is why it is important to look at the whole cycle. There are several measures to reduce NH_3 emissions, the aim of the research of Groenestein et al. (2011) was to explore the possibilities to reduce NH_3 emissions. The measures mentioned in this paragraph were all indicated as effective in this study.

1.2.1 Diet

Changing diet composition of livestock; more carbon instead of proteins, implicates less nitrogen in the nutrient cycle and a higher efficiency's to a certain extent (De Haan et al., 1994; Velthof et.al., 2002; Sonneveld & Bouma, 2005; Misselbrook et al., 2005c; Reijs 2007; Sonneveld, 2008) Nitrogen retention of the cow is in practice about 20% of nitrogen intake, while in theory 35-43% is possible (Bussink, 1996; Tamminga, 1996). When the manure has a higher C:N ratio and higher TAN content, more nitrogen is immediately available, while with a wider C:N ratio and lower TAN content the nitrogen release is slower and less predictable (Amon et al. 2005). Therefore this measure takes changes in the whole farming system, the nitrogen availability for the plants becomes more dependent on soil micro-organisms and the knowledge of the farmer (Reijs, 2007). Model simulations done by Reijs (2007) indicate that the reduced nitrogen availability will, on the long term, be compensated by higher mineralization. Mosquera et al. (2012a) reports that with these diets more methane emission occur.

1.2.2 Keep faeces and urine separated

Prevent or delay faeces and urine to come together, so NH_3 can't be formed is another measure to reduce NH_3 emission (Heiden, 1887; Kristensen, 1907; as cited by Bussink, 1996; Van Dooren & Smits, 2007). Not much literature is found about the primary separation of faeces and urine, De Haan et al. (2003) compared different stable systems, for example stables with a sloping floor. These types of stables reduce NH_3 emissions, however, this effect was abolished by the storage of solid manure and urine. De Haan et al. (1994) report about several researches were considerable NH_3 emission reductions were measured from stables with a sloping floor compared to flat floors. Substantial emission reductions were also found by Kant (1992) where sloping floors were compared with cubicle stable. More recent, several projects started were innovative stable types were developed that primary separate faeces and urine. Stables with sand floors, a semi-permeable concrete floor and a floor with slots were discussed in the Dutch project Cow Power, that works on innovative designs for an fundamental different dairy farms. (Groot Koerkamp et al., 2008) Stables with sand floors were included in the end report as a good option (Bos et al., 2009). The innovative stable design Het Kwatrijn developed a floor with little holes. With a robot faeces is being pushed aside and urine can sink into the holes to be collected in a cellar (Vista landschapsarchitectuur en stedenbouw, 2012).

1.2.3 Additives

Additives like urease inhibitors and acidification or microbes and clay minerals are options to reduce ammonia emission (Groot et al., 2006; Soares et al., 2012). Acidification of manure has proven to be effective in many studies (Blanck, 1918b; Heiden, 1887; Wagner et al., 1897 as cited by Bussink, 1996; Bussink & Bruins, 1992; Bussink et al., 1994; Mulder en Huijsmans, 1994; De Haan et al., 1994; Kaj et al., 2008) because it lowers the pH of the manure, whereas the equilibrium of NH_4 and NH_3 is more in favour of NH_4 . Also Groenestein et al. (2011) conclude that this measure is effective to reduce NH_3 emission and mention that this technique was not recognized as measure to reduce NH_3 emission because it is difficult to verify. This study does not take into account the effect of manure with a low pH on soil pH.

1.2.4 Water

Addition of water, rain, irrigation or the combined application of manure and water is an effective way to reduce NH_3 emissions (Blanck, 1918a as cited by Bussink, 1996; Klarenbeek & Bruins, 1990; Sonneveld & Bouma, 2005; Sonneveld et al., 2008). Paragraph 1.4 explains this measure in more detail.

1.2 Policy

From the mid-eighties of the previous century the Dutch government realized the harmfulness of NH_3. The above mentioned measures are effective to reduce NH_3 emission, if strictly followed. Effectiveness and enforcement seemed to be the major reasons why Dutch government decided to focuses on reducing NH_3 emission through manure application (De Haan et al., 2009).
There are a few agreements on international level to reduce gaseous emissions: in 1997 the Integrated Pollution Prevention and Control Directive (IPPC) to control the integrated environmental pollution on air, water and soil, in 2001 the National Emission Ceiling Directive (NEC) an European emission ceiling on 4 gaseous emission (including NH_3) and in 1999 the Gothenborg Protocol that sets limits to NH_3 emission (Van Dooren & Smits, 2007; Groenestein et al., 2011). According to Groenestein et al. (2011) the emission target of the NEC for 2010 were more or less achieved. According to Erisman & Monteney (1998) the target of the Dutch government to reduce NH_3 emission were not achieved at the time of their research. Actually, they estimated that taking all processes into account the NH_3 emission reduction until 1998 by manure application was not more than 15%. They argue that other measures concerning the whole nitrogen cycle should have been taken to meet the targets.

In the early nineties the law 'Besluit gebruik meststoffen' (manure use regulations) was implemented, this law prescribes a new method of applying manure, instead of surface application (broadcast), manure has to be applied on (trailing shoe) or into (shallow injection) the soil in bands with a maximum width of 5 cm and 15 cm apart from each other (overheid.nl). These techniques are called Low-Emission manure spreading Techniques (LET). These techniques reduce NH_3 emission efficiently, and nitrogen recovery is increased (Groot et al., 2006; Huijsmans et al., 2008). Nitrogen efficiency of broadcast spreading is around 30% and for LET around 50% (Huijsmans et al., 2008) and respectively 31% and 43% according to Groot et al. (2006). But: 'long-term effects are often not considered, conclusions concerning nitrogen use efficiency of slurry applications are often drawn from experiments where the measures were studied in isolation, whereas interactions between factors and implications for the performance of the whole farming system are often omitted' (Groot et al., 2006).

Research from Sonneveld & Bouma (2005) showed that with suitable weather the emission of manure applied above ground and raining in the manure are comparable with the emission with the use of trailing shoe. Feed without protein and the use of litter can limit the ammonia emission substantially. The research of Sonneveld et al. (2009) shows that the 'Alternative Track' consisting of a combination of measures like feed (protein low/structure rich diet), surface spreading, lowering the artificial fertilizer and taking notice of the weather conditions while applying manure can result in an equal ammonia emission per kg/ton milk compared to farms that use emission low techniques. But there is a large variety in emission per kiloton milk. Also Monteney et al. (2005) conclude that favourable weather circumstances and farm management can lead to low NH_3 emission. Nitrogen already in the soil could be used more efficient, good soil life with high fraction of organic matter can increase nitrogen efficiency (Erisman, 2000).

In 2005 56% of the farmers used injection to apply their manure, 14% used shallow injection, 23% trailing shoe and 7% used other systems (Luesing, 2006 and CBS). 20% of the Dutch farmers are not happy with the current Low-Emission Techniques (De Haan et al., 2009). Boer et al. (2000) found that 40% of the organic farmers in their survey dispute the current LET's. According to an article in the magazine Boerderij (Wellink, 2007, as cited by De Haan et al., 2009) a group of 400 farmers want to surface spread their manure at all expenses. These farmers believe that the current techniques ruin the soil and that it is harmful for the health of the cows, human and environment. Farmers that participate in the 'natural cycle farming' are also concerned about the conditions of the soil (Boer, 2000; Taken et al., 2008). According to De Haan et al. (2009) there hasn't been done much research on these effects.

1.3 Impact of manure application

1.3.1 Sward and soil structure damage

One of the concerns of farmers about LET is the apparent damage to sward and soil structure. Few literature is known about these side effects and the literature found are not recent.

Korevaar et al. (1991) state that when manure is applied with LET, sward damage can occur in soils with little carrying capacity, sensitive texture and small moisture delivering capacity. Especially with very wet or dry weather sward damage is more likely. On dry sandy soils, the risk of demolishing grass roots which can lead to drought damage is high. On heavy clay soils, low dewatered peat soils other types of manure application can be necessary. (Korevaar et al., 1991). Huijsmans et al. (2008) state that for these situations the use of the trailing shoe is a good option.

Nitrogen recovery and dry matter content is higher for shallow injection compared to broadcast (Sommer & Hutchings, 2001; Schils & Kok, 2003), but dry matter uptake at a given N uptake (nitrogen conversion efficiency) is higher for broadcast (Groot et al., 2006).

Schreurder et al. (1995) found especially more yield reduction of the first grass cut when (shallow) injection was applied. This effect was found regularly on all types of soils, on sandy soils this effect was the lowest. Shallow injection did not lead to yield reduction in the whole season. Especially on heavy clay and deeply dewatered peat soils cutting the soil had negative impacts. Hanegraaf (1995) report that slots are often long visible and that this in an indication for slower sward recovery. Schils & Kok (2003) and Uusi-Kämppä & Mattila (2010) also demonstrate that the difference between nitrogen recovery only occurred in later application times. Uusi-Kämppä & Mattila (2010) state that this might be due to the fertilizer applied in early spring.

Low Emission manure spreading Techniques were evaluated in 2009 by De Haan et al. (2009) and report that only the weight of the machines is indicated as reason why LET possibly damages the topsoil. These conclusions are based on the evaluation of Huijsmans et al. (2008). This research reports that, when dry weather follows after (shallow) injection this can lead to yield reduction on both sides of the slot. But they state that this yield should be compared the alternative for LET, namely broadcast manure spreading. These reductions don't appear when manure is applied with the trailing shoe. The weight of application techniques is a farmers concern, because compaction can have negative consequences for soil structure and the oxygen in the soil (De Haan et al., 2009).

1.3.2 Soil fauna and micro-organisms

Soil fauna and micro-organisms play a large role in a certain amount of soil ecosystem functions like the formation and maintenance of the soil structure, the nutrient cycle, soil fertility and disease and pest suppression. Agricultural activity can have negative effects on the presence of soil organisms (De Goede et al., 2003; De Haan et al., 2009). Especially earthworms have a lot of functions. degradation of organic material, availability of nutrients, redistributing of soil particles, improving soil structure by aggregates, pore volume, drainage, rooting, and increasing the grass harvest (Van Eekeren, 2003).

Boer et al. (2000) found that the farmers that dispute the use of LET believe these techniques have negative consequences for soil life. They experience that earthworms want to escape from the soil when manure is applied with LET. They believe that because manure has less contact with oxygen it has a more toxic composition.

The evaluation of De Haan et al. (2009) on the effect of manure application and earthworms points out that the effect is complex (Kruk, 1994; Oosterveld. 2006; De Goede et al., 2003). It is likely that this complex image is caused by the fact that the amount of earthworms and other organisms are fluctuating naturally and are influenced by weather.

Only few researches have been done on the effect of LET on soil life (Sonneveld et al., 2009; De Haan et al., 2009). Both LET and broadcast manure spreading have a negative effects on soil life (bacteria, funghi and mites), but LET has not a larger effect. Negative effects are often temporary (few weeks) (De Haan et al., 2009). The research of Sonneveld et al. (2009) hypothesized that broadcast potentially has positive effects on soil life because its exposure to ammonia is decreased and the soil is not disturbed. But the research showed that broadcast had more negative effects on soil life. The number of bacteria and fungi appeared to be two times lower when manure was surface spread, other found effects were not significant. However, no definite conclusions can be drawn because measurements were done on few farms, only one year after changing the management. Kruk (1994) did not found a significant difference between broadcast manure application and injection techniques. De Goede et al (2003) found that nematodes thrived under shallow injection, but only in the summer.

On the other hand, De Goede et al. (2003) found negative effects of shallow injection compared to broadcast on epigeic earthworms and explain this effect partly by physical damage. Anecic and edogeic have much lower risk of physical damage and exposure to manure, this is why these earthworms did not decrease with shallow injection and were even enhanced sometimes. Because less epigeic earthworms were found, this also reduced the calculated N mineralization for shallow injection. This research also conclude that soil respiration was positively affected by surface application.

This negative effect of shallow injection on earthworms is also found by and Oosterveld (2006) who compared LET with solid manure. In one year 54% and 60% less worms were found with shallow injection and trailing shoe, respectively. The population of the plots of solid manure remained the same. In another year the worm population increased for all manure types but 35% worms were found by shallow injection and 25% by trailing shoe, total weight of the earthworms did not differ in that particular year.

In a long-term (1982-1990, 2005) study Timmerman et al. (2005) concluded that 29% less earthworm were abundant in plots fertilized with slurry applied to the soil without cutting it, compared to unfertilized or farm yard manure. The variation between the years was high and winter coldness had big negative influence on earthworm population.

1.3.3 Meadow birds

Since the implementation of the 'Besluit Gebruik Meststoffen' law, the meadow bird population has decreased slowly despite measures to prevent this (Teunissen & Soldaat, 2006) This is possibly the effect of earlier grass growth, denser position of the grass and earlier application of manure. A direct relation between LET and this development cannot be proven (De Haan et al., 2009). Sonneveld et al.

(2008) points out that only few researches have been done on the effects of LET on soil, water quality and biodiversity despite desktop studies that indicate the possibility of severe effects.

On the basis several indicators like width of the technique Korevaar et al. (1991) estimated that with LET 90-100% of the clutches will be damaged, while with broadcast or watering 5-15% of the clutches will be damaged. Kruk (1994) estimated that minimal 85% clutches will be damaged with LET and minimal 15% with broadcast.

De Haan (1994), Kruk (1994) and Hanegraaf (1995) reported that manure application on soils with a lower carrying capacity will lead to problems for meadow birds because manure is applied later in the season due to the heavier weight of the technique. Ultimately this can affect the meadow birds when manure is applied for example in April when the meadow birds already start breeding.

According to the research of Oosterveld (2006) on a dairy farm and three different way of manure application (trailing shoes, shallow injection and solid manure) the godwits could find enough worms with all three manure types and did not have a preference. They state that even if the amount of worms would decrease, the critical boundary is not being crossed.

1.3.4 N_2O emission and oxygen in soil

N_2O emissions are approximately two times higher with LET (Kroeze, 1994; Hoek et al., 2007). Velthof et al. (2003) suggest that an increased N_2O emission of (shallow) injection can be explained by the decreased availability of oxygen in the soil, high local nitrogen concentrations and length of diffusion path. The evaluation of De Haan et al. (2009) also reports that manure applied in bands on the soil creates more anaerobe circumstances. The increased availability of nitrogen and higher local concentration which cause anaerobic circumstances inhibit nitrification and denitrification, therefor more NO^-, N_2O and N_2 emission during takes place (Hoek et al., 2007; Velthof & Mosquera, 2011). Denitrification is a far bigger source of N_2O emission than nitrification (Velthof et al., 2002) and denitrification is irreversible, the nitrogen will be lost to the environment (Erisman, 2000).
Also Misselbrook et al. (1996) found higher denitrification losses with shallow injection compared to broadcast. Decreased nitrification by anaerobe circumstances will decrease the availability of nitrogen for grass uptake (Mosquera et al., 2010). Availability of easily degradable carbon compounds also inhibit N_2O emission (Velthof et al., 2002). The faster the grass uptake of TAN the smaller the risk of N_2O emissions. This implies that smaller quantities reduce N_2O and NH_3 emission (Kroeze et al., 1994; Erisman & Monteney, 1998; Velthof et al., 2002).

N_2O emission contribute 298 times more to the greenhouse effect than CO_2 (Forster et al., 2007). Velthof & Mosquera (2011) found an average emission factor of 0.4% for shallow injection and 0.1% of the nitrogen applied for broadcast when cattle slurry was applied on grassland. The N_2O emission peaks for (shallow) injection occurs after one to two weeks, while the emission peak for broadcast and trailing shoe occurred in the first few days (Velthof et al., 2002). These emission factors are based on direct N_2O measurements, however, NH_3 has the potential to become N_2O by deposition. Since the NH_3 emissions of LET are lower compared to broadcast the calculated net N_2O emission is the same or even lower for LET (Velthof en Mosquera, 2011).

Hydrogen oxide (also called prussic acid) is often present in manure, when this toxic gas reacts with oxygen it will be degraded. Takens et al. (2008) argue that with surface application it is likely that more oxygen will be extracted from the air instead of the soil compared to when manure is applied in bands on or into the soil. This will contribute to anaerobic circumstances in the soil.

1.3.5. Harmful organisms & antibiotic resistant genes

There is no direct research available on the effects of manure application on harmful organisms in the soil like (myco)toxins and antibiotic resistant genes, but indirect researches suggest that trough UV light and oxygen broadcast could have a positive influence on decreasing their presence in the whole farming cycle.

Koch from Koch Bodemtechniek concludes in his research about toxins in the dairy chain that the fungi and bacteria responsible for toxin production partly end up in the manure. In the manure are possibilities for further development, and they end up on the parcel after manure application. Some bacteria and fungi can't handle light and oxygen, therefor broadcast manure application has the potential to limit the number of toxin producing fungi and bacteria. With (shallow) injection these toxin-producing organisms are more protected compared to broadcast. In 2012 Koch started a new research about this, which also involves soil and silage. Koch underlines that fungi not necessarily produces wastes like mycotoxins (Eurolab.nl; personal communication C. Koch, 30-03-12). However, the mycotoxins that can be inactivated by UV light (aflatoxins) are not a big problem in animal husbandry and other mycotoxins are only present in low concentrations in the manure (personal communication J. Fink-Gremmels 29-2-12).

Veterinary antibiotics can come into the environment through intensive farming. They potentially can cause damage to the environment (especially to soil and groundwater). Resistant genes are found in soil and groundwater, it is not clear if this refers to the natural concentration or an increased concentration by manure application. But it is clear that resistant bacteria are a problem in animal husbandry. In the Netherlands no field studies are known about antibiotics in soil and groundwater (Liefers, 2008). Fink-Gremmels and Liefers (2008) point out the possibility of UV light and inactivation of the stability of veterinary antibiotics.

The antibiotic group that is used the most in animal husbandry is tetracycline (Liefers, 2008). Da Costa et al. (2006) demonstrate that sunlight can decrease antibiotic resistant bacteria (among them tetracycline) substantially in sewage water. Sengeløv et al. (2002) measured the occurrence of antibiotic resistant bacteria (among them tetracycline) on farm soils with pig manure. They found that these bacteria temporally influence the levels in the soil, after six weeks levels both decreased and increased on the different farms. After five months the levels were similar to the reference. An increased amount of manure resulted in an increase amount of resistant bacteria, however the declination was similar. Engemann et al. (2006) compared in a laboratory study the antibiotic resistance (oxytetracycline) of American beef cattle waste water. Simulated sunlight was compared to dark conditions and a substantial higher decrease in antibiotic resistant genes levels. The degradation and inactivation is influenced by photo degradation and hydrolysis. The influence of photo degradation declines when the surface of the manure decreases (Thiele-Bruhn, 2003 as cited by Liefers et al., 2008), the level of degradation of tetracycline by photo degradation is unknown.

1.4 Manure and water

Ammonia has very strong affinity for water, therefore it's reactions is an important determinant for ammonia volatilization (Freney et al., 1983). The combined application of manure and water has several advantages:

- smell reduction;
- dissolves NH_4 in manure;
- infiltration into soil;
- NH_4 adsorpotion onto soil colloids;
- lowers soil temperature.

Rain dims the NH_3 emission during application, this effect can be imitated if irrigation is being applied right after manure application (Klarenbeek & Bruins, 1990; Sonneveld et al., 2008). By irrigation or the combined application of manure and water intrusion of manure into the soil and TAN infiltration into the inner side of manure clumps will be enhanced. If TAN infiltrates into the soil, volatilization is prohibited by the adsorption of NH_4 onto soil colloids. Infiltrated and adsorbed manure is more safe from temperature and wind influences (Mulder & Huijsmans, 1994; Sommer and Hutchings, 2001; Huijsmans, 2003; Misselbrook et al., 2005b; Huijsmans & Verwijs, 2008; Sonneveld et al., 2008; Shah et al., 2011).

Moreover trough irrigation or the combined application of manure and water, manure will be rinsed of the grass (De Haan et al., 1994, Huijsmans, 2003; Huijsmans & Verwijs, 2008), therefore this is more effective to reduce NH_3 emission than dilution alone (Bussink & Bruins, 1992; De Haan et al., 1994).

Finally, manure surface temperature is lowered and TAN concentration in manure is diluted, which both have a positive influence on reducing NH_3 emissions (Mulder & Huijsmans, 1994; Sommer and Hutchings, 2001; Huijsmans, 2003; Misselbrook et al., 2005b; Shah et al., 2011). According to Huijsmans, (2003) the effectiveness of this method depends strongly on the weather circumstances and soil conditions.

De Haan et al. (1994) report that smearing of manure occurred less when irrigation was applied compared with (shallow) injection. The distribution of manure is better when manure is broadcast applied with or by the combined application of manure and water (Hanegraaf, 1995). However, under windy conditions the opposite effect will be achieved.

Emission reductions

With solid manure Shah et al. (2011) found approximately 65% reduction in NH_3 emission with 5 mm of irrigation, while 10 mm irrigation led to a reduction of 93%. Nitrogen uptake increased from 18% to respectively 22% and 24%. McGinn and Sommer (2007), found 21–52% reduction in NH_3 emission with 6 mm of irrigation immediately after surface-application of solid beef cattle manure. Bussink & Bruins (1992) found with irrigation (3 mm with 10 m^3 ha^{-1}) an emission reduction of 70% and dilution (1:3) 59%.

Few researches have been done on the combined application of manure and water. Bode (1990) and Mulder & Hol (1992) measured NH_3 emission with the Duospray machine, this is a machine developed in the late eighties by Jan Teur were manure and water (ratio of 1:1) are applied at the same time. The emission reduction compared to broadcast of the first experiments was 25% (Bode, 1990), the second experiment two years later found emission reductions of 66-75% (Mulder & Hol, 1992). In their overview Mulder & Huijsmans (1994) explain these big spread in reductions to different weather circumstances and modifications on the machine, however the working group that deals with the guidelines of Low-Emission Techniques found that with this spread in results, the emission reduction was not ensured. This group also recommended that this measure should not be allowed because it is difficult to determine whether manure was applied with water (in the right proportion). Thereby, sight verification afterwards was not found to be meaningful and therefore (labour intensive) exclusive control in the act should take place (National Ombudsman, 1998).

1.6 Measuring NH_3

There are a lot of instruments and methods to measure the ammonia emission. Ammonia emission can be measured on small scale, medium scale and field scale. The Integrated Horizontal Flux (IHF, also known as the micrometeorological mass balance method) is a robust and often used method to measure NH_3 emission (Sintermann et al., 2011b). The IHF method measures NH_3 concentrations usually on medium scale at several heights in the middle of a circular plot and with a mast outside the plot that measures background concentrations. The concentrations of both masts are multiplied by wind speed and NH_3 flux is determined by the integration of this product. The flux is then divided by the fetch (length difference between windward and leeward boundaries) to derive the flux per unit of land area (Denmead, 1983; Ryden & McNeil, 1984). Wind tunnels measurements are done on small plots where a fan pushes air through the tunnel and NH_3 emissions are calculated by the same principle.

Sintermann et al. (2011b) compiled emission factors from over 350 measurements, published between 1991 and 2011 and came to the conclusion that different plot sizes and measurement methods show different results. Methods on medium scale mostly done with IHF resulted in a higher emission factor.
Emission is being stimulated if air with a low NH_3 concentration is forced over a surface with a high NH_3 concentration (the manured plot). This is called the oasis effect and concerns the circumstances in a wind tunnel (Loubet et al., 1999 a,b; Sintermann et al., 2012). Genermont & Cellier (1997) conclude that small scale experiments show a higher NH_3 emission compared to field scale, the influence of local advection is the possible explanation according to them. With their experiments, Sommer et al. (2003) and Spirig et al. (2010) also arrived at a scale effect on NH_3 emission and they found that there is almost no data available.

1.5 Research question

There are several measures to reduce NH_3 emission trough manure application. It is known that rain or water during manure application has positive effects on reducing NH_3 emission but there is not yet a technique where the combined application of manure and water is permitted. With modern techniques it is likely that the problems which the Duospray machine encountered twenty years ago with the enforcement and control are now not an issue anymore. In 2011 farmer Klaas Wolters developed a different version of the Duospray machine. Instead of a bow, this technique sprays the manure and water vertically on the soil and is called The Green Duo. As it was build, The Green Duo can contain 10 m^3 manure and 4,1 m^3 water.

The aim of this study was multiple, (i) to compare the NH_3 emission of The Green Duo with broadcast manure spreading and a low emission technique on field scale, (ii) to gain more inside in the NH_3

emission pattern of The Green Duo in time, and (iii) to gain more inside in the pattern of NH_3 concentration in the manured plot and with increasing distance behind the manured plot.

Main question
What are the effects of the combined application of liquid manure and water with The Green Duo compared to current low-emission techniques and broadcast manure spreading?

Sub questions:

1. What is the relative ammonia emission of The Green Duo compared to broadcast manure spreading and low emission techniques?
2. What is the ammonia concentration pattern on field scale at a height of 20 centimeter within and behind a manured grassland?
3. What is the time pattern of NH_3 emission when manure is applied with The Green Duo and what is the corresponding emission factor range?

1.7 The report

The next chapter of this report will explain the methods used to determine ammonia emission. Chapter three will present the results of four experiments where The Green Duo was compared with other application techniques. At the end of this chapter the NH_3 concentration pattern in the field will be addressed. Chapter four gives the results of the experiments where the NH_3 emission pattern of The Green Duo in time was measured. In chapter five, the discussion, not only the obtained results will be discussed, there is also attention for the absolute emission factors in case of broadcast spreading and shallow injection application. Finally, the conclusions give answers to the research questions. Appendix one contains detailed information about the measured results, appendix two provides more detailed information about all experiments.

The experiments where The Green Duo is compared with broadcast manure spreading and shallow injection are referred to as the *comparison experiments*. The experiments where the NH_3 concentration is measured in time will be referred to as the *time experiments* and the experiments where NH_3 concentration is measured over an increasing distance behind the manured plot will be referred to as the *distance experiments*.

2. Material and methods

Experiments were conducted in 2012 at the dairy farm of Mts. Wolters in Winsum (Groningen, latitude 53.33’N and longitude 6.54’E). In 2012 they had 80 milk cows, which produce 7,500 kg milk, 4.5% fat and 3.45% protein with an average milk urea content of 18. The farm comprises 41 hectares of grassland and a 3-4 hectares with maize on a marine clay soil. In February, 15 m^3 ha^{-1} solid cattle manure was applied to all grassland fields.

Figure 1. Paddocks surrounding the farm (A) (Google maps).

The NH_3 emission from a manured area near an environment with a low NH_3 concentration will be higher compared to that from an area that is near an environment with a high NH_3 concentration. Therefore measurements on field scale (0.5 ha) appeared to be the most reliable because this effect is negligible if the distance between the measuring site and the environment with a low NH_3 concentration is at least 50 meter (Sommer et al. 2003; Sintermann et al., 2011b).

2.1 Experimental setup

Four field experiments were conducted in April, May, July and August to compare the three or four liquid manure application techniques. Three field experiments with three replicates were conducted in June and August to measure NH_3 emission in time. And three field experiments were conducted in June and August to measure the NH_3 concentration with increasing distance behind the manured plot.

2.1.1 Comparison experiments

Experiments were conducted in April, May, July and August 2012 to estimate the effect of the combined application of water and slurry manure with The Green Duo which can contain 10 m^3 manure and 4,1 m^3 water (Figure 2). A comparison of this technique was made between broadcast spreading the manure (The Green Duo without water) and a commonly used Low Emission manure speading Technique in the Netherlands, for the purpose of this research taken as shallow injection (Figure 3). In front of every manure hose a coulter cuts a shallow slot in the grass sward wherein manure is applied a few centimeters deep. In addition to these two treatments, two experiments were done with The Green Duo with a manure : water ratio of about 1:1 and one experiments was done with a ratio of 1:2. More water was applied by adapting the pressure of the corresponding nozzle.

Application rates of the experiments varied between 17 and 39 kg TAN ha^{-1} due to different manure composition.

Figure 2. The Green Duo

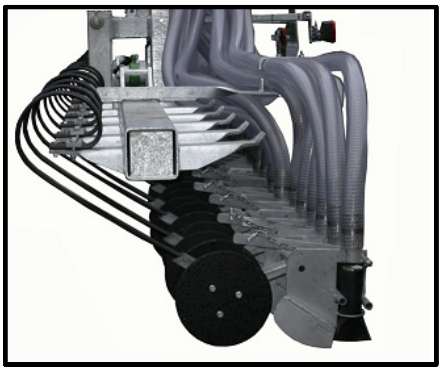


Figure 3. Shallow injection

The aim was to perform all comparison experiments on field scale (0.5 ha) to avoid interference. However, due to practical reasons the size of the plots of all experiments varied between 0.2 ha and 1.6 ha. Minimum distance between the individual plots was 13 meter. There were no buildings or trees near the plots within a radius of 100 meter, except for the experiment in August where there was a small bird-watch-shed (1x2m) at 30 meter distance of the leeward edge of the plots. The first measuring site was located on about one meter from the edge of the manured plot (except in May when it was about 7 meter from the edge). Five measuring sites were located downwind (Figure Figure 4). One fifth of the plot was manured like the grey strip in Figure 4 and immediately after the measuring site was manured, measurements were performed. After finishing the measurement, the next strip was manured and measured. The fetch, i.e. the length difference between the first measuring site windward and the last measuring site leeward, was between 90 and 160 meter. Measurements were done on one and the same large grassland field which was divided into four experimental plots. Except in April, when only three plots were used instead. Plots were chosen dependent on wind direction and suitability like equality in height (soil level as well as grass sward height). Every experiments was conducted on a 'new' plot that has not been used in previous experiments.

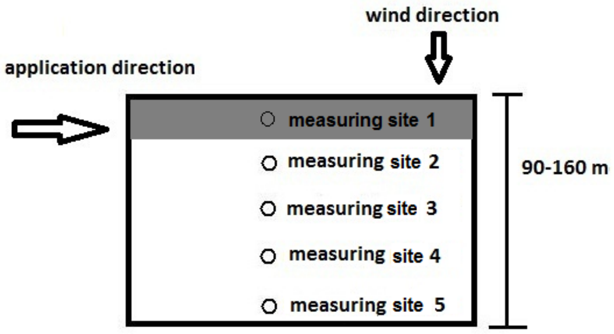


Figure 4. Schematic diagram of an experimental plot were one treatment was measured

The NH_3 concentration from the following five treatments was measured:
1) Broadcast (The Green Duo without water)
2) The Green Duo (TGD 2:1) ratio 10 m^3 manure, 4.1 m^3 water (0.6 mm water)
3) Shallow injection
4) The Green Duo (TGD 1:1) ratio 10 m^3 manure, 8.2 m^3 water* (1.0 mm water)
5) The Green Duo (TGD 1:2) ratio 10 m^3 manure, 20 m^3 water** (2.9 mm water)
* measured only in July and August
** measured only in May

The Green Duo with a manure : water ratio of 10:4 will be referred to as *TGD 2:1*, The Green Duo with a manure : water ratio of 10 : 8.2 will be referred to as *TGD 1:1* and he Green Duo with a manure : water ratio of 10 : 20 will be referred to as *TGD 1:2*.

NH_3 concentration was measured for four days during the first two experiments in April and May because it was found that by far the greatest part of the TAN would then have been emitted (Bussink et al., 1994; Huijsmans et al., 2001). However, after interpretation of two of the three time experiments described in the next paragraph it was concluded that no significant emission was measured already after six hours. Therefore the experiments in July and August ended after 24 hours.

The measuring sites were chosen in between the edge of the tires and the end of the range of the application method. With shallow injection two bands of equal length were covered by the ring of the flux chamber. The soil of the experiment in May was so dry that it took much time to hammer the rings into the soil. Therefore the day before the experiment, the measuring sites for the flux chamber were chosen beforehand, depending on the range of the application technique, and were watered so the ring would go in more easily. Rings were removed when manure was applied. Soil samples were taken near the measuring points, right before the start of the experiment.

2.1.2 Time experiments

Three field experiments were conducted in June and August to measure NH_3 emission in time with The Green Duo 2:1. The measuring sites were located in the middle of each plot and were measured approximately once an hour for a certain time period. After this period, there was more time in between measurements, the last measurement was after 24 or 72 hours (differed per experiment). With these measurements the absolute emission of the amount of TAN emitted in relation to the amount of TAN applied was calculated. The first experiment on June 1th started at 15:00, the second experiment on June 29th started at 13:00 and the third experiment on August 15th started at 9:00.

2.1.3 Experimental setup distance experiments

To measure NH_3 concentrations over an increasing distance, two plots of the time experiments on June 29th and August 15th were used. On August 17th another experiment was conducted where NH_3 concentrations behind the three plots were measured. Likewise, these experiments were done with The Green Duo 2:1. Originally all three manured areas were diveded into three plots, with one measuring site in the middle. The manured area of the experiment on August 17th was 150 meter wide and 50 meter long. But wind direction fluctuated slightly to both directions during this experiment. Besides some blank samplers were contaminated, this might be caused by the preparation of the samplers in Groningen, instead of the lab in Wageningen. For these two reasons the results of this experiment is not presented in the results.

The manured area on June 29th was 24 meter wide and 40 meter long, as visible in Figure 5 and Figure 6. There was a gap in the manured area and the measuring sites behind the manured area. Distances between the leeward edge and the measuring site of the manured area were 8, 18 and 32 meter. The fetch (difference between windward and leeward edge of the manured area) was approximately 20 meter.

On August 15th the measuring site was 48 m wide and 35 m long and measuring sites behind the manured plot were located at 5, 21 and 51 meter distance as illustrated by Figure 7 and in Figure 8 with the three black circles on the horizon. The manured area had a fetch of approximately 36 meter.

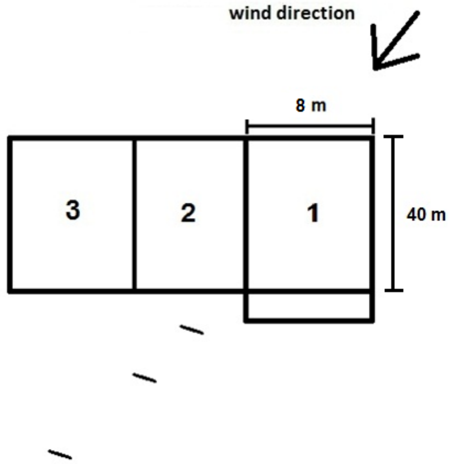


Figure 5. Schematic diagram showing the arrangement of the measuring sites of the distance experiments on June 29th . The bars represent the measuring sites at 8, 18 and 32 m distance from the leeward edge

Figure 6. Measuring site distance experiment June 29th

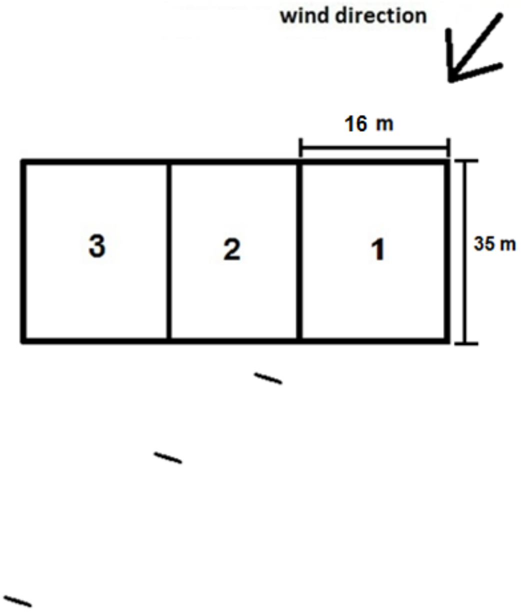


Figure 7. Schematic diagram showing the arrangement of the measuring sites of the distance experiments on August 15th . The bars represent the measuring sites at 5, 21 and 51 m distance from the leeward edge of the plot

Figure 8. Measuring site distance experiment August 15th

2.2 Method of measuring

NH_3 emission measurements were started within minutes after application using two methods: diffusion samplers (Figure 9: average NH_3 concentration) and a photo acoustic gas monitor (INNOVA 1412A) connected to a flux chamber (Figure 10: initial NH_3 emission rate and equilibrium NH_3 concentration). The flux chamber with photo acoustic gas monitor measured the NH_3 emission on small scale and the diffusion samplers measures NH_3 concentration on field scale.

2.2.1 Diffusion samplers

At every measuring site three (or more) diffusion samplers were placed in a wooden frame as used by Shah et al. (2011). From the used 50 or 65 samplers in total, two remained in the refrigerator of the lab and three remained in the cool box during and after installing the other 60 samplers. The samplers (three of fifteen, depending on the experiment) were made operational within five minutes after imposing the treatments and exposed for a period of 24 or 72 hours. All samplers of one experiment were analysed at the same time. The procedure described in the 4th version of the protocol "Measurement of NH_3 in ambient air using a modified palmes diffusion tube" by Hofschreuder and Heeres WUR-MAQ (2002) was followed to finally calculate the average NH_3 concentration with diffusion samplers. The wooden frame was installed at a height of 20 cm and the tubes were in a vertical position with the inlet facing down (Figure 9). Distance between the diffusion samplers was approximately 20 centimeters.

Figure 9. Diffusion samplers

A sampler consists of a small cylindrical tube with two stainless steel grids coated with 60 µL of 10%(w/v) sulphuric acid (H_2SO_4) at the bottom of the tube, placed in a cab with rim. This amount has a binding capacity of 9,1µg dissolved NH_4^+ in 5 ml of water. The tube is 0,041 m long and an area of $7{,}85*10^{-5}$ m^2. Only 45 tubes of this size were available, 15 tubes with a slightly different size: 0,035 m with an area of 9,5 $*10^{-5}$ m^2 were found and used to broaden the experiment. Both tube types were made of polyvinyl chloride (PVC), which is known for its low NH_3 absorption capacity (Shah et al., 2006). The cap on the entrance of the sampler was made of poly-ethylene and had a hole of 10 mm. A water repellent Teflon filter at the entrance prevents turbulence to enter the tube and disturb the molecular diffusion. Assuming a stationary layer between the inlet filter and the grid, the flow rate can be described using Flick's law of diffusion (Hofschreuder & Heeres, 2002).

People emit NH_3 by exhalation and from the skin, so the risk for contamination is high (Hofschreuder & Heeres, 2002). For this reason tubes were prepared with cleaned hands and without exhaling near the tubes. All tube materials were cleaned two times with water and two times with distilled water, everything was re-used except for the filters. The steel grids were cleaned with water and soap and afterwards rinsed with acetone. All material was dried for one hour in an oven at 60 °C. After coating and preparing the tubes were stored in a cool box. Transport can be done without cooling if the temperatures don't exceed normal outdoor temperature (Hofschreuder & Heeres, 2002). Within days after preparation the tubes were exposed in the field. After ending the measurements they went back in the cool box and stored in a fridge for a few days to be analysed within one week. The NH_4^+ containing samples were analysed by ion-exchange and conductivity detection in a ECN AMON detector as described by Houba et al. (1989). The NH_3 concentration was calculated using the following two equations developed by Hofschreuder & Heeres (2002) and Shah et al. (2010):

Equation 3.

$$C = \frac{17}{18} \ * \ \frac{Q.\ Z}{D.\ A.\ t}$$

Equation 4.

$$D = 1.1265 \ \ * 10^{-9} \ \frac{T^{1.75}}{P}$$

Where, C = concentration of NH_3 (µg m^3), Q = sampled amount of NH_4^+ (µg), Z = length of tube (m), D = diffusion coefficient (m^2 s^{-1}), A = area of the tube (m^2), t = sampling time (s), 17/18 = conversion from NH_4^+ to NH_3, T = air temperature (K) and P = air pressure (bar).

The RIVM (National Institute for Public Health and Environment) measures atmospheric NH_3 concentrations using diffusion samplers. To remove false or disrupted samplers the RIVM follows a validation procedure (Stolk et al., 2009). The RIVM uses many diffusion samplers per measuring site, thus reducing the Standard Error of the Mean (SEM). Because this research only uses three samplers per measuring site, and the variation is high, this procedure can't be followed. According to Shah et al. (2011) the individual result per measuring site can differ a factor four, and by comparing the individual results with the average result of the three samplers generally outliers were observed. In order to remove the outliers in an more objective way, a simple procedure was developed. The RIVM uses the Standard Error of the Mean as criteria to judge the sampled amount. Following this, in our case the average SEM of all (45 or 60) diffusion samplers of one experiment was calculated and this result was multiplied with 6. When the SEM of a given measuring site (three diffusion samplers) was higher than the average SEM times 6, an outlier was indicated.

2.2.2 Closed flux chamber and photo-acoustic infrared multi-gas monitor (INNOVA 1214A)

The use of a closed flux chamber on an emitting surface is a simple way to determine NH_3 emission. The NH_3 flux is derived from the temporal change in NH_3 concentration inside the chamber (Sintermann et al., 2011b). Accumulation of NH_3 (gas) inside the flux chamber is an air-born diffusional mass transport process (Szánto, 2009). Measurements will be stopped once the concentration of NH_3 (gas) inside the flux chamber reaches the equilibrium state with NH_3 (aqueous) in the top layer of the soil. It was assumed that the system then had reached a steady-state with a gas-liquid phase ratio of 1:1 (Shah et al., 2012). The simplicity, limited costs and possibilities of many replicates are advantages of chamber measurements. On the other hand, the limited spatial representativeness and the potential of inner walls to absorb and release NH_3 molecules are disadvantages. Besides, it is possible that the concentration-increase inside a chamber is strongly damped because of the sink activity of the chamber walls due to the sticky nature of NH_3 molecules. Even with a non-linear fit, this can lead to a severe underestimation (Sintermann, 2012).

To determine flux rates of NH_3, a photoacoustic gas monitor (INNOVA 1412A, LumaSense Technologies, Denmark) connected to a closed flux chamber (0.3x03 m) by two Teflon tubes was used. This monitor was connected by two 0.5 m long Teflon inflow and outflow tubes (volume 0.00001413 m^3) to the closed flux chamber. The flux chamber has a separate ring with a sharp bottom edge and an internal diameter of 0.3 m and it is made of PVC (polyvinyl chloride). The total internal volume of the chamber is 0.0212 m^3 and the volume of the air in the monitor is 0.0001 m^3. At each measuring site, the ring of the flux chamber was hammered four to five cm deep into the surface of the soil, this ads 0.0021 m^3 to the total volume. The total actual air in the flux chamber is 0.0235 m^3 (Shah et al., 2012). However, the volume of the grass and the unequal soil level is not included in this calculation. A plumb rule is used for levelling the ring. Thereafter the edge of the ring and the chamber will be closed with water, so no air can come in or out the chamber. Subsequently, NH_3 concentrations were recorded for 10 to 35 minutes until the equilibrium was reached.

The detection limit of INNOVA for NH_3 is 0.2 ppm. The following equation can be used to convert this to mg m^{-3} (LumaSense Technologies).

Equation 5.

$$C = \frac{ppm * M}{V}$$

Were C is the concentration of the gas in mg m^{-3}, ppm is the concentration in parts per million and M is the weight of the gas in g mol^{-1} , at 20°C and 1 atmosphere M becomes 24.04 g mol^{-1}.

The detection limit of 0.2 ppm is calculated with Equation 5. to 0.141 mg m^{-3} NH_3.

Figure 10. Ring

Figure 11. INNOVA and flux chamber

Figure 12 shows an example output from the INNOVA. The slope of the gas concentration (mg m^{-3}) in the first minutes represents the initial emission rate. The actual initial NH_3 emission rate can be determined with a non-rectangular hyperbola (Equation 6). The NH_3 concentration at time 0 (D), initial slope (B), equilibrium (C) and curvature parameter (A) are needed to obtain the instantaneous NH_3 emission rate while fitting the data (Shah et al., 2012).

Equation 6.

$$[NH_3] = D + \frac{1}{2A}\left\{B_1 \times t + C - \sqrt{(B_1 \times t + C)^2 - 4A \times B_1 \times C}\right\}$$

NH_3 concentrations at time 0 were not always reliable in this research, after the second experiment it was concluded that this was due to the air that was still left in the tubes of the flux chamber at the beginning of the measurement. The tubes of the experiments conducted thereafter, were ´cleaned´ by sucking air with a low NH_3 concentration after each measurement by holding the chamber in the air at a height of 1,5 meter. Therefore, instead of determining the emission rate with Equation 6. each single initial slope (the maximum difference between two measured concentrations) represents the (maximum) instantaneous NH_3 emission rate.

The volume and surface of the chamber together with this emission rate is used to calculate emission flux (µg $m^{2\ -1}$ sec^{-1}). For example, with an initial slope of 4.5 µg NH_3 m^{-3} min^{-1} the initial flux becomes 25 µg NH_3 m^{-2} sec^{-1} and this is equivalent to 0.9 kg NH_3 ha^{-1} $hour^{-1}$.

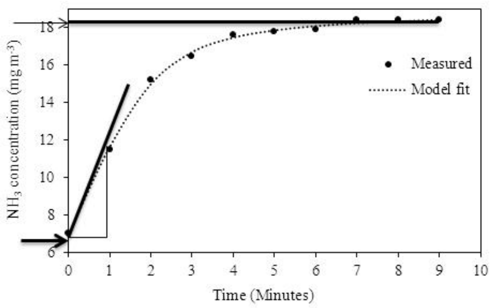


Figure 12. Example output INNOVA (Shah et al., 2012) illustrating the NH_3 concentration (mg min^{-1})

Not all of the obtained results with the INNOVA followed the normal emission pattern due to e.g. leaking of NH_3. In April this was probably due to incorrectly levelling the rings without a plumb rule and the long grass. This is one of the reasons why the INNOVA results of April won't be presented in the results. It is not known how NH_3 could escaped during the experiments. Therefore it happened that the equilibrium did not always remained at a steady level, in that case the maximum measured concentration was used when comparing equilibrium concentrations. A critical selection was made by judging the results using the pattern presented in Figure 4. In Appendix 1 the encountered problems with INNOVA and how they were prevented in the following experiments are described.

2.2.3 Emission calculations

In the time experiments NH_3 concentrations were measured with the diffusion samplers and the INNOVA connected to the flux chamber.

Every hour after manure application the time pattern of NH_3 concentrations were measured with the chamber connected to the INNOVA, until saturation was reached. It was assumed that saturation was reached when the results did not show an increase in NH_3 concentration. From each measuring site, the initial emission rates of each hourly measuring event were plotted together in a graph and an exponential trend line was used to fit the data. By integration the absolute emission can be calculated by corresponding equation:

Equation 7.

$$\int A\, exp^{-Bx} \quad dt = \frac{A}{B}$$

Where A is the initial NH_3 emission rate (kg ha^{-1} h^{-1}) right after manure application, B the curvature of the graph following the subsequent emission rates and x the time in hours. With the exponential trend line parameters A and B can be derived.

Diffusion samplers were installed approximately five centimeter apart from each other in two or three wooden frames in a row (Figure 9 and Figure 8) close to the flux chamber. Three diffusion samplers from each measuring site were closed and removed every hour until no significant difference in NH_3 concentration (slope) was measured with the INNOVA (saturation was reached). Thereafter samplers were closed after 12 of 24 hours. For this purpose the amounts of collected NH_4 instead of calculated NH_3 concentrations were used. The data points were fit by using the non-rectangular hyperbola (which is a very flexible and accurate function), in order to demonstrate the pattern of collected NH_4 in time as realistic as possible.

This non-linear regression analysis was performed for the dataset of each of the three experiments, by using the model given in Equation 6. Where A, the sharpness of the parameter, was set to a constraint smaller or equal to 1. B, the initial slope of the curve, was estimated first from the average amount of collected NH_4 in the diffusion samplers which were closed after one hour. C, the equilibrium, was estimated with the average amount of collected NH_4 for the last closed diffusion samplers. And D, the concentration at time 0 was set to 0.009, thus just above zero. This equation is used with a whole different purpose than estimating the emission rate from the INNOVA results.

Table 1. Model parameters of Equation 6. the non-rectangular hyperbola were A is the sharpness of the parameter. B is the initial slope of the curve (estimated from the average amount of collected NH_4 in the diffusion samplers closed after one hour) , C the equilibrium of the curve (estimated with the average amount of collected NH_4 for the last closed diffusion samplers) and D, the concentration at time 0, before manure was applied

	June 1th	June 29th	August 15th
A (constrains)	<=1	<=1	<=1
B	0.66	0.8	0.58
C	1.56	1.44	0.95
D	0.009	0.009	0.009

2.3 Soil, manure and water samples

Since soil, manure and water composition can influence NH_3 emission (Huijsmans, 2003) samples were taken to determine the total N, NH_4^+-N, NO_3^--N, dry matter and pH (Table 2, Table 3, Table 11, Table 12, Table 13 and Table 14). With total N and NH_4^+-N the organically bound N in the manure was calculated (Table 2 and Table 3,.

Ten soil samples of the first 20 cm were taken from each plot with an auger. The samples were mixed and subsamples were taken for further analysis. Manure samples were taken from the tank and the mixed manure cellar. Nitrogen content and pH were determined in wet samplers. Differences between the two manure samples were little and therefore averaged. Water samples were taken to determine the pH, NH_4^+-N and NO_3^--N content. Manure, soil and water samples were airtight stored in the refrigerator at 4 ºC before analysing.

Available NO_3^- -N and $NH4^+$-N were quantified following the methods described in Houba et al. (2000). In this case, manure and soil samples were extracted in 0.01M $CaCl_2$. They were shaken for two hours, diluted, centrifuged and finally together with the water samplers analyzed spectrophotometrically using a segmented-flow system (Auto-analyzer II, Technicon). To determine total N, manure and soil samples were digested with a mixture of H_2SO_4–Se and salicylic acid as decribed by Houba et al. (1997). In these digests total N was measured spectrophotometrically with a segmented-flow system (Auto-analyzer II, Technicon). pH of the soil was measured in a 1:10 (m/v) soil/0.01 M $CaCl_2$ extract as described in Houba et al. (1997). The samplers were shaken for 2 hours before the pH was measured. Manure and water samples were shaken and measured directly with a pH meter. After 24 hours of drying the soil and manure samples at 103 ºC, dry matter content was determined (Houba et al., 1997).

Table 2. Manure characteristics comparison experiments

Date	g NH_4-N kg^{-1}	g org-N kg^{-1}	g N kg^{-1}	% dry matter	pH	% TAN
April	1,7	0,6	2,3	2,8	7,5	74
May	2,4	1,2	3,6	6,3	7,4	67
July	1,4	1,7	3,1	7,2	7,5	45
August	1,3	1,6	2,9	6,4	6,9	45

Table 3. Manure characteristics time and distance experiments

	g NH_4–N kg^{-1}	g org-N kg^{-1}	g N kg^{-1}	% dry mater	pH (KCL)	% TAN	kg NH_4-N ha^-
June 1th	1.4	1.6	3	7.4	7.2	47	19
June 29th	1.4	1.6	3	6.5	7.4	47	54
August 15th	1.3	2.5	3.8	6.7	6.8	34	39
August 17th	1.4	2.4	3.8	6.7	7.4	37	56

It was expected that the manure in April had a low dry matter content and a relatively high TAN content, because straw was used in combination with a closed floor in the stables. This leads to more or less separated faeces and urine. To make the experiments more comparable with average (Dutch) dairy farms, thicker manure (slurry) was needed, therefore before all the other experiments this thin manure (urine) was removed from the bottom of the cellar before the cellar was mixed. The cows were grazing protein rich grass in the spring before the experiment in May, and this explains the high $NH4^+$ content in the manure.

Manure quantities

By weighing The Green Duo empty and full at the weighbridge in Baflo (Gn) in combination with the area of the manured plots, the applied amount of manure was calculated. If the tank was not empty at the end of the plot, the remaining manure and / or water was applied on another field. With a GPS system the speed was followed, larger amounts of manure were applied by slowing down the speed. The Green Duo is equipped with a meter that roughly measures the manure volume still in the tank and functioned as an extra check. The weight of shallow injection was not measured, instead the volume according to the manufacturer was used.

2.4 Weather

The weather station in Winsum (3000 meter near the experimental plots) measured the minimum and maximum temperature, the average percentage of cloud cover and wind speed expressed in Beaufort (Table 4). For temperatures, humidity and wind speeds during the whole day, two weather stations nearby Winsum (Eelde and Uithuizermeden) were used and averaged (Appendix 2). The data from Uithuizermeden was read from the graphs.

Table 4. Weather characteristics comparison experiments on the day of the experiment average from weather station Winsum

	April	May	July	August
Cloud cover %	25	1	55	10
Minimum temperature °C	-1.3	14.4	10.6	12.2
Maximum temperature °C	9.9	24.9	23.7	24.0
Wind Beaufort	2-3	3-4	3	4-3
Minimum air humidity %*	55	28	50	43

* Average from weather stations Eelde and Uithuizermeden

Table 5. Weather characteristics time and distance experiments on the day of the experiment, average of weather station Winsum

	June 1th	June 29 th	August 15 th	August 17th
Clouds cover %	65	70	5	20
Minimum temperature °C	7.3	13.9	16.2	12.8
Maximum temperature °C	13.9	22.1	25.7	26.5
Wind Beaufort	4-5	3	4	3
Minimum air humidity %	62	62	45	45
Rain mm*	0.5	0.4	3	0

*No rain was observed in the first 8 hours except for June 1th it rained a little during the experiment

Vapour pressure deficit

Vapour pressure deficit is calculated to compare weather circumstances. Figure 13 shows the Vapour Pressure Deficit for the four trails, which is calculated using the following equations (Allen at al., 2005):

Equation 8.

$$ea = es\frac{RH}{100}$$

Equation 9.

$$es\,(T) = 0.6108\exp\frac{17.27\,T}{T + 273.3}$$

Equation 10.

VPD = es-ea

Were, ea = actual vapour pressure (kPa), RH = relative air humidity (%), e_s (T) = saturation vapour pressure (kPa) at given temperature, T = temperature (°C), VPD = Vapour pressure Deficit (kPa).
All experiments were done on the same day, but circumstances differed during the day, therefore Table 15 in Appendix 3. shows the starting and ending time of the experiments

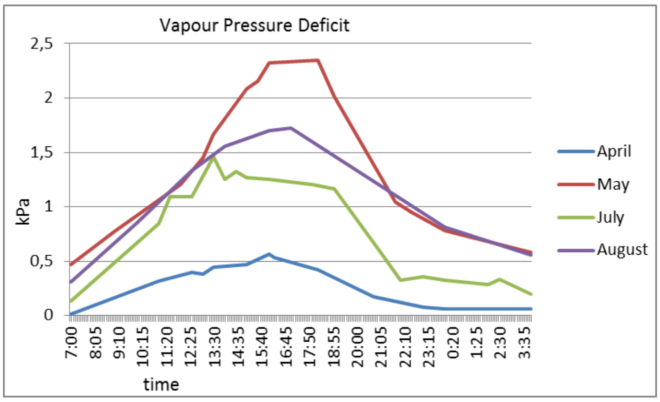


Figure 13. Average Vapour Pressure Deficit (KPa) of weather stations Eelde and Uithuizermeden for the comparison experiments on the day of the experiment

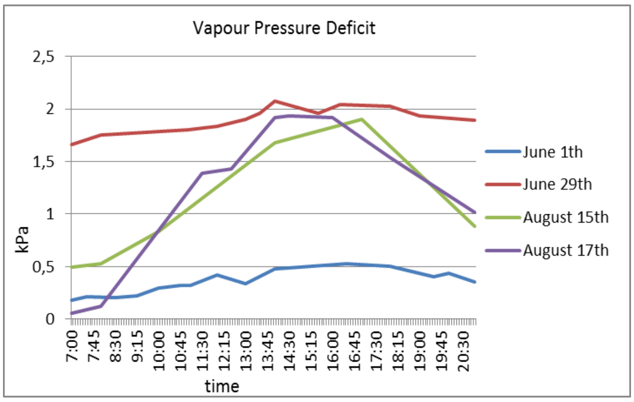


Figure 14. Average Vapour Pressure Deficit (KPa) of weather stations Eelde and Uithuizermeden for the time and distance experiments on the day of the experiment

3. Results comparison experiments

The first four paragraphs of this chapter present the results of one experiment, different circumstances are mentioned per experiment. NH_3 concentrations in the diffusion samplers are calculated with the collected amount of NH_4 in the tube and Equation 3. *and Equation 4., by using the actual tube sizes per treatment and average temperature and air pressure per experiment (Table 4). The error bars correspond with the Standard Error of the Mean of the three diffusion samplers. Both initial slope and equilibrium concentrations are presented per measuring site. Manure was not applied in equal quantities during the experiments, because it was difficult to drive fast with shallow injection, therefore larger amounts were applied in most cases. The validation procedure in this chapter refers to the procedure described in Paragraph 2.1.1. The results of all experiments are summarized in paragraph 3.5 and finally paragraph 3.6 presents results about the horizontal transport of NH_3.*

3.1 April

In April manure was applied before the herbage was cut, the first measuring sites of all three treatments had a grass length of approximately 10 centimeter. Grass lengths of the other measuring sites of the broadcast and The Green Duo 2:1 treatments were approximately 20-25 cm and those of shallow injection treatment 15-20 cm. For most farmers it is not common to apply manure at this grass length. On these measuring sites grass could have touched the samplers (Figure 15). 22 kg TAN ha^{-1} was applied on the plots of broadcast and TGD 2:1, 39 kg TAN ha^{-1} TAN on the plot of shallow injection. A double amount of manure was applied by accident on the 5th measuring site of shallow injection.

Figure 15. Grass could touch the samplers

Dry matter content in the manure was with 2% substantially lower compared to the other experiments; the weather in April was cool and humid, with about 25% cloud cover. The plot of broadcast was approximately 2.5 ha with a fetch of 105 meter, those for shallow injection and The Green Duo were 2.4 and 1.5 ha, respectively, and had a fetch of 160 and 150 m, respectively. Diffusion samplers were exposed for 72 hours (Figure 16).

3.1.1 Diffusion samplers

When applying the validation procedure, two samplers for The Green Duo treatment had to be rejected (one out of three for both measuring sites 2 and 5). The average temperature and air pressure of the first 24 hours were used in Equation 4 to calculate the NH_3 concentration.

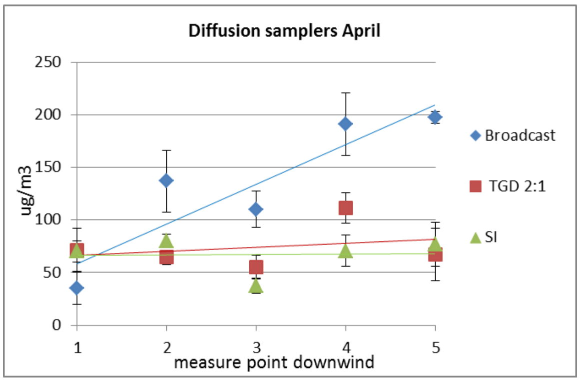


Figure 16. NH_3 concentration (µg m^{-3}) average of three diffusion samplers per measuring site downwind over 72 hours. The error bars correspond with the Standard Error of the Mean for three diffusion samplers

Only the NH_3 concentration of broadcast showed increasing values along the fetch, the concentrations of TGD 2:1 and shallow injection remained on average unchanged along the fetch (Figure 16).

3.2 May

A few days before the experiment started, grass was cut for the first time that year and had a height of approximately seven centimeter. The relative and absolute TAN content of this experiment was higher compared to the experiments in July and August (Table 2), but relative TAN content of the manure was lower compared to the experiment in April. The weather was summer-like; hot and dry with much wind. Due to droughtness of the soil, rings were hammered into the soil the day before the experiment after watering the sites.

31 kg TAN ha^{-1} was applied on the plots of broadcast and TGD 2:1, 36 kg TAN ha^{-1} on the plot of shallow injection and 35 kg TAN ha^{-1} on the plot of TGD 1:1. At the first measuring site of the broadcast treatment the manure was not spread equally due to a blockade of the nozzle. At the first measuring site of shallow injection, less manure was applied because it took more time than expected to start the manure circulation. The plots were 50 meter wide and had a fetch of approximately 90 meter.

3.2.1 Diffusion samplers

NH_3 concentrations over 72 hours are given in Figure 17. After applying the validation procedure, 7 out of 60 samplers were rejected, four samplers of broadcast (measuring points 1,2,4,5), two samplers of TGD 2:1 (measuring point 2 and 4) and one sampler of shallow injection (measuring point 5). The diffusion samplers of TGD 1:2 had a different size compared to the other treatments.

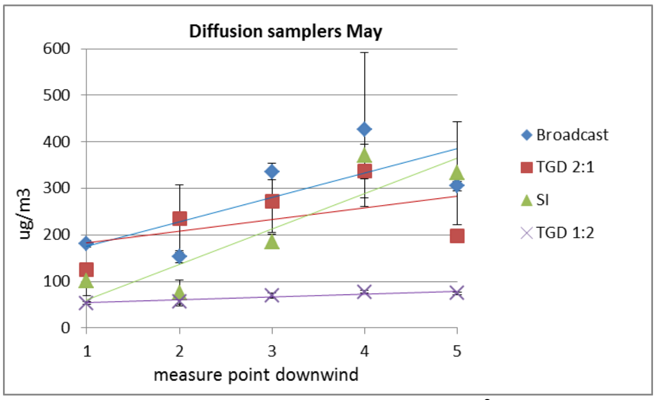


Figure 17. Average NH_3 concentration ($\mu g\ m^{-3}$) of 3 diffusion samplers downwind, over 72 hours. The error bars correspond with the Standard Error of the Mean for three diffusion samplers

The NH_3 concentrations of the diffusion samplers increased slightly along the fetch for broadcast, TGD 2:1 and shallow injection (Figure 17). It is interesting to note that the concentrations in the samplers of TGD 1:2 showed only a very small variation.

3.2.2 Initial slope & equilibrium concentration

At the fifth measuring point of The Green Duo 1:2, which was also the last measuring point of the whole experiment that day, some moisture in the tubes of the flux chamber was noticed and the measurement was stopped. All three approved measuring points of the plot of shallow injection did not get a representative amount of manure, especially measuring points 2 (Figure 18) and 5 (Figure 19) got less manure.

Figure 18. Measuring point 2

Figure 19. Measuring point 3

Figure 20. Measuring point 5

Figure 21. Manure applied with shallow injection

In Figure 22 and Figure 23 the results of the measurements right after manure application are shown.

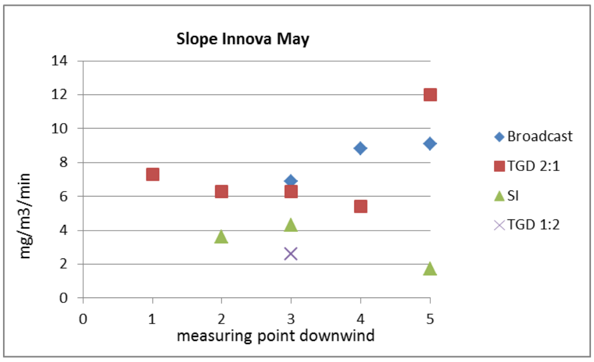


Figure 22. Initial slope (mg m^3 min^{-1}) in May, right after manure application

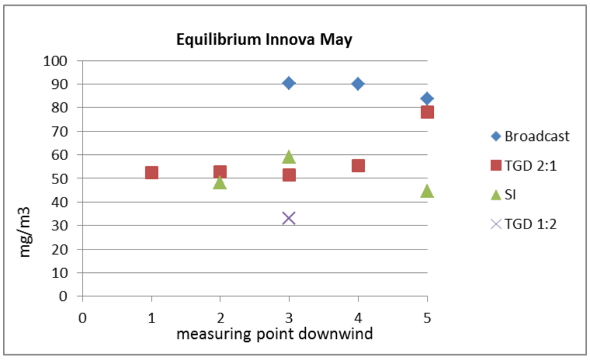


Figure 23. Equilibrium concentration (mg m^3) in May, right after manure application

The INNOVA results did not show great variations between the measuring points.

3.3 July

In July manure was applied one week after cutting the grass. 18 kg TAN ha^{-1} was applied with broadcast, TGD 2:1 and TGD 1:1, 27 kg TAN ha^{-1} was applied with shallow injection. Plots had a fetch of 90 meter and were 50 meter wide.

3.3.1 Diffusion samplers

Differences between treatments were not as clear as the experiments in April and May, but irregular and rather small (Figure 24). When applying the validation procedure one sampler of broadcast (measuring point 2) and one sampler of TGD 2:1 (measuring point 4) were rejected. The diffusion samplers of TGD 1:2 had a different size compared to the other treatments. The symbols of broadcast showing the concentration of measuring point two and five are hidden behind the symbols of TGD 2:1.

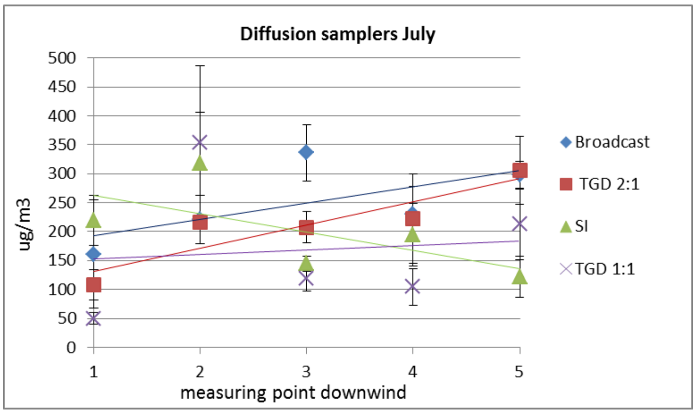
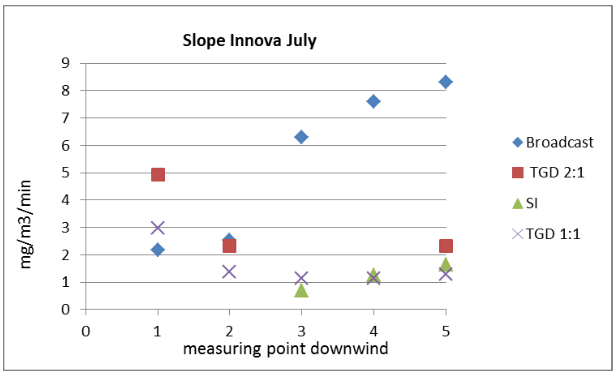


Figure 24. NH_3 concentration (µg m^{-3}) average of 3 diffusion samplers downwind over 24 hours. The error bars correspond with the Standard Error of the Mean for three diffusion samplers

3.3.2 Initial slope & equilibrium concentration

Figure 25 and Figure 26 showed a large variation in the plot of broadcast spreading.



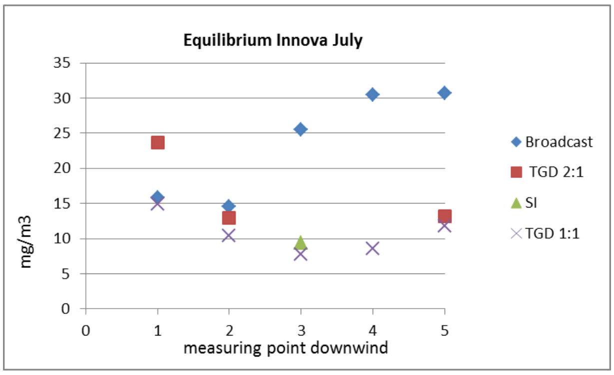


Figure 25. Initial slope (mg m^3 min^{-1}) in July, right after manure application

Figure 26. Equilibrium concentration (mg m^3) in July, right after manure application

The pattern of the initial slope and the equilibrium concentration are quite similar in both figures. Variation between the measuring points of broadcast are the greatest.

3.4 August

Grass had a height of approximately 10 cm during the experiments in August. 17 kg TAN ha^{-1} was applied with broadcast, TGD 2:1 and TGD 1:1, 27 kg TAN ha^{-1} was applied with shallow injection. Plots had a fetch of 100 meter and were 20 meter wide.

3.4.1 Diffusion samplers

At the third measuring site of The Green Duo 2:1 some technical problems occurred. It took about 1,5 hours to solve them and some manure was spilled on the plot, on the side of the treatment were manure was broadcast spread. Difference in general were not large between the treatments. With the validation procedure two samplers of TGD 2:1 were rejected at measuring sites 3 and 5. Also in August differences between the treatments were small. Although the result of measuring point two of shallow injection looks non-representative in Figure 27, during the experiment the measuring point was judged as representative. It was not visible that extra manure was applied, therefore this results was included in the average result. In this experiment the diffusion samplers of broadcast had a different size compared to the other treatments.

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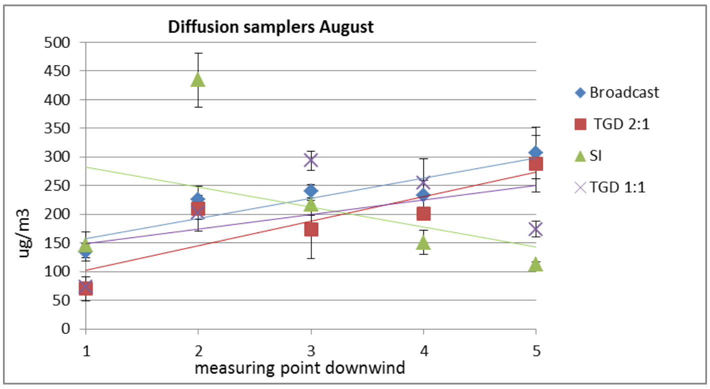

Figure 27. NH_3 concentration (µg m^{-3}) average of three diffusion samplers downwind over 24 hours. The error bars correspond with the Standard Error of the Mean for three diffusion samplers

3.4.2 Initial slope & equilibrium concentration

The initial slope and equilibrium concentration in August illustrate clearly the effect of application technique on concentration patterns (Figure 28 and Figure 29). Again, the initial slope follows the same pattern as the equilibrium concentration. Although, if the initial slope is compared with July, differences between treatments are even smaller compared to the equilibrium concentration.

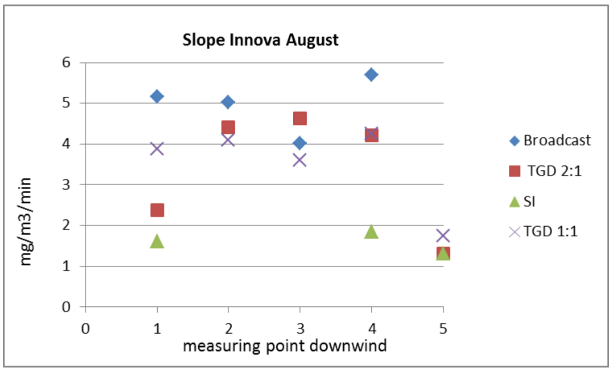

Figure 28. Initial slope (mg m^3 min^{-1}) in August, right after manure application

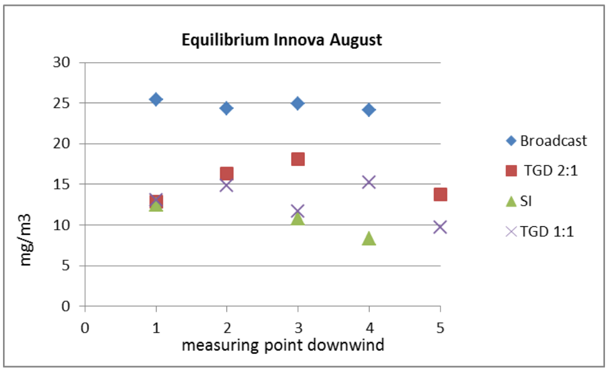

Figure 29. Equilibrium concentration (mg m^3) in August, right after manure application

3.5 General results

13 m^3 manure per hectare was applied for all experiments by broadcast, TGD 2:1 and TGD 1:1, due to different manure content the amount of TAN applied differed among the experiments. In April 22 kg TAN per hectare was applied, in May 31 kg TAN ha^{-1}, 16% more manure was applied for shallow injection and 13% more manure for TGD 1:2. In July 18 kg TAN ha^{-1} and in August 17 kg TAN ha^{-1} was applied. During the experiments in April, July and August a little less than ½ more manure was applied with shallow injection.

For each measuring method (the concentration of the diffusion samplers, the emission rate and the equilibrium concentration) the average of all approved measuring points of one treatment were calculated, thus the average of the data presented in the previous paragraphs. Subsequently, treatments of one experiment were compared with broadcast and relative values were obtained.

3.5.1 Diffusion samplers

The diffusion samplers collect the emitted NH_3 in total and is internationally excepted to compare treatments. The diffusion samplers in April and May were exposed for 72 hours and in July and August for 24 hours. To compare the results of the diffusion samplers, it was necessary to set the sampling time for April and May to 24 hours in Equation 3. when calculating the concentration. Instead of dividing the sampled amount to 72 hours, to get a concentration over the actual exposure time, the sampled amount was divided by 24 hours. According to the time experiments (Chapter 4) it could be assumed that no significant emission would have been occurred after 24 hours. The NH_3 concentrations per experiment are show in Figure 30. Because no equal amount of manure / TAN was applied for all experiments and treatments, emission was calculated for 20 kilo TAN ha^{-1} applied in order to compare the experiments in Figure 31. It was tentatively assumed that under equal circumstances a double amount of manure / TAN applied results in a double amount of emitted ammonia.

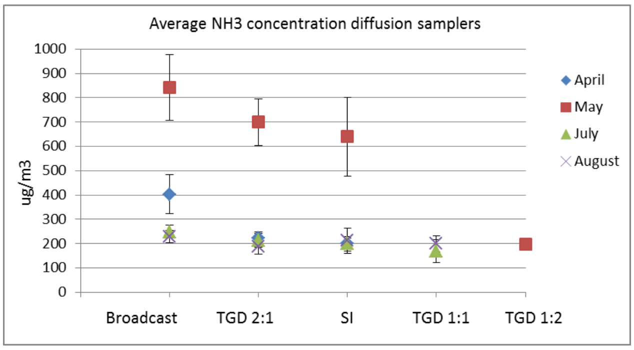

Figure 30. Measured NH_3 concentrations (µg m^{-3}) over 24 hours, of all experiments together. For amounts of applied TAN see Table 6.

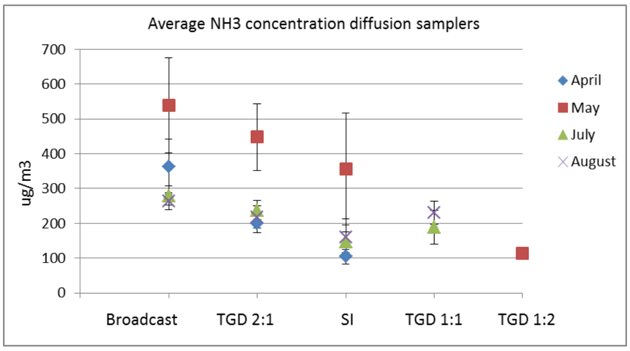

Figure 31. NH_3 concentrations (µg m^{-3}) over 24 hours, of all experiments together, assuming (i) 20 kg TAN ha^{-1} applied for all experiments and (ii) a linear relation between TAN applied and NH_3 emitted

When comparing the average concentration of the diffusion samplers, TGD 2:1 reduces the NH_3 concentration with 23% compared to broadcast. The two experiments with TGD 1:1 reduced NH_3 concentration with on average 22%, however, difference between those particular two experiments were little. The relative emissions per experiment are shown in Table 6. Assuming a linear relation between TAN applied and NH_3 emitted shallow injection reduced emission with 48% and TGD 2:1 with the experiment in May with 79%.

Table 6 shows the relative emission as measured (A) and by assuming a linear relation between TAN and NH_3 emission (B) for these two treatments.

Table 6. Relative concentration diffusion samplers compared to broadcast. TAN applied in kg ha^{-1} is mentioned between brackets. A = as measured B = assuming a linear relation between TAN applied and NH_3 emitted

	April	May	July	August
Broadcast	100 (22)	100 (31)	100 (18)	100 (17)
TGD 2:1	55 (22)	83 (31)	85 (18)	83 (17)
Shallow injection A	50 (39)	76 (36)	80 (27)	93 (27)
Shallow injection B	29	66	52	61
TGD 1:1			68 (18)	88 (17)
TGD 1:2 A		24 (35)		
TGD 1:2 B		21		

3.5.2 Initial slope & equilibrium concentration

The NH_3 concentrations were measured with the closed flux chamber only right after manure application. So the emission rate right after manure application is calculated with the maximum initial slope and the dimensions of the chamber as described at the end of paragraph 2.2.2. The different emission rates are visible in Figure 32. Because it is likely that the initial slope and thus the emission rate of May does not represent the actual emission rate, these results are not presented. It is striking that in August the NH_3 concentration of TGD 1:1 did not differ from TGD 2:1.

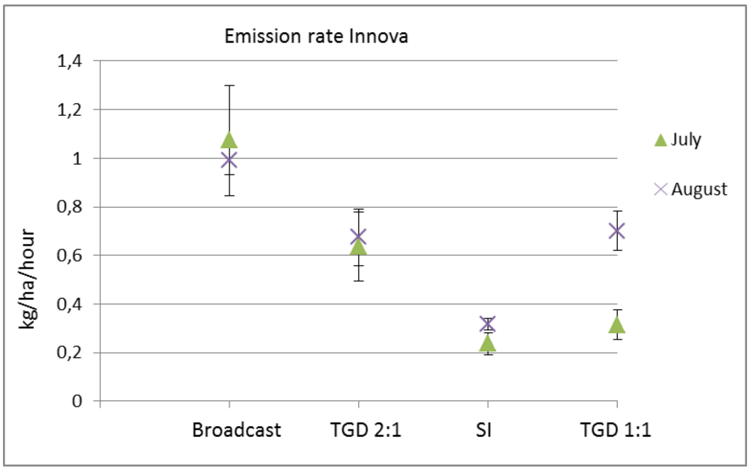

Figure 32. Average ammonia emission rate (kg NH_3 ha^{-1} h^{-1}) just after manure application. For amounts of applied TAN see Table 7.

No linear relation can be assumed between emission rate or equilibrium concentration and amount of TAN applied, therefore Table 7 shows the emission rates relative to broadcast together with the amount of TAN applied.

Table 7. Relative values of the initial emission rate just after manure application compared to broadcast, TAN applied in kg ha^{-1} is mentioned between brackets.

Emission rate	July	August
Broadcast	100 (18)	100 (17)
TGD 2:1	59 (18)	68 (17)
Shallow injection	22 (27)	32 (27)
TGD 1:1	29 (18)	71 (17)

The relative emissions of all application techniques are higher in August, but it is remarkable that the relative emission of TGD 1:1 is even higher than TGD 2:1.

If the equilibrium concentration of the experiment in May is compared with broadcast, TGD 2:1 reduces NH_3 concentration with 34%, shallow injection with 42% and TGD 1:2 with 62% (Figure 33 and Table 8).

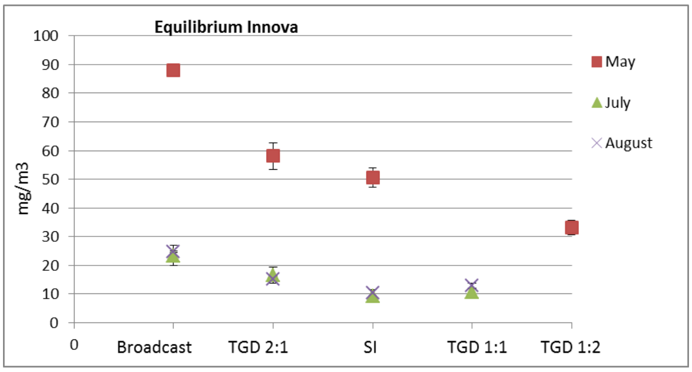

Figure 33. Average ammonia equilibrium concentration (mg $NH_3 m^{-3}$) just after manure application. For amounts of applied TAN see Table 8).

Table 8. Relative equilibrium concentration compared to broadcast. TAN applied in kg ha^{-1} is mentioned between brackets.

Equilibrium	May	July	August
Broadcast	100 (31)	100 (18)	100 (17)
TGD 2:1	66 (31)	71 (18)	61 (17)
Shallow injection	58 (36)	40 (27)	43 (27)
TGD 1:1		46 (18)	52 (17)
TGD 1:2	38 (35)		

Overall, the average results showed large variations between measuring techniques, although the general pattern is clear. The NH_3 concentrations of the experiment in May are much higher compared to the other experiments. Shallow injection appeared to be best technique to reduce NH_3 concentration when compared with the standard version of The Green Duo (manure : water ~ 2 : 1). As expected, although there were only little experimental data, applying more water with The Green Duo led to a significant reduction in the NH_3 concentration.

3.6 Transport of NH_3

3.6.1 NH_3 concentration pattern in the field

The first measuring sites of all comparison experiments were located about one meter from the edge of the manured plot, except in May about seven meter from the edge. Time between manuring and instalment of the first and last diffusion samplers of one plot (five measuring points) was within about 1.5-2 hours. Most of the concentrations of the first measuring sites of broadcast, TGD 2:1 and TGD 1:1 were the lowest compared to the other measuring site for all experiments. However, the lowest concentrations of shallow injection were not located on the edge.

In general the results with the diffusion samplers show that NH_3 concentrations do not show higher concentrations along the fetch at a height of 20 cm. Instead, starting from the edge of the field, a quick increase in NH_3 concentrations within the first 20 tens of meters occurred. Thereafter, the average NH_3 concentration remained unchanged up till the downwind end of the field. This is illustrated by Figure 34, where the relative NH_3 concentration at each of the five measurement locations downwind is presented. Due to grass height the diffusion samplers of the experiment in April are not representative (see Paragraph 5.4) and therefore excluded in this graph.

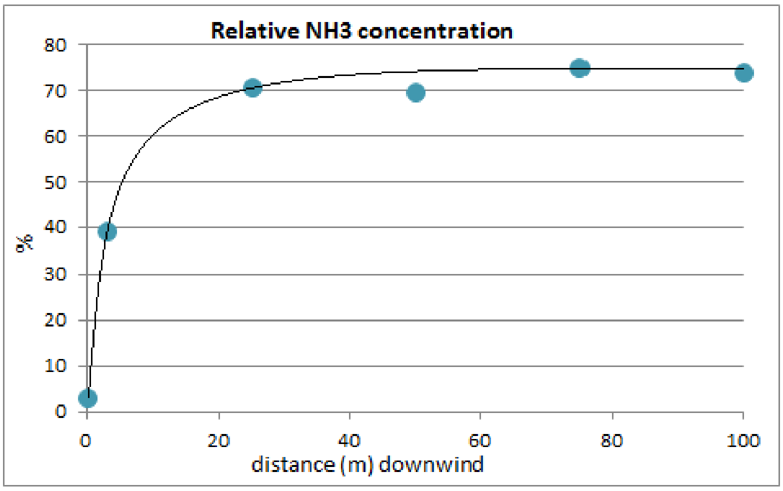

Figure 34. Relative NH_3 concentration downwind at 20 centimeter height of the experiments in May, July and August. Per application technique and experiment, the highest concentration of a single measuring point is taken as 100% and the relative NH_3 concentration of the other measuring points are calculated. Then the average relative NH_3 concentration of each of the five measuring points could be calculated and is represented by the blue dots in the graph. On average, the first measuring point was located at 2 meters from the edge, the second, third, fourth and fifth measuring point at 25, 50, 75 and 100 meter respectively. The relative NH_3 concentration at the beginning of the plot (0 meter) represents the background concentration of about 5 µg m^{-3}.

3.6.2 NH_3 concentration of increasing distance behind the manured plot.

NH_3 concentrations of all distance experiments were calculated over 24 hours. On June 29th 54 kg TAN per hectare was applied, on August 15th 39 kg TAN per hectare. Figure 34 illustrates that the NH_3 concentration behind the manured plot decreases exponentially with increasing distance.

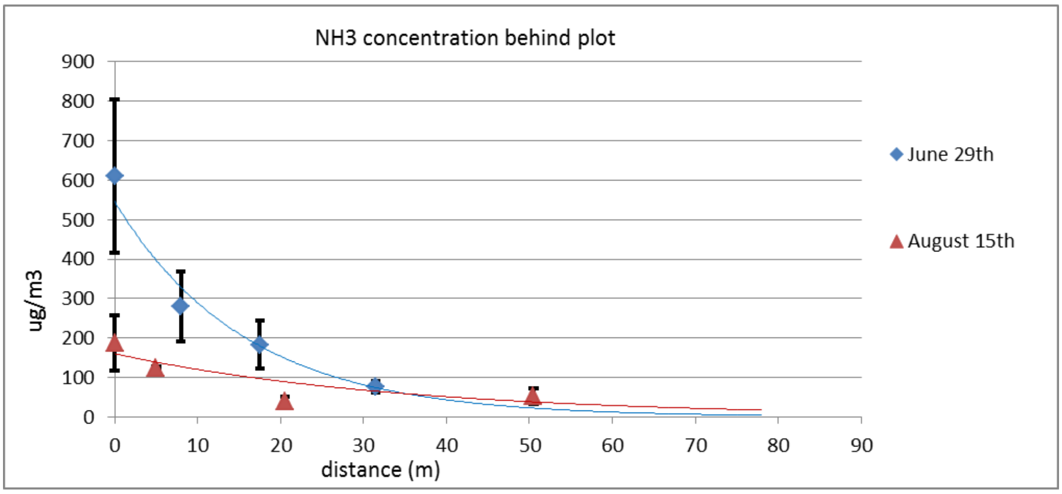

Figure 35. NH_3 concentration (µg m^3) over 24 hours behind the plots of all three distance experiments. The concentration shown at 0 distance are in the middle of the manured plot. The distance behind the manured plot is given from the leeward edge of the plot

4. NH_3 concentration pattern in time

The time experiments were performed with The Green Duo 2:1 on June 1th, June 29th and August 15th, were 19, 54 and 39 kg Tan per hectare was applied respectively. All three experiments had three plots, when one plot was manured the diffusion samplers were installed near the flux chamber, in the middle of the plot. After finishing the measurement, the next plot was manured.

4.1 Collected NH_4 time experiments

Diffusion samplers were installed in a row next to each other, facing the wind in such a way that the fetch was the same for all samplers. At the experiment on June 1th one or two samplers were closed every hour, and from eight hours onwards, two samplers were closed per time period. During the experiments on June 29th and August 15th three samplers were closed every time period. Figure 35, Figure 36 and Figure 37 illustrate the collected NH_4 for the experiment on June 1th, June 29th and August 15th respectively. With the model parameters of Table 1 the non-rectangular hyperbola (Equation 6) was fitted.

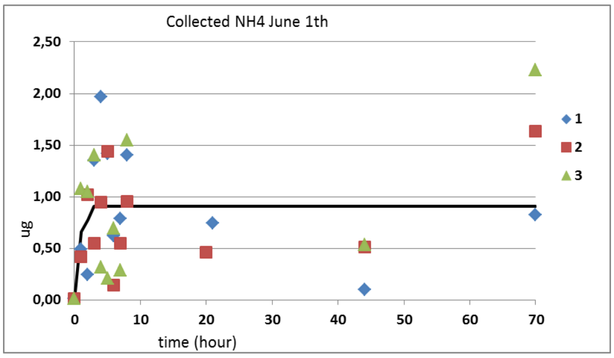

Figure 36. Collected amount NH_4 (µg) over time on June 1th of all three replicates (symbol 1,2 and 3) and the fit with the non-rectangular hyperbola (Equation 6)

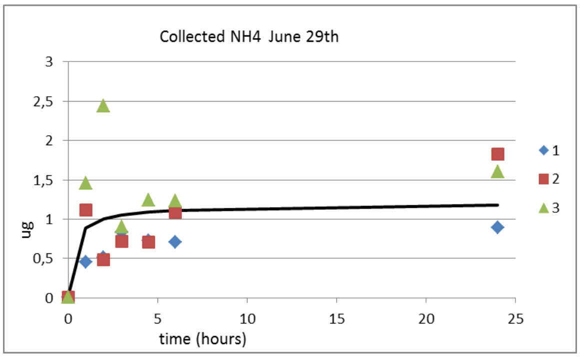

Figure 37. Collected amount NH_4 (µg) over time on June 29th of all three replicates (symbol 1,2 and 3) and the fit with the non-rectangular hyperbola (Equation 6)

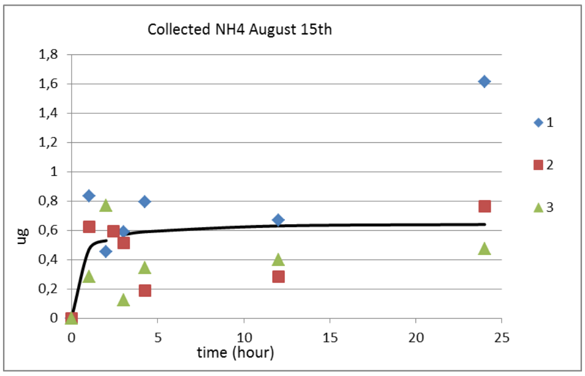

Figure 38. Collected amount NH_4 (µg) over time on August 15th of all three replicates (symbol 1,2 and 3) and the fit with the non-rectangular hyperbola (Equation 6)

These figures illustrate that the variation between the different diffusion samplers is large and the collected amounts of NH_4 are not increasing any longer after two to six hours.

4.2 NH_3 flux INNOVA time experiments

Right after manure application the NH_3 concentrations were measured with the INNOVA and this is called time 0, after one hour (or another time period) the same measuring point was measured again, this procedure was repeated until saturation was reached. Not all measurements with the INNOVA could be used in the three time experiments. On June 1th the first and second measuring site did not follow the normal emission pattern of Figure 12 (see also Appendix 1), for the same reason measuring site two on June 29th and all results of August 15th were not approved.

4.2.1 NH_3 flux June 1th

On June 1th only the third measuring site was approved, Figure 38 shows the measured concentration of each hour after the manure was applied. Time 0 was within minutes after application and time 4 was 4 hours after manure application. After time 5, the time period elapsed between measurements became smaller than one hour, time 8 was 7 hours after manure application.

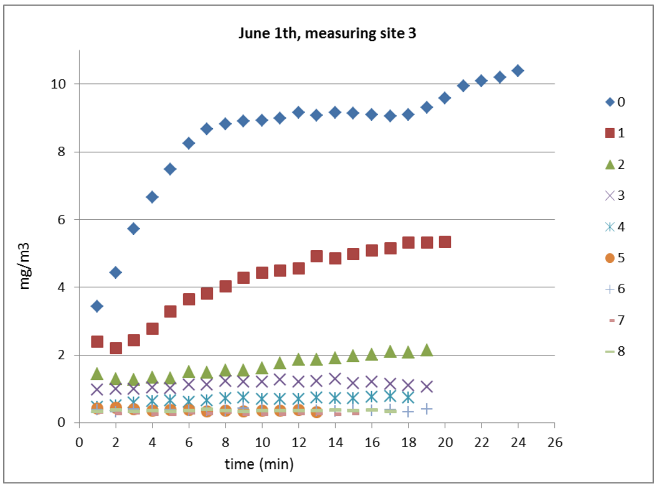

Figure 39. Measured concentrations of measuring site 3 from all time periods(0-8)

The initial NH_3 emission for each hour varied from 1.3 mg m^{-3} min^{-1} at time 0, to 0.07 mg m^{-3} min^{-1} at time 4. These slopes are calculated to a flux rate expressed in kg ha^{-1} hour^{-1} and are shown in Figure 39. With the exponential trend line parameters A and B were derived to fill in Equation 7, 0.259 was filled in for A and -0.795 was filled in for B, thereafter 0.325 kg emitted TAN ha^{-1} was calculated in case 19 kg TAN per hectare was applied. This application rate corresponds with the management of the farm. The flux rate of June 29th is low compared to the flux rates of other experiments.

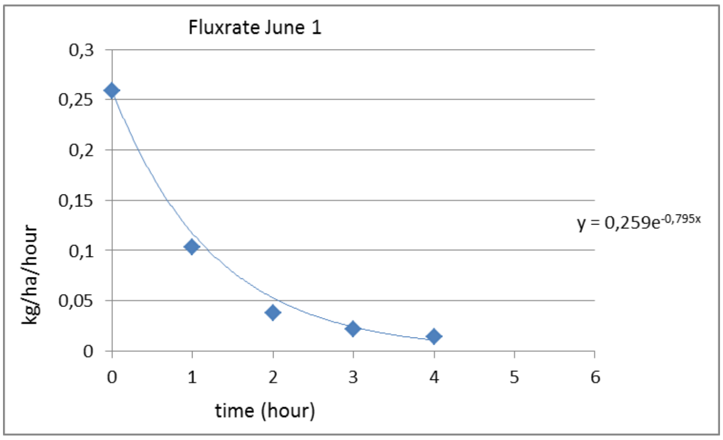

Figure 40. Hourly flux rate, on June 1th in kg ha^{-1} hour^{-1}

4.2.2 NH_3 flux June 29th

For June 29th the first and third measuring site were approved. Figure 40 and Figure 41 show the measured concentration of each time period after the manure was applied. Time 0 was within minutes after application but time periods differed between the measurements. Figure 42 illustrates the actual time between the measurements. To make this research more comparable with other foreign investigations it was decided to apply manure in larger quantities than is normal in the farm management. Therefore 54 kg TAN ha^{-1} was applied. Accidently, a double amount of manure was applied at the third measuring site.

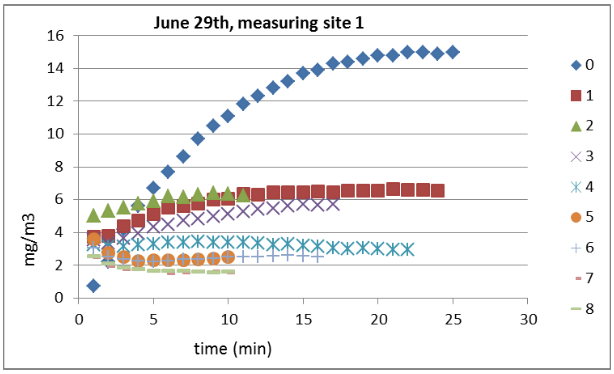

Figure 41. Measured concentrations of measuring site one from all time periods (0-8) on June 29th

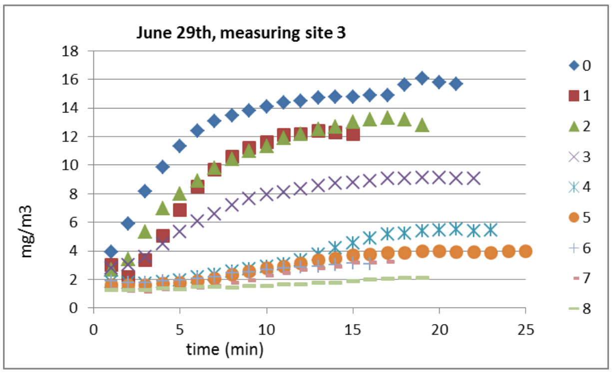

Figure 42. Measured concentrations of measuring site three from all time periods (0-8) on June 29th

The slopes of measuring site one varied from 1.95 mg m^{-3} min^{-1} at time 0, to 0.09 mg m^{-3} min^{-1} at time 4. And those of measuring site three from 2.24 mg m^{-3} min^{-1} at time 0, to 0.15 mg m^{-3} min^{-1} at time 8. These slopes were re-calculated to a flux rate expressed in kg ha^{-1} $hour^{-1}$ and shown in Figure 42.

With the exponential trend line parameters A and B were derived to fill in Equation 7. For calculating the absolute emission of measuring site one, 0.3886 was derived from the exponential trend line for A and -0.799 for B, whereafter 0.486 kg emitted TAN ha^{-1} was calculated
For measuring site three, 0.5463 was derived for A and -0.479 was derived for B and resulted in 1.14 kg TAN ha^{-1} that was emitted.

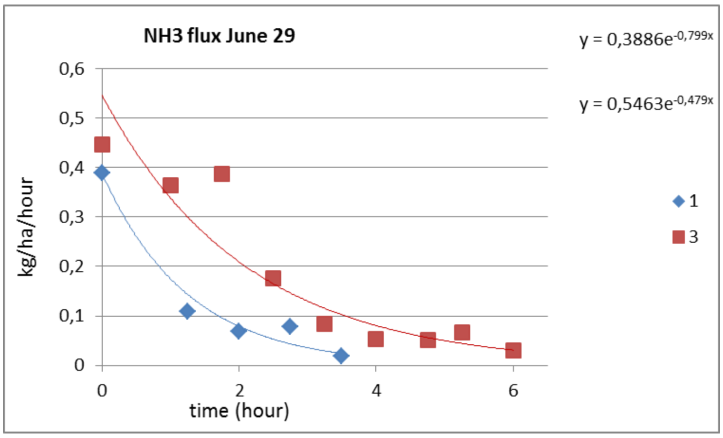

Figure 43 . Hourly NH_3 flux on June 29th

4.2.4 Total
In Table 9 the amount of TAN applied is compared with the measured emission in the flux chamber, the result show that the absolute emission of TGD 2:1 is not higher than 2%.

Table 9. Overview of the TAN applied, TAN emitted and the percentage of TAN that was emitted (emission factor)

	June 1st	June 29th	
		Point 1	Point 3
kg NH_4 -N ha^{-1} applied	19	54	109
kg NH_3-N ha^{-1} emitted	0.3	0.5	1.1
Percentage emitted (%)	1.7	0.9	1

5. Discussion

In this chapter an attempt is made to place the results in a context as regards to reliability and representativeness. The results will be summarized and factors and circumstances influencing emission will be discussed. Thereafter, extrapolating speculations are addressed and future research and recommendations will be discussed.

5.1 Representativeness

This research compared broadcast spreading, TGD 2:1 and shallow injection four times with each other, two experiments were done with TGD 1:1 and one experiment was done with TGD 1:2. The results of broadcast, TGD 2:1 and shallow injection were based on twenty measuring sites in total. The data of most of the passive diffusion samplers could be used, thirteen outliers were removed in total. Each measuring site contained three diffusion samplers, hence the results are based on almost 60 diffusion samplers per treatment in total. Not all data of the measurements with INNOVA could be used, especially in April most data was rejected and in May, TGD 1:2 had only one useable measurement. The time experiment of INNOVA on June 1th is based on one measuring site, the experiment on June 29th on two measuring sites. Although measuring sites were judged on representativeness, the spatial representativeness is low with measurements on 0.07 m^2 with INNOVA.
The variation in the field is likely to be high if one looks at the results of the diffusion samplers, the INNOVA results of the experiments in July and August however, show that the variation in the field is not that great. The distribution of the manure could certainly be improved for both techniques in the future. However, the NH_3 concentrations of TGD 1:2 measured with the diffusion samplers indicate that here the distribution pattern seemed to have been very good. The emission reduction of shallow injection depends a great deal on the depth of the slots, since poor manure distribution with shallow injection regularly occurred in this research, it is likely that the emission reduction achieved with shallow injection could be larger.

5.2 Reliability

The weather data used can only be seen as an indication of the weather circumstances, since the data for the temperature, humidity and wind speed during the day were obtained from weather stations within the Provence and data from the weather station in Uithuizermeden was read from the graphs. The data from the weather station 3000 m near the experimental plots did not give precise data during the day.

Ten soils samples from each experimental plot, two manure samples from the tank and the mixed cellar and one water sample from each experiment were taken. Variation in the field, manure and water can be high, so these samples should be seen in that context.

A margin is recommended for the amount of manure applied. During the first field experiments in April the amount of applied manure was calculated by the amount of emptied tanks and the surface was calculated from the map. The tank with manure and water is weighted once. From May onwards plot sizes were measured and, if necessary, the remaining manure (and/or water) was applied until the tank was empty. During the comparison experiment in April, at the fifth measuring site half of shallow injection, slots did not receive manure, alternated per two slots. Measurements were performed on the two slots that did receive manure and it was assumed (with the surface of the area) that a double amount of manure was applied.

Hammering the rings into the soil the day before the start of the experiment in May could have affected the results. The water that was used resulted in a higher moisture content of the soil near the measuring points, compared to the soil of the other experiments done with summer-like weather (Table 11). Measuring sites were chosen on beforehand and so the spots were not always representative, especially for shallow injection. During all other experiments spots were chosen the in between the edge of the tires and the end of the spraying width, this was not always the case during the experiment in May. During the other experiments two bands of equal length were covered by the ring, but this was not always the case in during the experiment in May.

5.2.1 Diffusion samplers

The field of the plot of shallow injection in August had a minor slope on the border in the middle of the plot, between measuring site three and four. In the past this used to be a ditch. The third and fourth measuring site were not located in this minor slope, but the pattern of turbulent diffusion of this plot will differ from the other experimental plots.

The average diffusion coefficient was calculated for each experiment with the maximum temperature and relative humidity of that day, but in reality the diffusion coefficient differed during the day. However, this minor change in diffusion coefficient can't have caused significant effects on the results.

In each of the comparison experiments of May and August and the experiments on June 29th and August 15th one blank sampler contained some NH_4. This could be due to accidently exhaling, skin contamination or some other unknown contamination.

NH_3 background concentrations appeared to be too low to be detected by the diffusion samplers accurately over a short time period. In the experimental area the average background concentration was 5-10 µg m^{-3} (Velder et al., 2012).

5.2.2 INNOVA
INNOVA can measure the NH_3 concentration accurately from 0.141 mg m^{-3} on (Gas Detection Limits, Luma Sense Technologies). Therefore the background concentration of 5-10 µg m^{-3} could not be measured and concentration readings between 0.1 and 0.3 mg m^{-3} were seen instead. Hood (2011) validated the INNOVA and predicted a relative error of 21% for the lower range of concentrations.

INNOVA results were judged based on the normal diffusion pattern as presented in Figure 12. Not all INNOVA results passed the selection because a leak of NH_3 to the outside the chamber occurred. The selection was made by two persons. In three cases a leak occurred before the equilibrium was reached. If the slopes of these measurements followed the same pattern as the corresponding other measurements, they were approved. The NH_3 concentration pattern of the time experiments in August did not follow normal emission pattern, the initial slopes could be approved, but the reliability of these experiments was found to be too low.

It seemed that air of the previous measurement remained in the circuit of INNOVA when the next measurement was started. Subsequently, the concentration at time 0 could have been higher than the actual concentration at time 0. Ultimately, this can affect the slope, especially when NH_3 concentrations are low. It is not certain how the slope changes if the concentration at time 0 actually represents the actual environment, but it is likely that there is an effect. The diffusions samplers and equilibrium concentration in May were both considerably higher compared to the slope of the experiments in July and August. Overall, the difference was a factor two. This is an indication that slopes are underestimated if air with a high concentration remains in the circulation system of INNOVA. Appendix 1 describes the learning process during the experiments.

From June 29th on, air from outside was circulated in the INNOVA for approximately two minutes before the next measurement started. During the last measurement of TGD 1:2 in May condensation was discovered in the tubes. Condensation in the chamber and high water solubility of NH_3 can cause NH_3 to absorb onto surfaces through the entire sampling system. This results in a time delay (or other errors) when large concentration differences are measured (Rom & Zhang, 2010) and thus affects the slope. An underestimation of a factor 2.4 was derived in this research. Hood (2011) also measured a delay. However the equilibrium concentration in the chamber is not affected by this because NH_3 absorption finally always reaches a saturation. From the experiment in May on, extra attention was paid to condensation. During the experiment on June 1th and 29th and August 13th condensation was discovered and tubes were 'cleaned' by the forced airstream of a compressor indoors. This might be the reason why not all measurements with INNOVA followed normal NH_3 concentration pattern and were rejected. Rom & Zhang (2010) conclude that a strategy need to be developed if measurements with high differences in concentration levels will be measured, to obtain a reliable dataset or reliable correction factors. Predotova et al. (2010 found that NH_3 N_2O, CH_4 and CO_2 have cross interferences with water vapour and gases in the flux chamber, when measured with INNOVA. The errors they found trough validations sessions point out that the average error is NH_3 is -13%.

Rings were not hammered into the soil at equal height, differences were only few cm. The decrease in chamber volume is minor and so is the influence on the result. Not using the non-rectangular hyperbola of Equation 6 can't lead to an underestimation of the initial slope since the each single initial slope (the maximum difference between two measured concentrations) is used to represent the (maximum) instantaneous NH_3 emission rate.

It was assumed that significant emission stopped when no increase in concentration was measured. In the time experiment this measured equilibrium concentration was not lower than 0.35 mg m^{-3}. The detection limit of INNOVA is 0.141, Even if the detection limit was more accurate and INNOVA would measure an increasing NH_3 concentration, it is not likely that this would have had significant contribution to the total amount emitted. NH_3 concentrations of the first hours are higher than 2 mg m^{-3} and contribute most to the total amount emitted. Moreover, NH_3 concentrations of 2 mg m^{-3} are already very low.

5.3 NH_3 emission pattern in time

The time experiments with The Green Duo 2:1 show that by far most of the emission takes place in the first hours. On June 29th 54 and 109 kg ha^{-1} TAN was applied and 0.9 and 1% TAN emitted respectively, this indicates a direct relation of TAN and NH_3 emission. At the time experiment on June 1th, a considerably lower amount of manure was applied (19 kg TAN per hectare) and more TAN was emitted (1,7%). The circumstances (manure and weather) were equal or in favour of lower emissions on June 29th (appendix page 58).

Spirig et al. (2010) found that emission becomes insignificant after three to six hours, when manure was broadcast applied. Sanz et al. (2009) found a similar emission pattern, emission became insignificant after 24 hours for broadcast applied manure but a fast decline was measured in the first few hours. Sintermann et al. (2011) also found a fast decline of NH_3 emission with broadcast spreading. It is likely that the emission in time for shallow injection differed from TGD 2:1. During the time experiments few diffusion samplers were closed from six hours on, since the variation in the field is high and the increase in amount of NH_4 is expected to be low, more samples are needed for a more precise determination of the decline in time.

Mosquera et al. (2012b) used absolute NH_3 emission measured with INNOVA in a laboratory study to compare the relative emissions of manure separation of different types of manure. The emission was measured from small jars containing soil and manure with a diameter and a length of 10 cm. Very low absolute emissions were calculated using a method similar to this research. 100 kg NH_4-N ha^{-1} was applied per treatment and the highest emission measured was 0.17% TAN. The emission rates were far lower on the first day, compared to this research. But minor emission rates were measured on the second and third day, these emission rates were similar to the measured concentration of this research after two or three hours. The soil in the jars were provided with water every day, although not suggested by the authors, this might have stimulated the NH_3 emission and can explain why this research did find emissions days after manure was applied. The measurements were not done in a field situation, Mosquera et al. (2012b) explained the low emission factors by the absence of wind and other weather circumstances that stimulate emission.

Absence of wind

Blanes-Vida et al. (2007) validated the flux chamber system by performing a comparison between the flux chamber emission rates and whole-building emission rates calculated from an NH_3 balance in a mechanically ventilated experimental test room. The authors mention in their report that the emission measured with a closed flux chamber can maximally be underestimated five to seven times, but this appears not from the article itself. By turning up the internal ventilation, the NH_3 emission decreases with maximal a factor three (Figure 43). However, the dotted horizontal line in the graph was determined by external air that had a far lower NH_3 concentration. Therefore, this is not realistic for a manured field, and it is likely that under real field conditions the underestimation is in all probability much less. It is also this principle why wind tunnels overestimate the NH_3 emission rate too.
The black squares in Figure 43 represent the NH_3 emission calculated with the flux chamber at eight locations. The disrupted line represents the NH_3 emission calculated from the NH_3 balance in the experimental room.

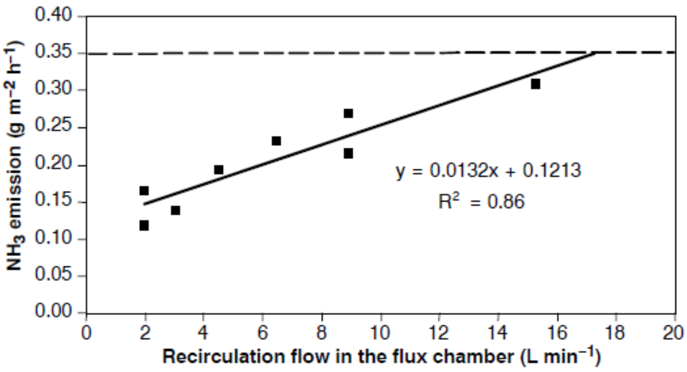

Figure 44. Underestimation INNOVA (Blanes-Vida et al., 2007)

If the time delay by interferences (factor 2.4) and the absence of wind (factor 2) of these laboratory studies (Blanes-Vida et al., 2007; Predotova et al. 2010; Rom & Zhang, 2010; Hood, 2011) would be extrapolated to this study, the maximum derived emission factor in our experiments is in the order of ten per cent.

5.4 Relative NH_3 concentrations

Only the diffusion samplers of the experiments in May, July and August can give a picture of the ammonia emission reduction of the different techniques compared to broadcast. The concentrations obtained with the diffusion samplers in April were not different from those found in July and August (Figure 34). This could be explained by grass length, the grass could have contaminated the diffusion samplers. Some diffusion samplers were dirty on the outside, but it is not certain if this was caused during the time the diffusion samplers were exposed. Moreover, the diffusion samplers were closer to the source compared to the other experiments, therefore higher concentrations are more likely. This means that the diffusion samplers of April are not representative and need to be excluded from the average emission reduction. The INNOVA results (equilibrium concentration and emission rate) right after manure application are excluded from the average emission reduction, because the emission right after manure application might be different from the total emission that will occur after 1-4 days. From the time experiments on June 29th it appeared that the a double amount of manure did not result in a double equilibrium concentration or emission rate right after manure application. Instead, the equilibrium concentration and emission rate in time were higher and continued longer.

When results of the experiments in May, July and August measured with the diffusion samplers are averaged it appears that The Green Duo 2:1, which standardly contains 10 m^3 manure and 4.1 m^3 water, reduces NH_3 concentration compared to broadcast with 23%, the two experiments with TGD 1:1 (10 m^3 manure and 8.2 m^3 water) reduced NH_3 concentration with 32% and 12% When a linear relation between NH_3 emission and TAN applied is assumed, shallow injection reduced NH_3 concentration with 49% compared to broadcast and the single experiment with TGD 1:2 reduced NH_3 concentration with 79%. The reductions found for all treatments are lower than expected, this might be an effect of low concentrations that were already measured with broadcast. The results hypothesize that a manure : water ratio of 1:1 is necessary to ensure emission reduction under all circumstances. There are still some technical improvements that can be done on The Green Duo, further research needs to be done to obtain a more reliable relative NH_3 concentration factor.

There is a large variation in the results and not everything can be explained because many factors influence NH_3 emission. Especially in August differences between the treatments measured with the diffusion samplers were not high. There was some manure spilled and the width of the plots was limited (20 meter). No change in wind direction was observed, not during the experiment nor in the data, however the wind could have changed direction unnoticed. These uncertainties together might explain the deviating results.

During the experiments of May (and April) samplers were exposed 72 hours. Because in the additional experiments after 6 hours no significant increase in NH_3 concentration were measured with INNOVA and no significant increase in collected NH_4 was measured, it was assumed that emission was insignificant after 24 hours. Therefore, samplers were exposed for 24 hours during the experiments in July and August. For comparing the results of the samplers, the sampling time in Equation 3. was set to 24 hours for the experiment in May.

5.5 Factors influencing NH_3 emission

There are a lot of factors influencing the NH_3 emission during manure application, literature gives a complex images of these factors (Cabrera & Kissel, 2005) and factors are interrelated.

5.5.1 VPD, TAN and dry matter content

Vapour Pressure Deficit in May was high and Total Ammoniacal Nitrogen content was above the average. Also NH_3 concentration of the diffusion samplers and equilibrium measured with INNOVA were relatively high. However, the VPD of the first hour of broadcast manure application was not much higher compared to July and August. The influence of TAN content on NH_3 emission concur with the results of Sommer & Hutching (2001) and Pinder et al. (2004). And the influence of air humidity is confirmed by Sommer (1991b).

Sommer et al. (1991b) concluded that an increasing ammonia emission with increasing VPD is especially an effect of temperature. Most literature indicate a significant relation between temperature and NH_3 emission, therefore temperature seems to be one of the main factors influencing NH_3 emission (Huijsmans et al., 2001; Pinder et al., 2004; Cabrera & Kissel, 2005). However, Misselbrook et al. (2005b) did not found this effect, they state that this might be due to interactions with other factors.

The water samples of July contained 1.65 NH_4-N l^{-1} and in August 2.38 NH_4-N l^{-1} this is substantially higher compared to the other experiments and could have resulted in a higher emission, however this is not visible in the results.

5.5.2 Soil CEC & pH

Although in May, July and August the experiments were done on the same plot there were some differences in soil characteristics, possibly due to the large variation in the field (Table 10). No relation between the differences in soil characteristics and the NH_3 emission of the treatments could be found. NH_3 emission depends on soil type, but infiltration is more influenced by dry matter content of the soil than by soil type. Because of improved infiltration, Sommer (1991a) found lower emission with dry soils. The results of this research did not indicate such a relation, probably because other factors were dominant.

Higher Cation Exchange Capacity results in a lower NH_3 emission (Freney et al., 1983; Cabrera & Kissel, 2005) because dissolved NH_4 is positively charged and will be attracted to negative charges in the soil and its organic matter. In 2007, the soil of the comparison experiment in July had an CEC of 22 cmmol kg^{-1}, the soil of the distance experiment in August had a CEC of 20 cmmol kg^{-1}, other soils surrounding the farm had a CEC of 12,18 and 22 cmmol kg^{-1}. The region's average of clay soils is 24 cmmol kg^{-1}, none of the CEC's measured in 2007 on the farm were higher than the region's average. Freney et al. (1983) summarized literature and concluded that CEC has to be higher than 25 cmmol kg^{-1} to reduce NH_3 emission substantially. Therefore, it is not likely that CEC is an explanation for the low emission factors. Higher pH results in a higher NH_3 emission (Freney et al., 1983; Pinder et al., 2004; Cabrera & Kissel, 2005). The pH of the manure as well as the soil was high compared to the average pH, therefore this doesn't neither explain the low emissions found.

5.5.3 Wind speed and solar radiation

Sommer et al. (1991b) conclude that the influence of wind on NH_3 emission increases at wind speeds until 2,5 m sec^{-1} between 2,5 and 4 m sec^{-1} no consistent increase was found. Génermont & Cellier (1997) also didn't found a direct relation between NH_3 emission and wind speed.

Solar radiation increases NH_3 emission (Sommer & Hutchings, 2001) because it increases the turbulence in the atmosphere, which leads to and increased transport of NH_3. Moreover, it increases evaporation which leads to a higher TAN concentration in the manure and it increases temperature of the manure (Sommer & Hutchings, 2001). Sommer et al. (2003) found with low solar radiation an increased NH_3 emission with increasing wind speed, while they found a NH_3 reduction when wind speed increases with high radiation. Lower surface temperature caused by the wind is the explanation. To decrease the number of toxins and antibiotic resistant genes higher solar radiation is preferred, although cool and dark weather in general result in lower emissions.

5.5.4 Earthworms

Especially during manure application in May and July it was observed that many worms came to the surface while manure was applied with shallow injection. It was also observed that a lot of worms came to the soil surface and died during the time experiments were manure was applied in large quantities (30-40 m^3 ha^{-1}) with The Green Duo 2:1. However, the earthworms in this research were not quantified, so no conclusion can be drawn.

5.5.5 Implications of The Green Duo

The controllability of The Green Duo can be improved with modern techniques. Farmers can give information, for example via a website, about the time of application. In this way satellite images of that time can be found, or the controlling body can visit the farmer during application (personal communication E. Lantinga, 31-01-2012; De Haan et al., 2009). In addition, a GPS system combined with a flow meter can be installed on the tank (personal communication E. Lantinga, 31-01-2012; K. Wolters, 10-4-2012). When manure is applied with broadcast equipment, nitrogen recovery is lower compared to Low Emission Techniques (Groot et al., 2006; Huijsmans et al., 2008), less NH_3 emission result in a higher nitrogen availability for the plant. Since TGD reduces NH_3 emission, it is likely that this will be noticed in the nitrogen recovery. Therefore, registration of nutrients with Farm-specific EXcretion (BEX) should indicate if The Green Duo was used together with water.

Not all farms are located near a water source, a water reservoir where rain water can be collected might be a solution. Because TGD contains water the weight of the tank increases. For this reason TGD can have the same negative effects on soil structure and compaction like other LET's.

5.5.6 N_2O emission

Besides NH_3, the INNOVA measures N_2O, CO_2 and CH_4 concentrations. N_2O emissions were measured for four days in April and May, but have not been analysed in detail so far. However, the first impression is that considerable N_2O losses occurred, not only immediately after manure application but also during the days thereafter. These measured N_2O data need further analysis, before a conclusion can be drawn. According to Velthof et al. (2002) N_2O emission not only occurs in the days after manure application, but can continue even for several weeks.

5.6 NH_3 transport

NH_3 concentrations obtained with the diffusion samplers at a height of 20 cm in the manured fields show that starting from the edge of the field, a quick increase in NH_3 concentrations over a few tens of meters occurred (Figure 34). Thereafter, the average NH_3 concentration remained unchanged up till the downwind end of the field. Diffusion samplers behind the manured plot decreased exponentially (Figure 35). Most of the concentrations measured at the edge of the manured plot were lowest compared to the other measuring sites downwind, except for the concentrations of shallow injection. The start of the experimental periods were carefully chosen, on the day of the comparison experiments no significant changes in wind direction were visually detected. However, this was not measured. The time between manuring and instalment of the diffusion samplers of the first and last measuring sites downwind (1.5-2 hours) can't explain the found distribution of ammonia concentrations because even after that time emission still occurs and time between the individual measuring sites was much shorter.

Ryden & McNeill (1984) demonstrated that the NH_3 concentration at an height of 25 centimeter of the air from a manured plot was usually at least twice that observed at a height of 3 to 3.5 meter. In the horizontal flux density profiles of Denmead (1983) it is shown that the NH_3 concentration just above the grass are highest and that the decline in height is rapid. Part of the emitted NH_3 might have been past above the diffusion samplers. Therefore NH_3 concentrations have to be measured at several heights in future research. The wind speed layers of the air above the plant canopies does not reach 0 at ground level (Denmead, 1983, but at some height above ground between 0.2 and 14 centimeter (Ryden & McNeil 1984). Moving of grass was observed in all experiments and wind speeds measured a few meters above the soil were considerable (Table 4 and Table 5).

When calculating the NH_3 flux with the mass balance method, the measured NH_3 concentration is multiplied by the wind speed and divided by the fetch. This implies that when the fetch increases two times, the sum of the captured NH_3 concentration should increase two times as well. (Ryden & McNeill, 1984). When this mass balance principle is applied to the results of this research, higher NH_3 concentration downwind and NH_3 concentrations in the same range as the manured plot are to be expected. When it would have been possible to calculate the NH_3 emission with the mass balance method between two measuring points in the current research, this value would have been very low. This is in contrast with one of the assumptions of the mass balance method, i.e. that the NH_3 concentrations are low at the edge of the windward plot and increase gradually along the fetch. However, we only found a quick increase along the first tens of meters of the fetch, thereafter concentrations remained unchanged.

5.7 Absolute emissions

The time experiments were performed with The Green Duo 2:1, these results were extrapolated to the results of broadcast from the comparison experiments by considering in detail the relative emissions. TGD 2:1 reduced emission compared to broadcast with ¼ , therefore it was tentatively assumed that the absolute emission of broadcast was relatively ¼ higher than TGD 2:1. The maximum found emission factor in the experiments with TGD 2:1 is in the order of ten per cent, based on the above assumption, the emission factor for broadcast is then in the order of a few tens of per cent.

The emission factors formulated by the Commission Experts Manure Policy (CDM) for broadcast manure spreading is 74% and for shallow injection 21% (Huijsmans & Vermeulen as cited by De Haan et al., 2009; Groenestein et al., 2011). The emission factor for shallow injection as used in this research has never been measured to our knowledge, but has been simply derived as the average of trailing shoe application and a less shallow injection application technique. Like in our research, Spirig et al. (2010) and Sintermann et al. (2011a,c) also derived emission factors far below the official emission factor for broadcast manure spreading. Although the manure in these researches had favourable properties for a low NH_3 emission this could only explain part of the low emissions found. The experimental data were based on Aerodynamic Gradient Methods. However, by applying these methods also a number of assumptions have to be made.

5.8 Implications and future recommendations

We have been facing a lot of unforeseen calamities (leaking of NH_3, too high NH_3 concentrations at the start of a new measuring session, etc.), but were able to solve them for the greater part. This can also be regarded as a learning process.

This research should be repeated on different soil types, different farm managements and different weather circumstances to draw firmer conclusions about NH_3 emission reductions. It is also important that effects of factors like weather circumstances and manure quantities (and content) will be better quantified. Future research would be more reliable if weather data were obtained from the experimental site itself. It is recommended to practice more with equal distribution of manure and adjusting the manure application rate, so this will be equal for all treatments. A flow meter can contribute to a more precise application rate.

Simple experiments with the diffusion samplers installed on several heights and several distances on field scale combined with measuring wind profiles could further verify the mass balance principle. More details needed to be collected about the circumstances in the chamber, like temperature and air humidity.

Besides, broadening of this research, e.g. in a long term study, can also include these focus points:

- effects on soil fauna and micro-organisms;
- effect on toxins and antibiotic resistant genes;
- effect on sward and soil structure and compaction;
- effect of different manure : water ratio's;
- possibilities of controllability;
- effect on nitrogen recovery and dry matter yield;
- the time pattern of NH_3 emission for the different treatments.

6. Conclusion

The results of this research are exploratory, repetition of this research in more detail is necessary to draw firm conclusions. Though, the following answers can be given to the research questions:

1. **What is the relative ammonia emission of The Green Duo (manure:water=2:1) compared to broadcast manure spreading and low emission techniques?**

The Green Duo reduced ammonia emission compared to surface spreading with about 25% and in case of shallow injection the average reduction was in the order of 50%. However, when the manure:water ratio was 1:1 the Green Duo was just as effective as shallow injection and with a manure:water ratio of 1:2 the relative reduction was about 75%. The amount of applied water in the latter case corresponded with only 3 mm rainfall. During the experiment in May, when manure composition and weather circumstances were in favour of ammonia volatilization, absolute emissions as measured with diffusion samplers were two to three times higher compared to those obtained during the other measurement events. For example, the ammonia emission from shallow injection was then higher than from broadcast application in the other experimental periods. Therefore, it seems that manure composition and weather circumstances have a greater influence on ammonia emission than application technique.

2. **What is the ammonia concentration pattern on field scale at a height of 20 centimeter?**

NH_3 concentrations right at the windward edge of the plot were lowest in most of the cases, except for shallow injection. NH_3 concentrations close to the edge of the field were already substantial compared to the other measuring sites along the fetch. The results of the current experiments clearly demonstrated that downwind starting from the edge of the field, a quick increase in NH_3 concentrations within the first 20 meters occurred. Thereafter, the average NH_3 concentration remained on average unchanged up till the downwind end of the field. This implies that the ammonia emission measurement method which has been used in the Netherlands during the last decades (only considering the first 20 m of a manured field) has led to significant overestimations.
The NH_3 concentration behind the manured plot decreased exponentially with increasing distance. Within several tens of meters the concentration was already half of the concentration measured in the middle of the plot. These findings question the general assumption that ammonia is transported mainly by advection over the manured surface with wind, rather than through turbulent vertical diffusion.

3. **What is the time pattern of NH_3 emission when manure is applied with The Green Duo and what is the corresponding emission factor range ?**

The time patterns obtained with The Green Duo demonstrated that NH_3 emission becomes insignificant after two to six hours. The ammonia emission factor established with The Green Duo using a static chamber connected to a gas monitor was only 2% at the highest. Even when levels of underestimation determined in laboratory studies due to the absence of wind and other meteorological factors, the “sticky” nature of ammonia, time delay in the measurement equipment due to interferences with other gases and water vapour are taken into account, the emission factors were still in the low range. Manure, soil and weather conditions could only explain part of the lower emissions found.

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Appendix / supplementary

1. INNOVA selection

As mentioned in Chapter 2 not all results of INNOVA followed normal emission pattern due to leaking of NH_3. A selection was made by judging the results on pattern like figure Figure 44. For some measuring points in July and August the slope appeared reliable but a NH_3 leaked before NH_3 emission reached an equilibrium. This chapter of the appendix describes the encountered problems with INNOVA and how they were prevented in the following experiments .

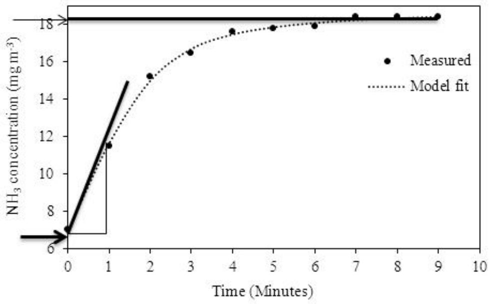

Figure 45. Example output INNOVA (Shah et al., 2012)

INNOVA results: learning process

Problem
During the first experiment in April leaking was likely to occur due to incorrectly levelling the rings without a plumb rule and the long grass that was difficult to keep away from the edge of the ring.

Learned:
Within the next experiments not only a plumb rule was used, also a steady template in the same size of the ring was hammered into the soil before hammering the actual ring into the soil. This was necessary because the soil was dry and it took force to hammer the rings into the soil.

Problem:
At the last measuring point of TGD 1:2 in May some condense was discovered in the tubes, this might be due to the low air humidity and high outdoor temperatures while much water was applied to the soil. In this experiment high NH_3 concentrations were measured, it appeared that the concentrations at time 0 were influenced by the air still left in the tubes and INNOVA. This is demonstrated in Figure 45, this was the first measurement of the experiment in May. Therefore the concentration at time 0 from first measuring point was low while the concentration at measuring point 3, 4 and 5 even decreased.

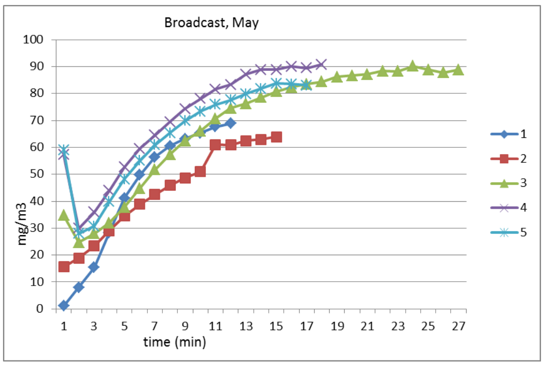

Figure 46. INNOVA results of broadcast in May, measuring points 3, 4 and 5 are approved

Learned:
From the experiments in May on extra attention was paid to condensation and tubes were ‘cleaned’ by a the forced airstream of a compressor. The tubes of the experiments from June 29th were ´cleaned´ by sucking air with a low NH_3 concentration after each measurement. In Figure 45 it is visible that the concentration at time 0 are lower and all measuring point are approved. Only the equilibrium concentrations of the experiment in May are approved due to this problem.
Measuring point 1 follows normal emission pattern, however the equilibrium concentration was not reached completely. Measuring point 2 is disapproved because the pattern is different from the others, less steep and the curve deviates.

For in total three measuring points in July and August the slope appeared reliable but a leak before NH_3 reached an equilibrium. Although the results of measuring points 1 and 2 are low for broadcast in July (Figure 46) they seem to follow normal emission pattern. The other measuring points don’t show a constant equilibrium, however, given the curve the equilibrium seems reliable. Figure 47 shows that the equilibrium of measuring points 1,3 and 4 are reached, the whole measurement of measuring point 2 is very doubtful because the pattern deviated much from the normal emission pattern. The equilibrium concentration of measuring point 5 is not constant and therefore it is rejected. The slope of measuring point 3 was not reliable because INNOVA was not connected to the laptop for 2 minutes. The slope of measuring point 1,4 and 5 were reliable, given the high slope it is likely that the equilibrium of measuring point 5 was higher compared to the measured value.

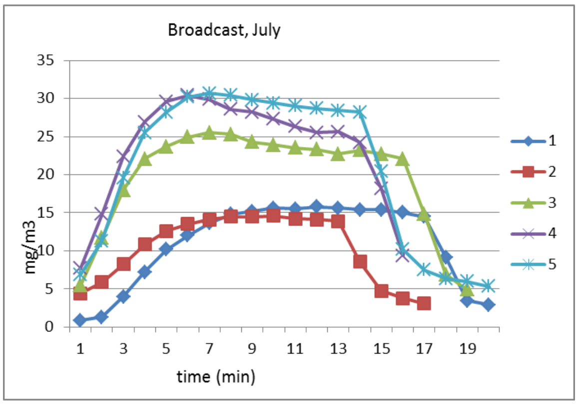

Figure 47. INNOVA results in July of broadcast, measuring points 1,2,3,4 and 5 are approved

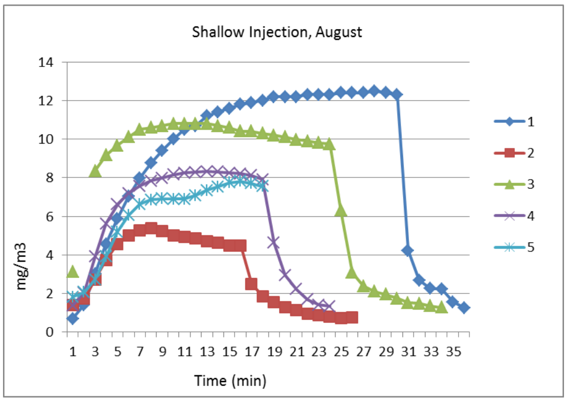

Figure 48. INNOVA results in August of shallow injection, measuring points1, 3 and 4 of the equilibrium and 1,4 and 5 of the slope are approved

Table 10. gives an overview of the approved INNOVA results of all comparison experiments.

Table 10. approved measuring point, the number corresponds to the measuring point for that particular treatment

	Broadcast	TGD 2:1		Shallow injection		TGD 1:1	TGD 1:2
May	3,4,5	1,2,3,4,5		2,3,5			3
July	1,2,3,4,5	1,2,5		E 3	S 3,4,5	1,2,3,4,5	
August	1,2,3,4	E 1,2,3,5	S 1,2,3,4,5	E1,3,4	S 1,4,5	1,2,3,4,5	

E=equilibrium
S= slope

2. Weather

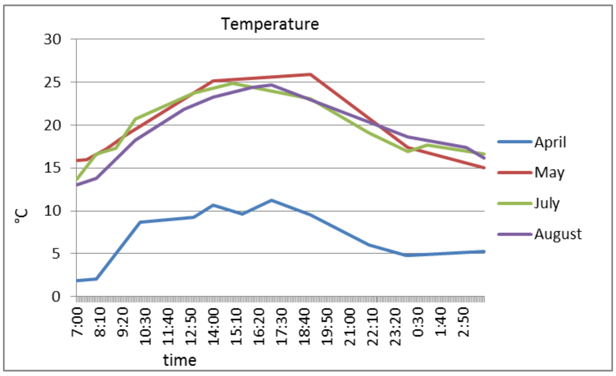

Figure 49. Average temperature weather station Eelde and Uithuizermeden of the comparison experiment on the day of the experiment

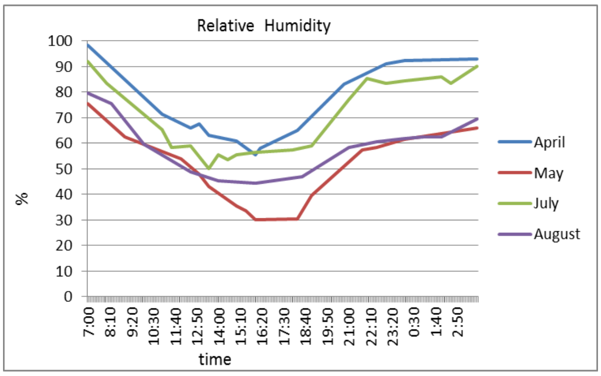

Figure 50. Average relative humidity of the air from weather station Eelde and Uithuizermeden of the comparison experiment on the day of the experiment

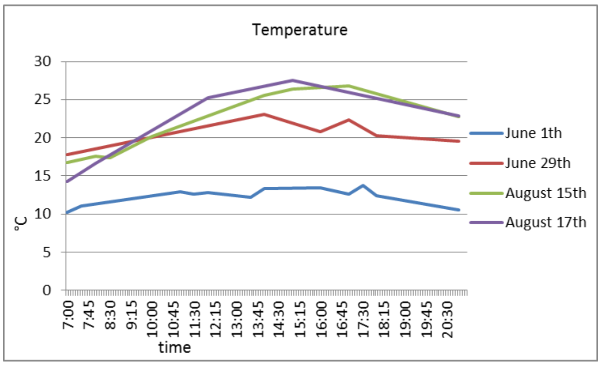

Figure 51. Average temperature weather station Eelde and Uithuizermeden of the time and distance experiments on the day of the experiment

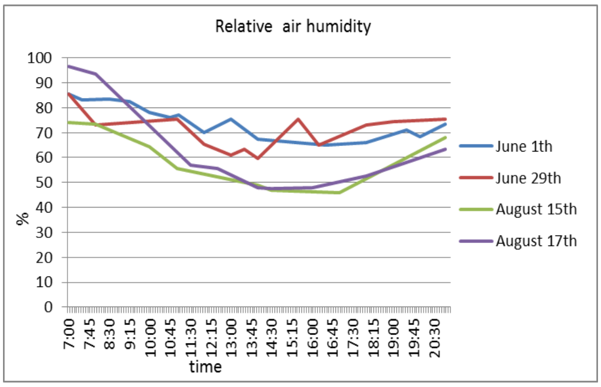

Figure 52. Average relative humidity of the air in Eelde and Uithuizermeden, of the time and distance experiments on the day of the experiment

3. Soil and water characteristics and time schedule

Table 11. Soil characteristics comparison experiments

Soil samples	**April**				**May**			
mg/kg	Broadcast	TGD 2:1	SI		Broadcast	TGD 2:1	SI	TGD 1:2
NO_3-N	40.5	27.3	44.9		38.1	52	52.7	43.2
NH_4-N	4.4	3.5	3.8		6.7	12.5	9.6	7.6
pH	6.4	5	5.2		5.1	4.2	4.7	4.8
DM	71	74	73		73	71	71	74
	July				**August**			
mg/kg	Broadcast	TGD 2:1	SI	TGD 1:1	Broadcast	TGD 2:1	SI	TGD 1:1
NO_3-N	11.6	19.4	12.3	14.7	23.47	24.1	31.3	29.8
NH_4-N	8.1	7.6	7.5	6.7	10.76	11.2	13.2	11.2
pH	5.5	6.1	5.8	6.1	5.4	5.8	5.6	5.5
DM	68	70	67	68	68	65	66	68

Table 12. Soil characteristics time and distance experiments

mg/kg	June 1th	June 29th	August 15th
NO_3-N	11.1	23.3	16.3
NH_4-N	7.4	5.1	5.4
pH	5.5	5.0	5.6
DM	70.9	67.7	75.5

Table 13. Water characteristics comparison experiments

	pH	NO_3-N mg l^{-1}	NH_4-N mg l^{-1}
April	8.58	0.03	0.22
May	7.46	0.03	0.69
July	7.6	0.02	1.65
August	6.89	0.21	2.38

Table 14. Water characteristics time and distance experiments

	pH	NO_3-N mg l^{-1}	NH_4-N mg l^{-1}
June 1th	7.66	0.08	1.2
August 15th	7.38	0.21	2.38

Table 15. Start and end time of the comparison experiments

	April				**May**			
	Broadcast	TGD 2:1	SI		Broadcast	TGD 2:1	SI	TGD 1:2
Start	12:33	10:33	14:38		9:16	11:20	14:17	17:05
End	14:08	12:11	16:04		11:10	12:48	16:42	18:47
	July				**August**			
	Broadcast	TGD 2:1	SI	TGD 1:1	Broadcast	TGD 2:1	SI	TGD 1:1
Start	10:24	13:52	16:01	12:09	10:15	12:58	18:29	16:24
End	12:05	15:40	18:55	13:49	12:51	13:44	20:45	18:18
Start 2.3*						15:19		
End 2.3						16:17		

* A technical problem with The Green Duo caused a delay