UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI SCIENZE AGRARIE E AMBIENTALIPRODUZIONE, TERRITORIO, AGROENERGIA

Effects of slurry treatments on gaseous emissions from storage and evaluation of models to predict ammonia release

Dr. Francesca Perazzolo

PhD thesis

PhD in Technological Innovation for Agro-Alimentary and Environmental Sciences

XXVII° CICLO

Tutor: **Prof. Giorgio Provolo**

PhD course coordinator: **Prof. Roberto Pretolani**

Academic year: **2013-2014**

Abstract

Liquid manure storage facilities are sources of methane (CH_4), nitrous oxide (N_2O) and ammonia (NH_3) emissions. CH_4 and N_2O are relevant greenhouse gases in terms of climate change because of their strong absorption of infrared radiation. NH_3 causes various environmental problems, such as odour, eutrophication, acidification of soils and atmospheric particulate matter formation.

To mitigate the effect of these emissions on the environment, many guidelines and regulations have been established by governments in various countries. Mitigation options during storage have been proposed, but they are not always easy to be implemented and their adoption in some areas, including Italy, is limited. Furthermore, the introduction of new slurry treatment technologies brings new challenges that require a better knowledge of their effect on the emissions during subsequent storage of the treated manure. This is particularly relevant also in the context of emission inventories, which aim to establish the state of implementation of environmental policies.

The research carried out aims to improve the knowledge about the effect on emissions of some slurry management techniques.

The activities carried out can be divided in two main groups:

1) Experimental activities
    a) Pilot scale experiments in controlled temperature conditions which aim to study comparatively the emission and the chemical evolution of treated and untreated slurries during one month storage. In particular it was evaluate how mechanical separation and anaerobic digestion affect NH_3 and greenhouse gas emissions from the storage. The experimental plan was designed in order to apply mechanical separation on untreated slurries and digestates and to consider different typologies of slurries, whose characteristics can be considered representative of the average for the region considered.

    b) Pilot scale experiments in field conditions which aim to study the effect on NH_3 and greenhouse emissions of the following treatments and mitigation option:
        b.1) mechanical separation
        b.2) application of a coat of clay granules on slurry surface
        b.3) acidification with sulphuric acid

    Activities a) and b.1) were carried out at the experimental farm of Landriano (Italy) while Experiments b.2) and b.3) took place at Rothamsted Research Center (UK). The methods used for gas measurement in all experimentations are based on dynamic chamber technique, while the effective nutrient losses have been determined by chemical analyses.

2) Modelling activity: the overall objective of this activity was to identify and calibrate some models, pre-existing in literature, to simulate ammonia emission factors from different storage conditions, suitable over a range of slurry chemical and physical properties. Therefore, 13 different models have been evaluated and a calibration procedure was set using the data obtained in the experimental activities in order to find the best prediction models for each storage condition considered.

The main results obtained from experimental activities were the following:

- Mechanical separation can cause a significant increase (up to 85%) of ammonia e nitrous oxide emission during storage: the first one is related to the presence of the liquid fraction while the second is mainly caused by the solid fraction

- Anaerobic digestion can also increment significantly nitrogen losses up to 45 %, but at the same time it represents a treatment that can effectively reduce methane emissions during storage of digestate
- Handling operation have to be carefully considered: increments of nitrogen and carbon losses were observed from mixed slurries. Furthermore it was found that when slurries are mixed, the main factors influencing nitrogen emissions are the TAN concentration and the TAN/TKN ratio. After mixing, the unseparated slurries were associated with higher NH_3 emission factors
- Floating clay granules proved to be a very effective NH_3 (mean reduction 72 %) mitigation technique but had no significant effect on CH_4 emission from pig slurry
- Acidification of cattle slurry proved to be a very effective mitigation technique for both CH_4 (mean reduction of 88 %) and NH_3 (up to 100% when pH is kept below 5)
- The derivation of country-specific emission factors for pig and cattle slurries in a revised inventory approach need to take into account duration and temperature of storage

In general, the results obtained from the experimental activity carried out can be used to estimate the variations of the emissions during storage induced by treatments or mitigation techniques. It is thus possible to quantify the reduction of emissions that can be obtained if best practices are applied with reference to the standard techniques.

On the other side, the emissions from the standard technique can be based on models in order to consider the manure characteristics and the local conditions, as demonstrated by the results in the assessment of model to estimate ammonia emissions.

In particular models have proved to be very helpful instruments to predict ammonia emission factors in different storage conditions. In some cases, they can also evaluate the effect of a treatment when the latter influence the input variables of the model.

In conclusion the use and evaluation of models coupled with the study of slurry treatment effects is advisable for an improved inventory approach and to develop operational guidelines for improved manure management practices to reduce environmental impacts.

Further research is necessary to improve models and to better understand the effect of some treatments techniques on emissions. Specific experimentations have to be set in order to validate the models and, at the same time, a wider assessment of treatments across different slurry types is advisable to provide robust values of emission factors, which are the base for a “good” model development.

Acknowledgements

My PhD has been a great opportunity for learning and for professional development. I am also grateful for having had the chance to meet so many wonderful people and professionals who have accompanied me in this path. All the activities carried were are part of two projects one Italian (NER0: N-Emission Reduction Zer0) and one English (Defra project AC0114).

I would like to express my deepest gratitude and special thanks to my tutor Professor Giorgio Provolo who has always taken the time to listen to me, guide me and keep me on the right path and has eventually allowed me to carry out my project within the university.

I do also express my sincere thanks to Dr. Tom Misselbrook, for the fundamental advice and guidance provided during my Erasmus Placement experience at North Wyke. I think this is the right opportunity to say I owe much to him.

I am grateful to all people that supported my activity, especially to Dr. Aldo Calcante, Mr. Emanuele Cattaneo (Agroenergie Bergamasche sca), Ms. Arjana Doda, Dr. Alberto Finzi, Mr. Roberto Galassi, Professor Marcella Guarino, Mr. John Hunt, Dr. Gabriele Mattachini, Mr. Ezio Naldi, Professor Roberto Oberti, Ms. Paola Rinaldi, Dr. Elisabetta Riva, Dr. Fulvia Tambone, to all the people that work at Menozzi farm in Landriano, in particular Mr. Mauro Colnago and Mr. Davide Reginelli, who have given me precious insights, both theoretical and practical. All the activities carried out were a part of two projects one Italian (NER0: N-Emission Reduction Zer0) and one English (Defra project AC0114).

I wish also to thank all the people working at DISAA – Engineering Section, and at the Rothamsted Research Centre for their availability and kindness to helping me to work out any kind of problem and difficulty.

Last but not least, I wish to truly thank my family and all my friends that have always been supporting me throughout my PhD studies. I would like to dedicate this work to them.

Index

1 Introduction 7

2 General aspects 10

  2.1 Environmental issues 10

  2. 2 Legislation 13

    2.2.1 Global regulation 13

    2.2.2 EU directives 15

    2.2.3 National regulations 17

  2.3 Background information on greenhouse gas inventories and climate change 18

  2.4 Processes involved in gas formation and effect of main mitigation techniques and slurry treatment 20

    2.4.1 Methane and Nitrous Oxide 20

    2.4.2 Ammonia 23

  2.5 Methods for gas measurements from slurry storage 26

    2.5.1 Main Methodologies used in field/pilot scale experiments 29

  2.6 Technologies used for gas concentration measurements 31

    2.6.1 Ammonia 31

    2.6.2 Greenhouse gas 35

  2.7 Ammonia release models 37

    2.7.1 Introduction 37

    2.7.2 Process involved in ammonia emission 38

    2.7.3 Ammonia in the liquid phase: dissociation constant (k_d) determination 41

    2.7.4 Ammonia in the air boundary layer 43

3 Aim of the research 45

4 Material and methods 47

  4.1 Pilot scale experiments in controlled temperature conditions 47

  4.2 Pilot scale experiments in field condition 51

4.3 Models 59

    4.3.1 Reproduction of models in literature and their application 59

    4.3.2 Model calibration 59

    4.3.3 Model evaluation 63

5 Results and discussion 65

  5.1 Pilot scale experiment in controlled temperature conditions 65

    5.1.1 Effect of mechanical separation on emissions from digestates 65

- 5.1.2 Effect of mechanical separation on emissions from livestock slurries 72
- 5.1.3 Effect of anaerobic digestion on emissions from raw livestock slurries 77
- 5.2 Pilot experiments in field condition 84
  - 5.2.1 Effect of mechanical separation (Group A) 84
  - 5.2.2 Effect of slurry acidification and clay granules (Group B and C) 97
- 5.3 Models 107
  - 5.3.1 Results of calibration 107
  - 5.3.2 Model evaluation 108
  - 5.3.3 Considerations 111

6 Operative application of the research 112

7 Conclusions 115

8 References 116

Appendix 1: description of the models evaluated 124

Appendix 2: simulation results 140

1 Introduction

Globally, agriculture contributes significantly to both greenhouse gas (GHGs) and ammonia (NH_3) emissions. In Europe and the US approximately 75% of NH_3 emissions derive from livestock production (Webb et al., 2005). NH_3 emissions are partly a local-regional environmental issue, because approximately 50% of the NH_3 may be deposited near the source (Sommer, et al., 2013), but there is also a contribution to trans-boundary transport (Directive 2001/81/CE). Deposition of NH_3 gas and NH_4 particulate can cause eutrophication of surface waters and acidification of ecosystems. Enteric fermentation of organic matter by ruminants is the major source of methane (CH_4) emission, contributing 35-40% of atmospheric CH_4. The CH_4 losses from manure management are approximately 20% of total agricultural CH_4 emissions for most countries. In addition, approximately 30 – 40% of the total global nitrous oxide (N_2O) emissions are caused by livestock production systems (Sommer et al., 2013).

To mitigate the effect of these emissions on the environment, many guidelines and regulations have been established by governments in various countries. Most of these regulations encourage manure recycling and a more efficient use of slurries by promoting the introduction of specific abatement strategies and technologies at the farm level. Among these, reducing emissions from storages is a relevant issue. The storage of effluents is strictly regulated and must be compatible with the time of spreading and with crop requirements. This often results in long slurry storage periods, leading to substantial organic matter degradation with subsequent uncontrolled release of CH_4, N_2O and NH_3. Storage accounts for 20-30%, ≈100% and 9 -10 % of the total respective NH_3, CH_4 and N_2O emissions produced during manure management (housing, storage and spreading) (Hutchings et al., 2001, EEA, 2013). Mitigation options during storage (e.g. cover, acidification) have been proposed, but they are not always easy to be implemented and their adoption in some areas, including Italy, is limited.

Furthermore, the introduction of new treatment technologies brings new challenges that require a better knowledge of their effect on the emissions during subsequent storage of the treated manure. This is particularly relevant in the context of emission inventories that every year member states has to upload in order to evaluate the state of the implantation of legislation concerned the gas emissions reduction (e.g. Kyoto Protocol, Gothenburg Protocol). Currently emission inventories are based on annual emission factors, which do not capture effects of all management options discussed above. Another major difficulties is the large variability in manure characteristics, which is not taken into account in the estimation of average emission factors, which makes the effect of mitigation effects uncertain (Petersen et al., 2013). In this context, modelling is required for more precise estimates of emissions and mitigation potentials. Furthermore emissions rates from slurry stores are difficult to measure, requiring specialised equipment and appropriate technology to obtain realistic emissions in relation to variable climatic and management conditions where animal production occur. The development of models permit to accurately simulates emission based on easy measurable variable, allowing a better assessment of emission factors from stored slurry and design practical solutions to reduce the impact.

The work carried out in this thesis concerned an experimental activity and a modelling activity.

During the first one, through direct measurements, the effects of the following treatments and mitigation options on gaseous emissions were evaluated with pilot scale laboratory and field experiments:

1) Mechanical separation

very widespread treatment, which is applied either on raw slurries and after anaerobic digestion as a second treatment.

This treatment separates slurry into a larger liquid and a minor solid fraction, with nutrients being more concentrated in the solid fraction (Dinuccio et al., 2008). This could improve nutrient management especially in areas with a high livestock density. Some studies have already investigated the effect of mechanical separation on untreated slurries. Fangueiro et al. (2008) reported higher NH_3 emission from separated cattle, with the highest amount of NH_3 lost from the liquid fraction. Dinuccio et al. (2008) showed contrasting results depending on the origin of slurries: separation of pig slurry resulted in reduced NH_3 losses compared with storage of untreated pig slurry, while for cattle slurry the combined NH_3 losses from the storage of the liquid and solid fractions were higher than those from the untreated slurry. Greenhouse gas emissions from manure storage are predominantly as CH_4. Greater CO_2 and NO_2 emissions are observed during the storage of solid fractions and of liquid effluents with a high total solids concentration and a tendency to develop a crust (Misselbrook et al, 2005, Hansen et al., 2006, Fangueiro et al., 2008).

In this theses the effect of mechanical separation on untreated and digested slurries was investigated. In particular very few data are currently available concerning NH_3 and GHG emissions during storage of separated and unseparated digested slurry.

2) Anaerobic digestion

Over recent years, anaerobic digestion has been increasingly adopted as a treatment for energy production, especially at farm facilities, and the management of digestate is crucial to address concerns regarding possible negative impacts on the environment. In Italy during the last three years, the number of biogas plants (more than 1000 as stated by Piccinini, 2013) increased substantially as the result of incentive policies. Some authors (Amon et al., 2006; Clemens et al., 2006) have already shown that anaerobic digestion is an effective means to reduce GHG emissions. In contrast, slurries which have been codigested anaerobically in biogas production plants have a higher NH_3 volatilization potential than untreated slurries because pH and TAN (NH_3 + NH_4^+) concentrations are higher (Sommer, 1996). In this thesis two digestates obtained from a cattle and a pig slurry were considered.

3) Acidification: the effect of acidification on ammonia emissions have been already investigated but less emphasis to date on methods to mitigate CH_4 emissions, with the exception of the deliberate promotion and capture of CH_4 in purpose-built anaerobic digestion plants. Slurry acidification to pH values <6 can be very effective at reducing NH3 emissions, but has also been shown to inhibit methanogenic activity (e.g. Berg et al., 2006).
4) Clay granules consists on covering the surface of slurry with a layer of this material. NH_3 emission are expected to be reduced but no clear are the effects on CH4. Petersen et al. (2005) reported CH_4 oxidation through the presence of a slurry crust, and the presence of a floating layer of inert clay granules might be expected to have a similar effect by allowing a more aerobic surface layer in which methanotrophic activity can occur as the CH_4 generated within the stored slurry passes through.

In the second part some models for NH_3 emission prediction were evaluated. In particular the overall objective of this activity was to individuate and calibrate some models, pre-existing in literature, to simulate ammonia emission factors from different storage conditions, suitable over a range of slurry chemical and physical properties. Many models can be found in literature, those evaluated in this work include statistical and mechanistic models of NH_3 release from liquid manure available in nine publications. The general structure of the models is described and discussed. The problem of applying these models is that, very often, they are suitable over a strict range of conditions. Therefore a calibration procedure was set using the data obtained in the experimental activity in order to find at least one “good” prediction model for each storage condition considered.

2 General aspects

2.1 Environmental issues

The greater size and intensity of farms and concentrated animal-feeding operations have increased the emissions of odorous compounds (e.g., organic acids) and trace gases (e.g., carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), nitrogen oxides (NO_x), ammonia (NH_3), and reduced sulphur compounds, such as hydrogen sulphide (H_2S) to the atmosphere (Aneja et al., 2008).

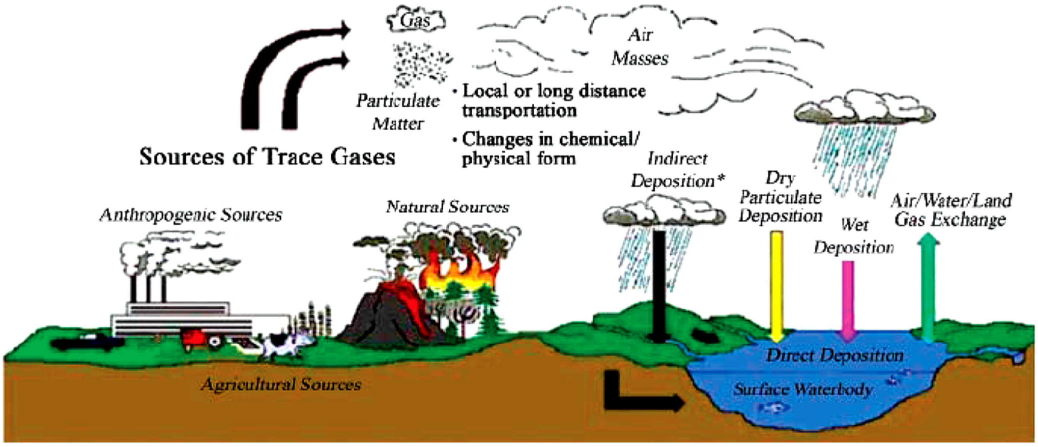
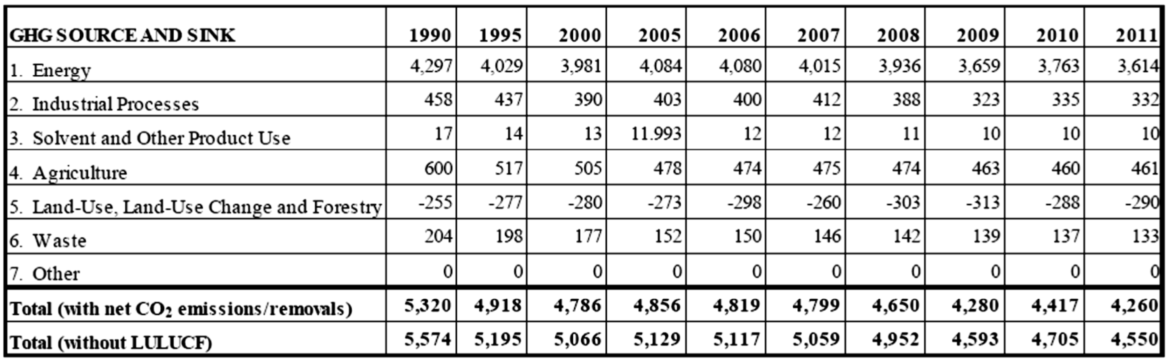


Figure 1. Atmospheric emissions, transport, transformation, and deposition of trace gases. Source: Aneja et al., 2006

Globally the livestock sector (beef and dairy cattle, swine, and poultry) is estimated to be responsible for 18% of all greenhouse gas emissions measured in CO_2 equivalents, 65% of anthropogenic N_2O, 37% of anthropogenic CH_4, and 64% of anthropogenic ammonia (FAO, 2006). the livestock sector is a major driver of deforestation, as well as one of the leading drivers of land degradation, pollution, climate change, coastal sedimentation, and invasion of alien species (Aneja et al., 2009).

In Europe agriculture sector contributes for 10.1% (Tab. 1) of greenhouse gases emissions (the first source is Energy with 79.4%) (European Environmental Agency, 2013). Regarding only the Agriculture sector (Fig. 2) the main sources of greenhouse gases are CH_4 produced by cattle livestock (27%) and N_2O emission from soils (26%).

Table 1 Overview of EU-27 GHG emissions in the main source and sink categories 1990 to 2011 in CO_2 equivalents (Tg) (LULUCF = Land Use, Land-Use Change and Forestry). Source: EEA, 2013.



GHG SOURCE AND SINK	1990	1995	2000	2005	2006	2007	2008	2009	2010	2011
1. Energy	4,297	4,029	3,981	4,084	4,080	4,015	3,936	3,659	3,763	3,614
2. Industrial Processes	458	437	390	403	400	412	388	323	335	332
3. Solvent and Other Product Use	17	14	13	11.993	12	12	11	10	10	10
4. Agriculture	600	517	505	478	474	475	474	463	460	461
5. Land-Use, Land-Use Change and Forestry	-255	-277	-280	-273	-298	-260	-303	-313	-288	-290
6. Waste	204	198	177	152	150	146	142	139	137	133
7. Other	0	0	0	0	0	0	0	0	0	0
Total (with net CO_2 emissions/removals)	**5,320**	**4,918**	**4,786**	**4,856**	**4,819**	**4,799**	**4,650**	**4,280**	**4,417**	**4,260**
Total (without LULUCF)	**5,574**	**5,195**	**5,066**	**5,129**	**5,117**	**5,059**	**4,952**	**4,593**	**4,705**	**4,550**

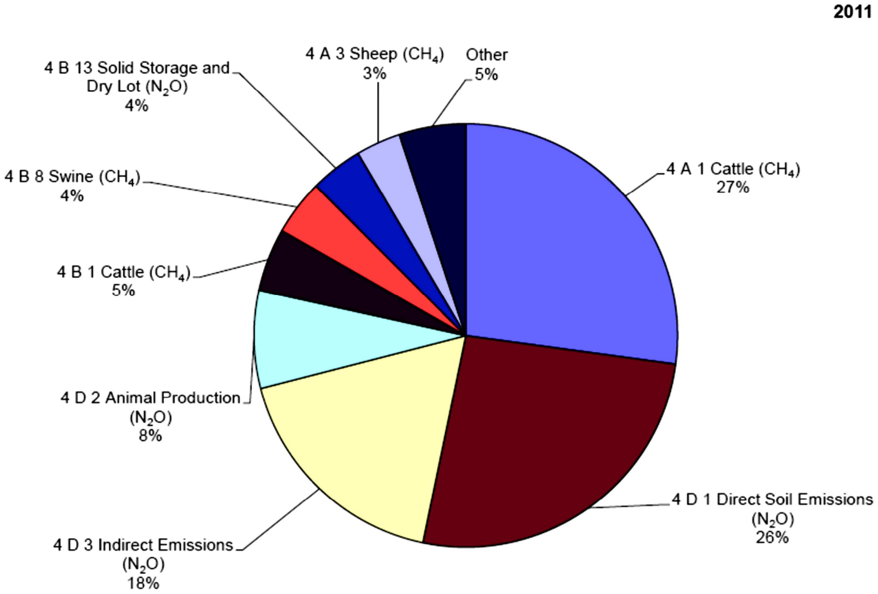


Figure 2 'European Agriculture' and share of largest key source categories in 2011. Source: EEA, 2013.

N_2O emissions are responsible for 7.2 % of total EU-15 GHG emissions and decreased by 34.1 % to 264 Tg CO_2 equivalents in 2011 (Environmental European Agency, 2013). The three largest key sources (direct emission from soil, indirect emission, animal production) account for about 72 % of N_2O emissions in 2011. The main reason for large N_2O emission cuts were reduction measures in the adipic acid production (EEA, 2014). Indirectly, the NH_3 emissions also contribute to N_2O emissions by increasing the N cycling in natural ecosystem (Sommer et al, 2013). N_2O is a greenhouse gas with an atmospheric lifetime of approximately 120 years. N_2O is about 298 times more effective in trapping heat in atmosphere than CO_2 over a 100-year period (IPPC, 2007). It is produced naturally in soils through the microbial processes of denitrification and nitrification. These natural emissions of N_2O can be increased by a variety of agricultural practices and activities, including the use of synthetic and organic fertilizers, production of nitrogen-fixing crops, cultivation of organic soils, and the application livestock manure to cropland and pasture. Some N_2O emissions can also be produced from the storage of solid manure (Montes et al., 2013)

Globally agriculture is the most important source of anthropogenic **CH_4**. Among domesticated livestock, ruminant animals produce significant amounts of CH_4 as part of their normal digestive process. CH_4 emissions account for 8.0 % of total EU-15 GHG emissions in 2011 and decreased by 34 % since 1990 to 289 Tg CO_2 equivalents in 2011. The main reasons for declining CH_4 emissions were reductions in managed waste disposal on land and coal mining. The largest source of CH_4 in 2011 is Cattle (35%) due to the enteric fermentation (EEA, 2014). The CH_4 losses from manure management contribute approximately 20% of total agricultural CH_4 emissions for most countries. Between countries, the variation in the percentage contribution of manure to CH_4 emissions reflects differences in the duration of manure storage, the proportion of ruminant livestock relative to other livestock types and livestock production system (Chadwick et al., 2011). Furthermore CH_4 is about 25 times more effective on trapping heat in atmosphere than CO2 over a 100-year period and it has a lifetime of approximately 14 years (IPPC, 2007).

Although not a GHG, **NH_3** (and its ionized form, NH_4^+) is an important component of the environment because it is the dominant gaseous base specie present in the atmosphere. Its properties (e.g., water solubility) make NH_3 important in atmospheric chemistry and physics. NH_3 is known to affect ecosystems at relatively low concentrations (Aneja et al., 2001). Once released into the atmosphere, NH_3 has a lifetime of less than 1 day to 5 days (Aneja et al., 2001). It will, therefore, most likely deposit to the Earth's surface close to its source: it’s estimated that 50% of the NH_3 is deposited close to the source (Sommer et al., 2009). However part of NH_3 can react with acidic species such as sulphuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) to form ammonium sulfate, ammonium nitrate, or ammonium chloride, respectively. Once transformed into ammonium (NH_4^+) aerosol, the lifetime of the species increases (ranging from 1 to 15 days) (Aneja et al., 1998b) as its dry deposition velocity decreases. Thus, NH_4^+ aerosol can be transported over larger distances downwind of sources than NH_3. The rate of conversion of NH_3 to NH_4^+ is largely unknown, but it is expected to have an important bearing on the spatial scale of NH_3 deposition from individual sources. The reaction rates depend mostly on the acid concentration, humidity, and temperature of air. Environmental consequences associated with atmospheric NH_3 and its deposition includes eutrophication, soil acidification, and aerosol formation. In the vicinity of sources, direct absorption into some plants through needles and leaves may impact vegetation. It is believed that atmospheric deposition is a significant source of nitrogen to coastal waters (Moore et al, 2013). In Europe and the US approximately 75% of NH_3 emissions derive from livestock production (Webb et al., 2005).

2. 2 Legislation

2.2.1 Global regulation

Intergovernmental Organisations, such as United Nations, and multilateral environmental agreements, such as conventions and protocols, have greatly contributed to considering seriously many of the known environmental problems, continuing to address outstanding issues of international concern. These organizations have also done much to harmonise the efforts of governments, and have provide important driving forces for international and national action on environmental matters, including manure management. The UN, founded in 1945, with the aim of maintaining international peace and security, developing friendly relations among nations and promoting social progress, better living standards and human rights. The UN works on a broad range of fundamental issues, including sustainable development and environment protection. The UN has been at the core of the multilateral environmental agreements on combating climate change through the UN Framework Convention on Climate Change (UNFCCC) and its Kyoto protocol, which outlines regulations aimed at decreasing greenhouse gas emissions, including those from manure management. Another example is the UN Economic Commission for Europe (UNECE), which hosts five conventions including the Convention on Long-Range Transboundary Air Pollution (CLRTAP). the CLRPTA was established in 1979 to address air pollution problems. It has eight protocols that identify specific measures to be taken by its 51 parties (countries) to cut their emissions of air pollutants including the 1999 Gothenburg Protocol, which addresses emissions of SO_2, O_3, NOx, NH_3 and volatile compounds (VOCs). It sets ceilings on the annual emissions of these pollutants and requires the implementation of measures to decrease emissions Methodology for estimating CH_4 and N_2O emissions factors has been devised by the Intergovernmental Panel on Climate Change.

Gothenburg protocol

Besides emissions and depositions on a local scale, it has become clear that air pollutants, e.g., NH_3, can travel several thousands of kilometres before deposition and damage occurred. In response to this issue, in 1979 the Convention on Long-range Trans boundary Air Pollution (CLRTAP) was signed by 34 governments and the European Community. The convention was the first international legally binding instrument to deal with problems of air pollution on a broad regional basis. In 1999, the CLRTAP was extended by the protocol to Abate Acidification, Eutrophication and Ground-level Ozone in Gothenburg, Sweden. At the beginning of 2007, this *Gothenburg protocol* was signed by 31 and ratified by 23 parties (UNECE, 2007).

The Gothenburg protocol sets emission ceilings for 2010 for four pollutants: sulphur, NO_x, volatile organic compounds (VOCs) and NH_3. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Once the protocol is fully implemented, Europe's sulphur emissions should be cut by at least 63%, its NO_x emissions by 41%, its VOC emissions by 40% and its NH_3 emissions by 17% compared to 1990 levels. The protocol requires that BATs are used to keep emissions down and describes specific measures that farmers will have to take to control NH_3 emissions. For the European Union Member States, EU Directive 2001/81/EC sets the National Emission Ceilings (NECs) for these emissions (EC, 2001). The first review of the Gothenburg protocol was started in December 2005 and was completed by the end of 2007.

In 2012 the protocol was amended and new emission ceilings for sulphur dioxide (SO_2), nitrogen oxides (NOx), $NH_3$and volatile organic compounds (VOCs) for 2010 up to 2020 were given. Concerning NH_3 Europe has to cut her emission of 5% compared to the level of 2005. Furthermore Annex IX of the amended Gothenburg Protocol contains specific measures to decrease NH_3 emissions from animal manure and fertilizers (UNECE, 2012).

Kyoto Protocol

The Kyoto Protocol was adopted in Kyoto, Japan, on 11 December 1997 and entered into force on 16 February 2005. There are currently 192 Parties to the Protocol. The Kyoto Protocol implemented the objective of the UNFCCC to fight global warming by reducing greenhouse gas concentrations in the atmosphere to 'a level that would prevent dangerous anthropogenic interference with the climate system' . As a result, it sets binding emission reduction targets for 37 industrialized countries, mostly Member States of the European Economic Area (EU + EFTA) in its first commitment period. These targets add up to an average five per cent emissions reduction compared to 1990 levels over the five-year period 2008 to 2012. Under the Kyoto Protocol, the EU agreed to reduce its GHG emissions by 8 % by 2008-12 compared to its ‘base year’ (the base-year emissions for the EU-15 have been fixed to 4 265.5 Mt CO_2 equivalent). Since 2009, total GHG emissions have been below the EU-15 Kyoto target.

With Doha Amendment a second commitment period was proposed in 2012 (UNFCCC, 2012).
The key aspects of the second commitment period (CP2) are as follows:

- CP2 will be eight years long, running from 1 January 2013 until 31 December 2020;

Parties taking on commitments in CP2 (CP2 Parties) are required to reduce their aggregate emissions by 18 per cent below 1990 levels in CP2. The commitments of individual Parties range from a 24 per cent reduction (in the case of Ukraine) to a 0.5 per cent reduction (in the case of Australia). The European Union, as a whole, is required to reduce its emissions by 20 per cent; and as part of a global and comprehensive agreement for the period beyond 2012, the European Union showed its conditional offer to move to a 30 % reduction by 2020 compared to 1990 levels, provided that other developed countries commit themselves to comparable emission reductions and developing countries.

- CP2 Parties are required to review their commitments by the end of 2014 with a view to increasing the level of their mitigation ambition;

The Doha amendment will enter into force on December 2015 during the Conference of Parties that will be held in Paris. Anyhow at the moment only 19 countries have finished their ratification process, considering that 144 are required. Furthermore, in Doha, parties confirmed their commitment to **Advancing the Durban Platform**, which was agreed in 2011, and cemented support for countries to achieve more ambitious emission reductions by agreeing a new, legally binding treaty in 2015 that would take effect in 2020. The Platform is notable because it's an agreement that involves action from all 194 countries, rather than just rich ones.

On November 12, 2014, China and the United States reached an agreement on greenhouse gas (GHG) emissions reduction commitments and issued a joint announcement in Beijing. According to the announcement, the U.S. intends to reduce net GHG emissions by 26–28% below 2005 levels by 2025 (consistent with prior U.S. Obama administration policy). China pledged that its GHG emissions will not increase after 2030 with an effort to reach peak emissions at an earlier date.
In addition, China has targeted a 15% increase in the use of non-fossil fuels in primary energy consumption by 2015 and 20% by 2030 (UNFCCC, 2014).

The significance of this agreement is both symbolic and practical. It reflects China's foremost commitment to limit GHG emissions and to change its energy consumption. In addition, this agreement is likely to spur other countries to tackle climate change issues and possibly achieve an agreement binding all parties at the United Nations Climate Conference in Paris in 2015.

2.2.2 EU directives

- **91/676/CEE Nitrates Directive**

  This Directive had a large impact also in greenhouse gases emissions control. The Nitrates Directive is now an integral part of the Water Framework Directive and is one of the key instruments for protecting water against agricultural pressures.

  AIM: "reduce water pollution caused or induced by nitrates from agricultural sources and prevent further such pollution". This Directive requires Member states taking the following steps:

  1. Identification of waters that are polluted or at risk of pollution
  2. Designation of vulnerable zones
  3. Establishment of codes of good agricultural practices and action programmes
  4. A review at least every 4 years of the designation of vulnerable zones and action programmes . waters must be identified as pollute or at risk of pollution, if nitrate concentrations in groundwater and surface waters could contain more than 50 mg NO_3l^{-1} if no action is taken, or if surface waters. Including fresh water bodies, estuaries, costal and marine waters, are found to eutrophic or in the near future may become eutrophic if no action is taken

The action programmes to reduce pollution must contain mandatory measures relating to:

1. Period when the application of animal manure and fertilisers to land is prohibited
2. Capacities of and facilities for storage of animal manure;
3. Limits to the amounts of animal manure and fertilisers applied to land, which balanced fertilisation. The Nitrate Directive has clearly a huge effect on manure management in practice and is one of the reason why manure management in the most advanced countries in EU-27 is more advanced than in, for example U.S, Japan and China.

- **96/61/EC Directive on Industrial Emissions concerning Integrated Pollution Prevention and Control (IPPC).**

  This Directive was substituted by 2008/1/CE Directive and after by 2010/75/EC. The latter integrates the Directive of 2008 with other 6 directives concerning the industrial emissions. It establishes a permit procedure and lays down requirements, in particular with regard to discharges. The objective is to avoid or minimise polluting emissions in the atmosphere, water and soil, as well as waste from industrial and agricultural installations, with the aim of achieving a high level of environmental and health protection.

  AIM: minimise the overall environmental impact of human activities. The IPPC directive sets common rules for permitting and controlling certain large-scale industrial and agricultural activities. Such activities need an operating permit that takes into account the whole environmental performance of the facility, covering *e.g.,* emissions to air, water and land, generation of waste, use of raw materials, energy efficiency, local disturbance (odour, noise), prevention of accidents, and restoration of the site upon closure.

To gain a permit operators have to show that no significant pollution is caused and that the BATs are applied, taking into account the technical characteristics, geographical locations and local environmental circumstances of the installations concerned. “Best” means the most effective in achieving a high general level of protection of the environment as a whole. “Available” means those techniques that have been developed on a scale that allows implementation under economically and technically viable conditions, but does not necessarily mean that the technique has to be an industry standard or indeed widely available, as the intention of IPPC is to change practices to new, less polluting alternatives. “Techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned. The environmental impacts of industry and agriculture can be significantly reduced through the use of new and more advanced techniques and technologies. Adoption of the BAT system aims to help to improve the management of material flows, increase energy efficiency, and cut emissions.

The EU member states' authorities and industry cooperate on the development of so-called BAT reference documents (BREFs). A BREF assists the regulatory authorities and those applying for licences by describing reference techniques and reference levels for a specific economical sector. One of the BREFs is dedicated to installations for intensive livestock production. This “Reference Document on Best Available Techniques for Intensive Rearing of Poultry and Pigs” covers intensive livestock farms with more than 40 000 places for poultry, or 2000 places for production pigs over 30 kg, or 750 places for sows. The BREF discusses good agricultural practice, nutritional management, housing systems, water and energy use, manure storage, manure processing, and land spreading of manure. The BREF document for intensive rearing of poultry and pigs is expected to be updated from 2008 on.

- **2001/81/EC National Emissions Ceiling (NEC) Directive.**

The Directive was amended on 2009 with the regulation n°219.
AIM**:** combat acidification, achieving long-term objectives of not exceeding critical levels and loads by establishing national emission ceilings, taking the years 2010 and 2020 as benchmarks.

This Directive sets upper limits (ceilings)from each member state for total emissions in 2010 and 2020 of the four pollutants responsible for acidification, eutrophication and ground-level ozone pollution (SO_2, NOx, VOCs and NH_3), but leaves it largely to the Member States to decide which measures to take in order to comply. The Directive is basically the EU translation of the Gothenburg Protocol.

Member States must prepare and annually update national emission inventories and emission projections for SO_2, NO_x, VOC and NH_3. These inventories and projections must be reported to the Commission and the European Environment Agency each year by 31 December at the latest.

- **2000/60/EC Water Frame Directive**

AIM: Protection of superficial, deep, transaction, coastal waters. Protection and reduction of pollution, promotion of a sustainable water use, environment protection, improvement of aquatic ecosystems and mitigation of flood and drought effects. Reach a “good status” form an ecological and chemical point of you of the all water within 2015.

Each member state have to find hydrographic districts and for each one management plans have to be established taking into account the results of previous studies and analyses. The management plans have to be redacted during 2012 and they aim at:

- Avoid the deterioration, improve and restore the conditions of the superficial waters, in order to reach a good ecological and chemical status within the end of 2015 and reduce the pollution related to discharges and Hazardous substances emissions.4
- Protect, improve and restore of the conditions of groundwater water, avoiding their pollution and deterioration.
- Preserve the protected areas

2.2.3 National regulations

Italy

Decreto Legislativo 152/2006 "Norme in materia ambientale"

This decree transposed numerous European directives modifying and repealing numerous decrees. It collected in one single act the majority of the decrees .

AIM: promoting the human life quality through the safeguard and the improvement of environmental conditions and the rational and shrewd use of natural resources. For this purpose it provides reorganization, coordination and integration of the laws relating to the environment.

Answering to the Nitrate Directive the vulnerable zone are identified and the criteria for agronomic use are given, delegating to the regions the laws actuation. Once the zones are designated the regions must intervene through an action plan that follows the indications of the Directive.

Decreto Ministeriale del 19/04/ 1999

AIM: approval of good practice codes.

The code aim is to promote the protection of waters from nitrate pollution reducing the environmental impact of agricultural activity through a careful management of the nitrogen balance.

The code is focus on the equilibrium between agriculture, nitrogen fertilizers and environment. Concerning the manure management, the dimension of storage is regulated. The necessity of a correct size of storage is highlighted in order to program the effluents distributions in the most suitable periods for crops. The sizing must be done taking into account the daily production of effluents (slurries, solid fractions, washing water, rainwater) and the storage period necessary to manage a correct utilization.

Decreto Ministeriale 07/04/ 2006

AIM: give technical criteria and general indications to discipline at regional level the agronomic use of livestock effluents in vulnerable and not vulnerable zones.

The application of the new this regulation concerns the whole cycle of agronomic utilization of the livestock effluents (production, collection, storage, fermentation and maturation, transport e spreading).

In this law the storage modalities, the storage capacity and the minimum storage period are given (from 90 to 180 days).

Decreto Legislativo 171/2004

AIM: transpose the 2001/81/CE Directive concerning the national limits of SO_2, NOx, COV, NH_3 emissions to achieve within 2010 and in the later years.

It defines the characteristics that the action plan must contain and the emission limits for the different composts.

2.3 Background information on greenhouse gas inventories and climate change

The challenge of climate policy is to achieve a long-term “stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system” (United Nations 1992, Article 2). A successful implementation of environmental policies, e.g. Kyoto protocol and NEC Directive, will depend on high-quality greenhouse gas (GHG) inventory data. A the moment the emission inventory used are prepared according to the guidelines given by the IPCC (IPCC, 1996).
Greenhouse gas inventories are necessary to run mathematical models. quality of emissions inventory depends on the quality of statistics available. The output of sophisticated models operated by scientific community will became the basis for policy development and implementation. Error in GHG inventory leads to erroneous output from mathematical models and ends in wrong policy like building infrastructure where it may not be needed.

Concerning estimation of CH_4 and N_2O, emissions from livestock manure has been indicated by the Intergovernmental Panel Climate Change (IPCC, 1996). It is based on emission factors estimating gas emissions as a proportion of the carbon or nitrogen pools in manure from a number of livestock categories and manure management systems by region. Nevertheless many studies have already shown that changes in manure management can induce significant changes in CH_4 and N_2O emissions and carbon sequestration, and that introducing environmental technologies may vary significantly with livestock farming practice and interact with climatic conditions (Sommer et al., 2009) at the moment a standard scheme for describing manure management systems across regions does not exist. When slurry is treated there is no information regarding the chemical composition of effluents obtained by the treatment technology. This lack of information avoids any progress in quantifying agricultural GHG emissions, and it prevents the adoption of effective GHG mitigation strategies. For mitigation strategies to be effectively implemented, such manure information and calculation schemes must be made available and applied within the national emission inventories for reporting under United Nations Framework Convention on Climate Change (UNFCCC) and related protocols in emissions reduction.
In this context there is a need to better understand the processes involved in greenhouse gas and NH_3 emission during manure management and a need for more precise models to estimate emissions at farm to national scale.

Concerning **NH_3** many countries recognize that in the agriculture sector the emissions from the different categories are inherently linked and are best estimated in a comprehensive model that covers not only greenhouse gases (CH_4 and N_2O) in a consistent manner, but also NH_3. Estimations of NH_3 emissions are required for reporting under the Convention on Long-Range Transboundary Air Pollution and are needed to estimate indirect N_2O emissions. The first inventories of NH_3 emissions from livestock production were calculated by multiplying livestock numbers by emission factors (EFs) per animal (Reidy et al., 2008). This approach did not allow for significant differences in the potential for NH_3 emissions due to differences in performance, diet and hence nitrogen (N) excretion, or differences in livestock and manure management practices among countries and regions.

Hence, some countries have developed comprehensive models covering consistently different source categories and different gases replacing EFs approach.

- Austria: For the calculation of the losses of gaseous N species the mass-flow procedure pursuant to EMEP/CORINAIR is used. A detailed emission model for NH_3, NMVOC and NOX has been integrated into the national inventory.

- Germany: Germany uses the emission inventory model GAS-EM to calculate consistently emissions of CH_4, NH_3, N_2O, and NO from agricultural sources. It is based on IPCC methodologies and has been developed in recent years with a comprehensive description found in Roesemann et al. (EEA, 2014). Basis of the model is the feed intake which determine emissions. Data are available at district (livestock characterisation, housing systems, manure management systems) and regional level. N-emissions are considered within an N-flow concept. In the N-flow concept, only remaining N in manure is transferred to storage systems, after subtraction of emissions in housing systems. Emissions are subtracted from the total N-pool.

- Denmark: The emissions from the agricultural sector are calculated in a comprehensive agricultural model complex called IDA (Integrated Database model for Agricultural emissions). The model complex is designed in a relational data-base system (MS Access). Input data are stored in tables in one database called IDA_Backend and the calculations are carried out as queries in another linked database called IDA. This model complex is implemented in great detail and is used to cover emissions of NH_3, particulate matter and greenhouse gases. Thus, there is a direct coherence between the NH_3 emission and the emission of N_2O.

- Finland: Finland uses a nitrogen mass flow model (except for N-fixing, crop residue and sewage sludge) accounts for nitrogen losses as NH_3 and N_2O emissions during manure management in animal houses, during storage and application; the calculation method was developed in order to avoid double-counting

2.4 Processes involved in gas formation and effect of main mitigation techniques and slurry treatment

2.4.1 Methane and Nitrous Oxide

CH_4 is only produced in strictly anaerobic environments, while N_2O is produced in more complex environments with low oxygen concentrations, typically mosaics of aerobics and anaerobic micro-environments or interfaces where aerobic and anaerobic conditions meet.

CH_4 is only produced in manure when the oxygen consumption rate is higher than the rate of oxygen supply to the site of consumption. The production of CH_4 involves degradation and hydrolysis of organic material to organic compounds, which are then degraded to long-chain acids, proteins or alcohols. These components are fermented to short-chain acids that are transformed to CH_4 and CO_2 by CH_4-producing Archea. Production of CH_4 from manure is affected by environmental factors such as temperature, biomass composition and management of manure (Chadwick et al., 2011) .

The N collected in manure is present in reduced form such as ammonium (NH_4^+), proteins and urea. Oxygenation via nitrification of NH_4^+ to nitrate (NO_3^-) is necessary for N_2O production. Nitrifiers increase their activity with temperature but at temperature above 40-45°C they become inactive. In an environment supporting nitrification, N_2O may be produced as a by-product of NH_4+ oxidation and emitted from the manure. Nitrite and NO_3^- produced via nitrification may, under anaerobic conditions, become reduced to gaseous N_2O and N_2. However, in micro-sites with low levels of oxygen there is a great tendency for N_2O emissions due to incomplete nitrification. Therefore, the spatial and temporal distribution of O_2 supply and O_2 demand may be of particular importance for the prediction of N_2O emissions (Petersen et al., 2011).

The population of microorganisms can be a significant factor affecting GHG production and emissions. For example, the substrates for nitrifers are NH_4^+ and N_2O^-, which are ineffective energy sources, and therefore the autotrophic nitrifiers grow slowly (Sommer et al., 2013). In environments with relatively few nitrifiers, such soil, the nitrification of total ammoniacal N in manure may become significant only after a lag phase of several days (Petersen et al., 1996).

Slurry stores

Storage systems are sources of **CH_4** because the environment in these stores, if not actively aerated, favours methanogenesis and because slurry is mostly stored over long period. Pig slurry generally has the potential to emit more CH_4 than cattle slurry, because it has a higher content of degradable organic matter than cattle slurry (Moller et al., 2004). In outside slurry stores, CH_4 emissions vary over the year due to the temperature variation and management practice. For example, in countries where stores are emptied in spring, only small amounts of slurry are exposed to high temperature during summer, whereas in countries where slurry is stores in lagoons which are never completely empty, emissions may be higher. A positive correlation between CH_4 emissions during storage and the temperature of manure or slurry has been observed (Massè et al., 2003; Moller et al., 2004). CH_4 production is low at temperatures < 15°C.

Mild agitation of slurry has been shown increase CH_4 emissions, as dissolved gas and bubbles are released, but losses from these route tend to be small and short-lived. Indeed, allowing a formation of a slurry crust can produce a CH_4 sink as a result of CH_4 oxidation (Petersen et al., 2005). Covering slurry stores with porous surface of straw, expanded clay pebbles or recycled polyethylene may reduce CH_4 emission during oxidation to CO_2. Amending slurry with straw may enhance methanogenic activity, thus a surface crust of slowly degradable manure material or inert leca pebbles may be more efficient at reducing CH_4 emission. Another way to reduce CH_4 emission is a frequent removal of slurry from store or channel (Chadwick et al., 2011). In fact while methanogenesis on the digestive track of livestock is mainly due to H_2-utilising methanogens, CH_4 production in slurry environment probably depends on the activity of slow-growing acetotrophic methanogens. If slurry pits or outside stores contain aged slurry with an adapted microflora, CH_4 production is not delayed by the microbial capacity to produce CH_4. In contrast, when slurry channels or a store has been completely emptied, the absence of old manure that may serve as an inoculum can result in low CH_4 production rates for several months (Sommer et al, 2013).

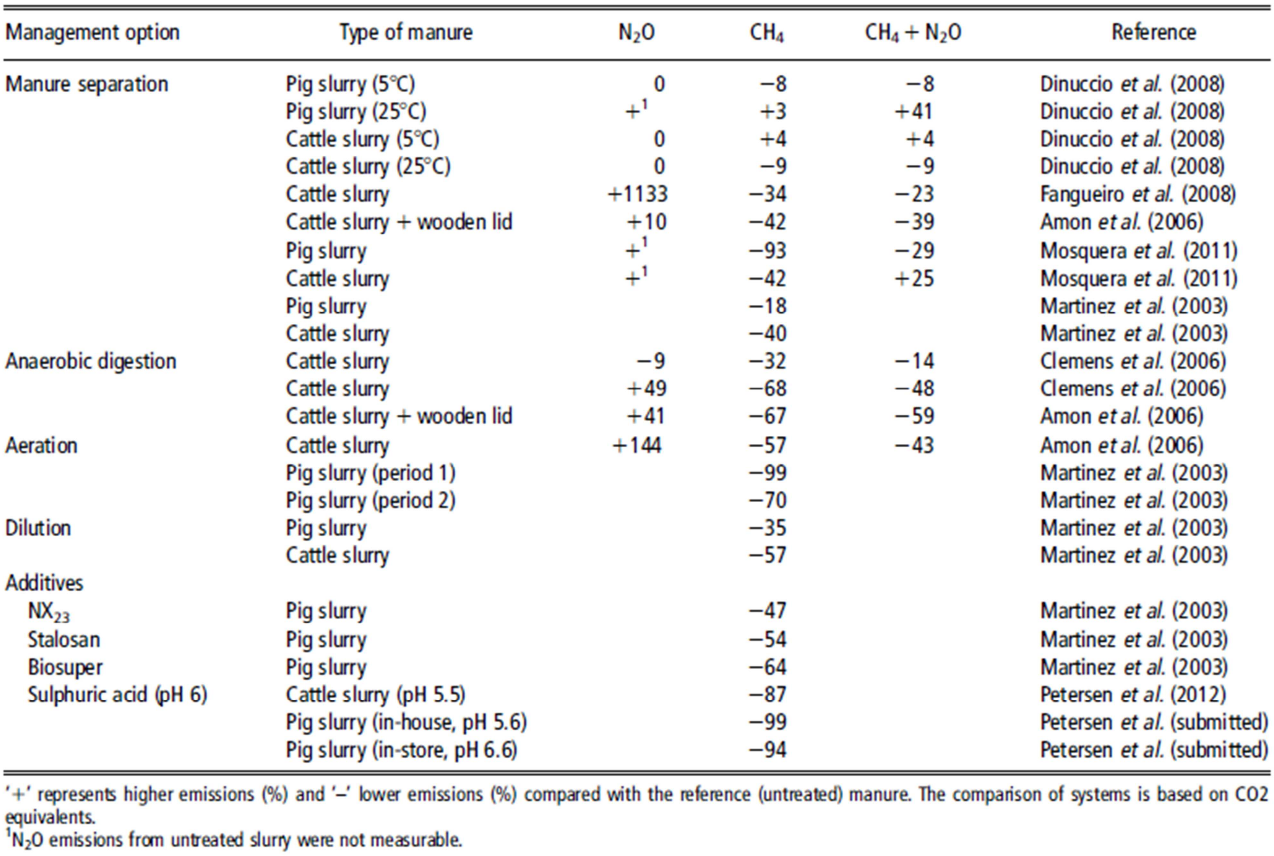
The storage of solid manure has also been shown to be a source of CH_4, with losses from cattle heaps representing between 0,4 -9,7 % of the total C content of small heaps, end loss can be higher in larger field-scale heaps (Chadwick et al., 2005). The large variation is due to the effects of air exchange and aerobic decomposition of the volatile solids, which increases the temperature and produces anaerobic sites in the heap where CH_4 is produced. Deep litter from pig and cattle houses and pig manure with large proportion of straw decompose aerobically because of the high permeability of the organic material, and little CH_4 is produced, because the temperature in the manure remains low (Webb et al., 2012). High CH_4 emissions may be expected from solid manure heaps, with porosities lying between these extremes of high and low porosity manures, with the porosity being affected by the amount of straw added to the manure. Manures from open beef feedlots are often so dry that aerobic decomposition will not occur without the addition of water. The gaseous emissions from stored solid manure therefore generally reflect the variation of manure composition. Covering and compacting could either increase or decrease CH_4 emissions. CH_4 emissions from stored solid manure can be reduced by two completely different strategies aiming at either promoting or preventing anaerobic conditions (Chadwick, 2005).

In animal house with slurry collection, the manure remains in a predominantly anaerobic state with little opportunity for the NH_4^+ to be nitrified. Here **N_2O** may theoretically be produced at air liquid interface of stored slutty or on slats and solid floors where urine and faeces are deposited. Emission of N_2O can be influenced by the temperature, pH and TAN concentration (high concentrations inhibit the process). The bulk of slurry stored outside is anaerobic, and therefore emissions of NH_3 via nitrification and denitrification from slurry without a floating cover are insignificant. However a natural or an artificial crust on top of the stored manure can become a mosaic of anaerobic and aerobic sites, creating a suitable environment for N_2O production (VanderZaag et al., 2009). Some materials used to cover liquid manure stores to prevent NH_3 emissions enhance crust formation and may lead to an increase in N_2O emissions during manure storage (Berg et al., 2006).

Porous solid manure heaps may be a source of N_2O during the initial phase or storage, before the temperature increases. During the composting phase little N_2O is produced, partly because NH_3 volatilisation depletes the pool of NH_4^+, and partly because nitrifying and denitrifying microorganisms are not thermophilic. When the temperature declines, conditions suitable for nitrification/nitrification are re-established. In general, emissions of N_2O are a function of production and consumption of N_2O and the air exchange rate in the heap. Thus emissions of N_2O typically range from less than 1% to 4,3% of the total N in stored cattle and pig manure heaps. The process mentioned above for the pig and cattle manure also hold for poultry manure. The N_2O emissions for poultry manure heaps in the one study known to us range between 0,2 and 0,8% N content of heap (Sommer et al., 2013).

Mechanical separation of liquid manure is practised to various extent in European countries (90% pig slurry in Greece, 10% of all slurry in Spain and in Italy 15% of cattle and 40% of pig slurry) (Burton and Turner, 2003). There are several advantages in using this treatment regardless nitrogen restraint: improvement in slurry management and handling, obtaining of a liquid fraction rich of mineral N and thus with a higher percentage of plant-available N, and there are several options for treatment with a potential to improve manure quality and reduce losses towards environment. However, the solid fraction is similar to untreated solid manure and has been shown to result in higher N_2O emissions during storage, relative to the untreated slurry due to the mix of aerobic/anaerobic conditions in the solid heap. Storage of the liquid fraction can lead to even lower N_2O emission relative to untreated slurry, and this decrease could be amplified if screw-press separation was combined with chemically enhanced settling to obtain a supernatant liquid fraction (Fangueiroet al., 2008). Concerning CH_4 emissions it is difficult to say if slurry separation increases or decreases CH_4 emissions (Table 2). Since it depends mainly on the storage conditions and the characteristics of the slurry fractions obtained (Petersen et al., 2013). Similarly, combined CH_4 and N_2O emissions from storage of both fractions have usually, but not always, been lower than from untreated manure (Dinuccio et al., 2008). This means that slurry separation requires additional measures to achieve GHG mitigation during the storage phase.

Table 2 Effect of different management options on CH_4, N_2O and combined CH_4 + N_2O emissions from manure treatment. Source: (Petersen et al., 2013)



Management option	Type of manure	N_2O	CH_4	$CH_4 + N_2O$	Reference
Manure separation	Pig slurry (5°C)	0	−8	−8	Dinuccio *et al.* (2008)
	Pig slurry (25°C)	$+^1$	+3	+41	Dinuccio *et al.* (2008)
	Cattle slurry (5°C)	0	+4	+4	Dinuccio *et al.* (2008)
	Cattle slurry (25°C)	0	−9	−9	Dinuccio *et al.* (2008)
	Cattle slurry	+1133	−34	−23	Fangueiro *et al.* (2008)
	Cattle slurry + wooden lid	+10	−42	−39	Amon *et al.* (2006)
	Pig slurry	$+^1$	−93	−29	Mosquera *et al.* (2011)
	Cattle slurry	$+^1$	−42	+25	Mosquera *et al.* (2011)
	Pig slurry		−18		Martinez *et al.* (2003)
	Cattle slurry		−40		Martinez *et al.* (2003)
Anaerobic digestion	Cattle slurry	−9	−32	−14	Clemens *et al.* (2006)
	Cattle slurry	+49	−68	−48	Clemens *et al.* (2006)
	Cattle slurry + wooden lid	+41	−67	−59	Amon *et al.* (2006)
Aeration	Cattle slurry	+144	−57	−43	Amon *et al.* (2006)
	Pig slurry (period 1)		−99		Martinez *et al.* (2003)
	Pig slurry (period 2)		−70		Martinez *et al.* (2003)
Dilution	Pig slurry		−35		Martinez *et al.* (2003)
	Cattle slurry		−57		Martinez *et al.* (2003)
Additives					
NX_{23}	Pig slurry		−47		Martinez *et al.* (2003)
Stalosan	Pig slurry		−54		Martinez *et al.* (2003)
Biosuper	Pig slurry		−64		Martinez *et al.* (2003)
Sulphuric acid (pH 6)	Cattle slurry (pH 5.5)		−87		Petersen *et al.* (2012)
	Pig slurry (in-house, pH 5.6)		−99		Petersen *et al.* (submitted)
	Pig slurry (in-store, pH 6.6)		−94		Petersen *et al.* (submitted)

'+' represents higher emissions (%) and '–' lower emissions (%) compared with the reference (untreated) manure. The comparison of systems is based on CO2 equivalents.

[1] N_2O emissions from untreated slurry were not measurable.

Anaerobic digestion potentially can reduce the emission of greenhouse gases. Emissions from digested slurry during storage were 30-60% lower than from untreated slurry (Table 2).Because the major part of the degradable organic matter is consumed during the process the emission of CH_4 can be very reduced at storage condition. At the same time it's important to consider that digestate contains an enriched methanogenic microflora that will continue to produce CH_4 during the cooling phase. Thus collecting CH_4 during this phase it's very important to improve the mitigation effect (Petersen et al., 2013). Also, acidification of slurry for the purpose of reducing NH_3 emissions from storage has been observed to reduce CH_4 emissions (Petersen et al., 2012). Concerning the N_2O there is little opportunity for nitrification of NH_4^+ to NO_3 so emission of these gas can be insignificant.

2.4.2 Ammonia

NH_3 is the gas measured in the highest concentration in animal houses, where concentrations up to 50000 ppb have been observed. The ambient concentration is about 1 ppb. NH_3 can be sensed at concentrations above 2500 ppb, which is significantly higher than the detection level of most odorants, which can be sensed at level about 1 ppb, apart from acetic acid with detection level of about 250 ppb (Sommer et al., 2013).

NH_3 is a risk to the health of people inhaling the gas of particles formed by the gas, and a component that cause nitrogen enrichment and imbalance of ecosystems.

NH_3 is a colourless gas with a low density (0.73 kgm^{-3} at 1.013 bar and 15° C). The N atom in the molecule has a lone electron pair, which makes NH_3 a base. The polarity and ability to form hydrogen bond makes NH_3 highly soluble in water.

NH_3 is produced as a consequence of bacterial activity involving organic N substrates. Farm animals consume a considerable amount of protein and other nitrogen (N) containing substances with their feed. The dietary N consumed by the animal is partitioned between products such as meat, milk, eggs, urine, and feces. The conversion of the dietary N to animal product is often inefficient and 50 to 80% of the N consumed is excreted. More than 50 to 60% of the excreted N by pigs and cattle is in the urine and over 70% of the N in the urine is urea-N. In poultry, more than 70% of the total N excreted is uric acid.

The primary sources of NH_3 in livestock and poultry production are urea and uric acid, respectively.

Urea is a diamide, which is transformed by urease to NH_4^+-N NH_3-N and bicarbonate:

$$CO(NH_3)2 + 2H_2O \leftrightarrow NH_3 + NH_4^+ + HCO_3^-$$

This reaction occurs very rapidly, requiring only hours for substantial conversion and days for complete conversion. Other organic N compounds in faces are a secondary source of TAN, which in this time frame (hours to few days) can account for up to 35% of the production. In total, rapid processes convert about 35% of the total organic N initially in manure to TAN. Over longer time periods, mainly during storage, a total of 50 to 70% of the organic N can be converted to TAN (Zhang et al., 2005).

Hydrolyses of urea is affected by pH and optimum pH for urease activity has been reported to range from pH 6-9. Animal manure is buffered to pH 7 – 8.4; therefore, hydrolyses of urea will not be greatly influenced by pH in manure that has not been treated with acids and bases (Sommer et al. 2006). Urease activity is affected by temperature and the activity is low at temperature below 5-10°C and at temperature above 60°C.

Slurry stores

Table 3 reports the main abatement techniques for NH_3emissions from storage reported in the Annual Inventory Guidebook of EEA. The baseline for estimating the efficiency of an abatement measure is the emission from the same type of store, without any cover or crust on the surface. Emissions from slurry stores can be reduced by decreasing or eliminating the airflow across the surface by installing a floating cover (different types), by allowing the formation of a surface crust, or by reducing the surface area per unit volume of the slurry store. Reducing the surface area is only a consideration at initial store design or at replacement. When using an emission abatement technique for manure stores, it is important to prevent loss of the conserved NH_3 during spreading on land by using an appropriate reduced-emission application technique (EEA, 2013).

The best proven and most practicable techniques to reduce emissions from slurry stored in tanks or silos are to provide a *'tight' lid, roof or tent structure*. The application of these techniques to existing stores depends on the structural integrity of the stores and whether they can be modified to accept the extra loading. While it is important to guarantee that such covers are well sealed or "tight" to minimize air exchange, there will always need to be some small openings or a facility for venting to prevent the accumulation of flammable gases, such as CH_4.

Floating cover sheeting may be a type of plastic, canvas or other suitable material. It is considered to be technique for *small* earth-banked lagoons. *Storage bags* for slurry on small farms (e.g. < 150 fattening pigs) also provide a system that reduces emissions.

If shallow earth-banked lagoons are replaced by *taller tanks or silos*, emissions will be reduced due to the reduced surface area per unit volume. This could be an effective (though expensive) NH_3 reduction option, particularly if the tanks are covered by a lid, roof or tent structure. However, the effectiveness of this option is difficult to quantify, as it is strongly dependent on the characteristics of the lagoon and the tank.

The Formation of natural crust by minimizing stirring of stored cattle slurry of sufficiently high dry matter content will allow the build-up of a natural crust. If this crust totally covers the slurry surface and is thick enough, and slurry is introduced below the crust, such a crust can significantly reduce NH3 emissions at little or no cost. This natural crust formation is an option for farms that do not have to mix and disturb the crust in order to spread slurry frequently. The emission abatement efficiency will depend on the nature and duration of the crust (Misselbrook et al, 2005) (Smith et al., 2007).

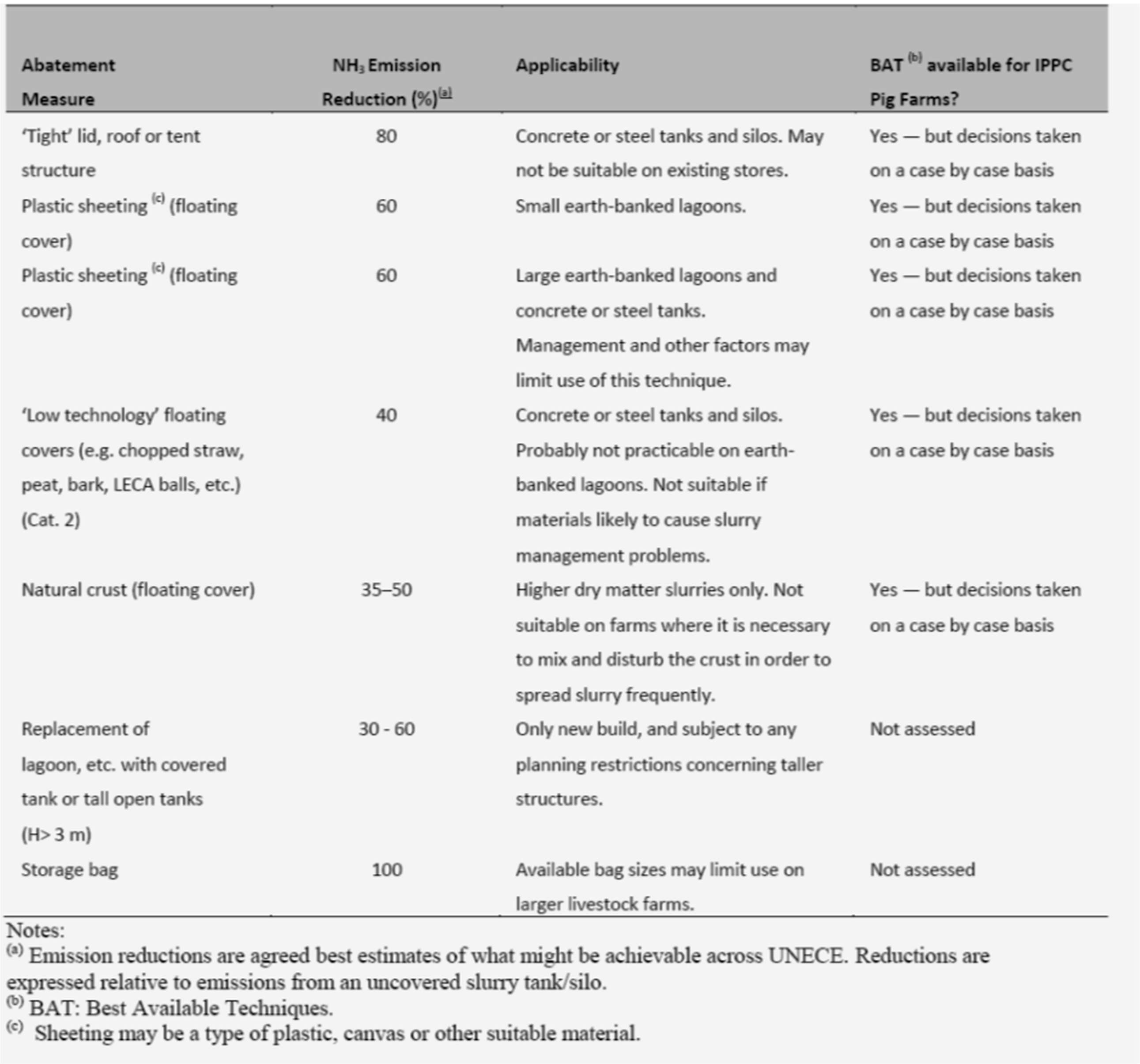
There are few options for reducing NH_3 emissions from stored farmyard (solid) manures for cattle and pigs. Experiments have shown that covering farmyard manure piles with plastic sheeting can substantially reduce NH3 emissions and did not show any significant increase in CH_4 or N_2O emissions (Chadwick et al., 2005) (Hansen et al., 2006).

Another very effective technique to reduce NH_3 emissions is slurry *acidification*. This treatment is not reported in Table 3 but is widely used in Denmark as a mitigation option. It was demonstrated that a pH reduction in the slurry by two units to about 5.5 reduces free NH_3 concentration by two orders of magnitude which practically eliminates NH_3 evaporation and loss from slurry (Ottosen et al., 2009). Generally the sulphuric acid has been suggested for economic reasons and its fertilizer value. The equipment currently used on several commercial farms in Denmark takes each day a portion of the slurry accumulating under slatted floor for pH adjustment; then the acidified slurry is sent to the slurries channels except for a part corresponding to the daily production of slurry, which is transferred to an outside storage tank with no further treatment (Petersen, 2012).

<u>Slurry separation</u> not always resulted in lowering the NH_3 emissions. When an increment is observed, this is related to the presence of a liquid fraction characterized by a higher TAN/TKN ratio and a lower TS% content, which slows the crust formation. In winter the increment can be also connected to the solid fraction: inside the heap the temperature can be very high promoting the NH_3 volatilization (Dinuccio et al., 2008).

<u>Anaerobic digestion</u> potentially can increase NH_3 emission due to higher TAN concentration and higher pH. Digestion of the slurry increases the concentration of TAN, reduces the concentration of volatile fatty acids (VFA) and increases the concentration of total inorganic carbon (Sommer, 1997). Since a crust do not develop, an increment of NH_3 volatilization is expected.

Table 3 NH_3 emission abatement measures for cattle and pig slurry storage (EMEP/EEA Emission inventory guidebook, 2013)



Abatement Measure	NH_3 Emission Reduction (%)[a]	Applicability	BAT [b] available for IPPC Pig Farms?
'Tight' lid, roof or tent structure	80	Concrete or steel tanks and silos. May not be suitable on existing stores.	Yes — but decisions taken on a case by case basis
Plastic sheeting [c] (floating cover)	60	Small earth-banked lagoons.	Yes — but decisions taken on a case by case basis
Plastic sheeting [c] (floating cover)	60	Large earth-banked lagoons and concrete or steel tanks. Management and other factors may limit use of this technique.	Yes — but decisions taken on a case by case basis
'Low technology' floating covers (e.g. chopped straw, peat, bark, LECA balls, etc.) (Cat. 2)	40	Concrete or steel tanks and silos. Probably not practicable on earth-banked lagoons. Not suitable if materials likely to cause slurry management problems.	Yes — but decisions taken on a case by case basis
Natural crust (floating cover)	35–50	Higher dry matter slurries only. Not suitable on farms where it is necessary to mix and disturb the crust in order to spread slurry frequently.	Yes — but decisions taken on a case by case basis
Replacement of lagoon, etc. with covered tank or tall open tanks (H> 3 m)	30 - 60	Only new build, and subject to any planning restrictions concerning taller structures.	Not assessed
Storage bag	100	Available bag sizes may limit use on larger livestock farms.	Not assessed

Notes:

(a) Emission reductions are agreed best estimates of what might be achievable across UNECE. Reductions are expressed relative to emissions from an uncovered slurry tank/silo.

(b) BAT: Best Available Techniques.

(c) Sheeting may be a type of plastic, canvas or other suitable material.

2.5 Methods for gas measurements from slurry storage

To obtain accurate measurements of emissions from stored slurries the most suitable techniques and methods must be adopted in relation with the aims of the research.

The choice depends on many factors: advantages and disadvantages of the methodology used, the techniques of the methodologies used, the times and the costs.

The experiments can be conducted in field or in laboratory condition, inside temperature controlled rooms. In the latter conditions it’s possible to study the different effluents in more standard conditions and repeatable conditions.

The chamber method has been developed in response to a need to measure emissions of nitrogen, sulphur, and carbon compounds for a variety of field applications. Basically a chamber involves a physical enclosure or a sampling chamber to create a limited headspace over the release surface that is physically separated from surroundings. In this space the substances emitted from the material can be analysed and accumulated. For measuring emissions, the chamber technique has the important advantage of association of a particular emission site and its measurable array of physical, chemical, and microbiological properties with emissions of particular compounds or their reaction products (Aneja et al., 2006).

A sampling chamber has an open-bottom face and is usually equipped with air inlet(s) and outlet(s). The chamber is placed on the floors of animal buildings or on the surfaces of liquid or solid manure storages that release NH_3.

The methodologies used are mainly two: the **closed static chamber** and the **open dynamic chamber**. The difference between the two is structural: the first ones isolate completely a small part of atmosphere, while the open chambers are crossed by an air flux continuously.

In the **static closed chamber** the adjective static underlines that there is not any flux except that one generated from the gradient concentration between the source and the headspace of the chamber. The sample of air is drawn by the headspace after a time interval during which the chamber is left on the emitting surface. This method gives information on the potential emission of the material without the presence of an air flow on the emitting surface.

When the measurement is taken the chamber is airtight. Some chambers utilized a stirring fan inside the chamber to mix air. Thus, through several samples, usually effectuated using a syringe, the saturation curve of the gas is obtained (Fig. 2). The time necessary to draw the curve is different depending on the gas considered.

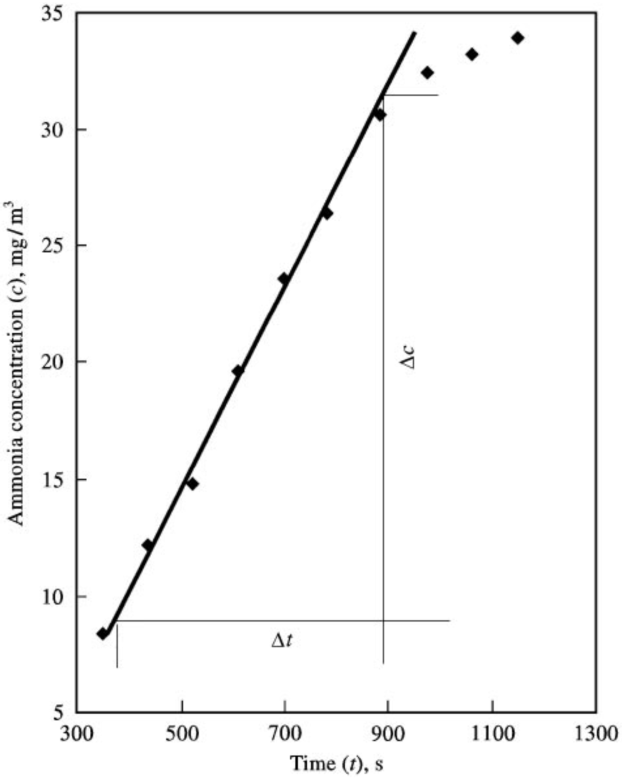


Figure 2 Example of saturation curve for NH_3 (Hornig et al., 1999)

Once the coefficient at the beginning of the flux curve is calculated then the equation for the flux calculation is:

$$F = \frac{\Delta NH_3}{\Delta t} \times \frac{V}{S} \qquad 1$$

Where:

$\frac{\Delta NH_3}{\Delta t}$ = angular coefficient of the curve (NH_3 = NH_3 concentration in terms of mg m^{-3}; Δt = time interval in s)

V = volume of the headspace (m^3)

S = emitting surface (m^2)

The most used instruments for determining the gas concentrations are:

- Trace gas analyser
- Gas chromatography

This method is typically used to measure emissions from soil (Cardenas et al., 2010, Velthof et al., 2011, Rodhe et al. 2012).

The dynamic chamber are often very similar to the static closed chamber, and they differ from the previous ones for the presence of two holes one representing the inlet and the other one the outlet of the air flow that is established in the headspace of the chamber (Fig. 3). This flow can be generated by the natural environmental wind naturally, more often, is produced artificially connecting a fan or an air pump to the sampling system that can work in compression or in aspiration. The sampling in this case occurs drawing air coming out form the chamber which drags the compounds emitted inside the chamber.

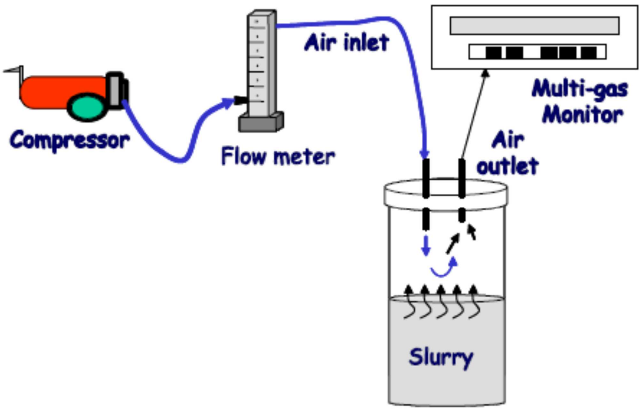


Figure 3 Schematic diagram of the sampling system (Dinuccio et al., 2008)

In this case the flow rate set is very important in the emission determination. In particular significant errors can be done if excessive or too low flow are adopted. In fact it was demonstrated that a too high flow or a too low flow can underestimate or overestimate the gas emission respectively (Gao et al., 1997). When the measurement is starting the methodology involves the enclosure of the containers. An air flow must be applied knowing his characteristics (flow, temperature). The air outlet, if the system is in aspiration, is connected to a flow-meter and to a pump. In this way the space between the emitting surface and the lid is ventilated and the air exchange can be adjusted with the flow meter.

In general measurements occurs in four phases:

1) At the moment zero the lid is closed
2) During the first 20-30 minutes the headspace is only ventilated in order to reach steady emission conditions
3) Start the sampling
4) End of the sampling

At the end of the sampling the lid can be reopen or left in place: in this case the air flow is over the surface and is maintained at the entire time of the experiment.

The flux in this case are calculated with the following equation:

$$F = \frac{Q(C_{in} - C_{out})}{A} \qquad 2$$

Where F is the flux expressed in terms of mgm^{-2}h^{-1}, Q is the air flux expressed in m^{3}h^{-1} C$_{in}$ is the NH$_3$/N$_2$O/CH$_4$/CO$_2$ concentration of the air inside the bottle, C$_{out}$ is the concentration of the air entering in the bottle. In alternative the fluxes can be expressed in terms of g t^{-1} d^{-1}. In this case the divisor is the volume instead of area (A).

The specific methodology used has been found to have a strong influence on the magnitude of NH$_3$ losses (Smith et al., 2007). Sharpe et al. (2004) reported that laboratory approaches showed greater losses than field systems, while dynamic flux methods (e.g. wind tunnels) have demonstrated greater losses than closed static systems, partly because of the influence of NH$_3$ gradients and wind. Moreover, NH$_3$ is a difficult gas to directly measure without disturbing its transport characteristics.

2.5.1 Main Methodologies used in field/pilot scale experiments

Micrometereologial systems

In these methods the flux density of the gas is measured in the free air above the surface. Advantage of these technique: they do not disturb the environmental or soil processes which influence gas exchange; they allow continuous rapid measurement, facilitating the investigation of environmental effects; they provide a measure of the average flux over a large area minimising the sampling problem created by point to point variation (Denmead et al., 1983). The difficulties of this methodology: their successful application requires a larger plot size (> 10 m^2) compared with the tunnels ($\approx$1 m^2), which at times may not be easily replicated (Smith, 2007).

Funnel system

Figure 4 Examples of funnel system.

This system (Fig. 4) consists of a PVC funnel covering 0.14 – 0.12 m^2 of slurry surface, connected to vacuum pump. A volume flow meter and a flow meter, and a floating platform. Because the no-wind condition under the funnel, the system enables to compare the emissions measured in different storage tanks. The Equation used to calculate the flux is N°2 (Balsari et al., 2007).

Wind tunnel

The wind tunnels (Fig. 5) consist of a fan, a hose, a mixing chamber, the tunnel body, an expansion chamber and a sampling point. Smith et al. (2007) reported the wind tunnel technique is just as robust as the preferred TPS method. The main advantage of the wind tunnel technique is that it is a relatively small, portable unit that is easily replicated in the field, requiring small plots compared with the micrometeorological method. The wind tunnel also offers the advantage of studying several treatments and making good comparisons between treatments.
The limitation with this methodology, however, is the initial set-up cost (~$3500.00 per tunnel), and the fact that the wind tunnel is a controlled system that may at times vary from ambient conditions (Smith et al., 2007).

Figure 5 Example of wind tunnel

Large Open Chamber

Measurement of NH_3 release from solids such as straw-based manure leads to a number of difficulties such as the recognition of significant local source and requires to operate with large sampling areas. With the aim to cover this gap of information the open dynamic chambers were realized.

Each device (Fig. 6) is made up of: a *chamber* covering a surface of ≈20 m^2 , a *fan*, connected to a galvanized sheet iron pipe (diameter 1 m, length 10 m) equipped with an internal flow conditioner (pipe and flow conditioner function is to avoid air rotation within the pipe, making homogeneous air sampling possible close to pipe outlet), an *air sampling system* made up of a pump, a flow meter, a volume meter (the system collects samples of outgoing air from 15 different sampling points spread on pipe), two *anemometers(* a first one for the measurement of the air velocity within the pipe and second one under the chamber) (Balsari et al., 2004).

Figure 6 A large open chamber

2.6 Technologies used for gas concentration measurements

2.6.1 Ammonia

To obtain atmospheric NH_3 concentrations, suitable techniques must be adopted and one or more measurement variables must be chosen depending on measurement objectives. Comparison of animal facilities, management and abatement strategies usually involves the determination of not only NH_3 concentration but also its emission (Ni, 2001). To obtain NH_3 emissions, whether for comparison or for baseline determination, from animal buildings or manure storages, measurements of NH_3 concentration difference between the outgoing and incoming air is essential along with the air temperature, air pressure, and air exchange rate (or ventilation rate). Most NH_3 concentration measuring devices provide volumetric concentrations directly. However, mass concentration are necessary to calculate NH_3 emissions. The volume of gas depends on both temperature and pressure and is therefore not constant. When converting to mass concentration, the volumetric concentration is multiplied by the molecular weight and the pressure, and divided by gas constant and the temperature. Temperature and pressure therefore needs to be known. Temperature and pressure therefore need to be measured. Atmospheric pressure varies between 980 and 1040 mbar. Any how the measurement of temperature and pressure is relatively easy with few technical challenges.

Ni and Heber define the NH_3 sampling as “the technique and the procedure that specifies the locations where air samples are taken, controls the time, interval, frequency and duration of samples taking, and regulates the volume or mass of the sample air to be measured”. We can extend this definition also to the other gases (CO_2, CH_4, N_2O).

This definition includes three elements: location, time, and volume/mass.

Concerning the sampling location at uncovered manure storage and lagoon the localized gas concentration depends on weather conditions such wind speed, wind direction, temperature and on emission mechanism of that particular gas. Large concentration gradient can exist at these areas when there is a poor dispersion due to slow air movement. Consequently, different sampling location may result in wide variations measurements data. Surely the number of sampling locations determines the spatial resolution of the NH_3 concentration profile.

The more the sampling locations are, the better the spatial resolution of the data. Unfortunately, in practical situation the number of sampling locations are comprised because the limitation of the budget, equipment, time and manpower.

Also the time is very important to consider in gas sampling. Very often results of gas concentration acquired at that specific time are usually and only valid for that time. Seasonal temperature change is the most important factors influencing seasonal gas concentration variations. In open animal feedlots and manure storage/lagoons, higher temperature means faster NH_3 release from liquid manure and hence higher NH_3 concentrations above the manure surface. In addition also precipitation and solar radiation can quickly change the emission pattern.

Another very important parameter during sampling is the sample volume: accurate control of air sample volume is indispensable for some measurements techniques such as acid traps. In these case volume control devices are needed.

The first reported measurements of NH_3 concentrations at animal facilities were in the 1960s using wet chemistry (Ni and Heber, 2008). Analytical methods of NH_3 can be categorized as "wet methods", which use aqueous media, and "dry methods" which use direct analysis of NH_3 in the gas phase.

Measurements can also be classifies as active or passive. An active device needs a pump, whether hand or electric powered, to provide controlled sample air flowing to the deice. A passive measurement device does not require a pump. It allows air to diffuse into the sensor. Passive measurement devices need to be placed right at the sampling location during measurement. Passive techniques that depend on diffusion take longer to finish a measurement.

In general the variety and the number of existing techniques show that there is not yet a standard technique for measuring NH_3 concentration under agricultural field conditions. Therefore standard techniques and relevant methodologies need to be developed, and the existing NH_3 concentration measuring devices need to be tested, compared and evaluated.

Wet methods

ACID TRAPS

Most wet methods are standardized methods that rely on collecting gaseous NH_3 into a suitable acid solution and then performing concentration determination in the laboratory. Wet method can be active or passive. In the active method the air is pumped through the acid solution during sampling and volume of air passing through the solution is recorded. The NH_3 concentration is calculated based on the volume of air. In the passive method NH_3 diffuses into the acid and no pump is required.

The most commonly used acid is boric acid (Curtis at al., 1975), orthophosphoric (Pertersen, 2013; Wood, 2012) acid and sulphuric acid (Dinuccio e al., 2012). To evaluate the NH_3 concentration in the acid solution several techniques are available which mainly consist on titration and spectrophotometric methods. the principle of the latter (Nessler and indophenol techniques) is that air samples are converted into coloured compounds that are than determined. Titration methods tend to be less sensitive than the colorimetric ones.

The Equation used for flux determinations is the following:

$$F = \frac{(mg_{out} - mg_{in})}{A * T} \qquad 3$$

Where F is the flux expressed in terms of mg m^{-2} h^{-1}, mg_{out} are the mg of NH_3 captured in the air outlet acid traps, mg_{in} are the mg of NH_3 in the blank acid trap, A is the bottle surface area, T is the length of the sampling period.

Gas detection tubes

Gas detection tubes are based in absorption of target air pollutants on solid surfaces accompanied by colour reaction. Usually the sensitive of the tubes (0.5 – 260 ppm) are too low for measuring outdoor concentrations. That's why one of their more typical application is for measuring NH_3 concentrations at animal house especially broiler and swine houses were NH_3 concentration are very high (Elwinger et al., 1996), swine houses, (Hinz et al., 1998).The most obvious advantage of the gas detection tube is its operational and functional simplicity. Active gas tubes require a hand-pump that suck a predefined volume of air for stoke. Both ends of the test tube are sealed when are produced and then are open just before the measurement. The open end tube is inserted tightly into the pump connector. By pumping the end-pump, the air sample flows through the tube. The colour that arises is evaluated to asses NH_3 concentration.

Like active tubes, passive sampling tubes are also sealed before using. However, only one sealed end of the tube is broken to commence measurement. The opened tube is exposed at the selected sampling location for a specific time, usually several hours. The gas concentration indicated in the tube should be interpreted with exposure time.

Dry methods

Fourier Transform infrared spectroscopy

Fourier transform infrared spectroscopy is a technique involving the interaction of IR electromagnetic radiation with the test sample. In this method the output signal is known as an interferogram and is produced by an interferometer. As the movable mirror is gradually displaced, a cycle of maximum and minimum intensity recurs. It yields specific information about chemical structure of organic compounds based on the technique of vibrational mode of different chemical bonds. The FTIR spectrum is rich with information because each vibrational mode adsorbs a specific wavelength of IR radiation. Each bond within a molecule may have several vibrational modes. The FTIR absorption spectrum is a “fingerprint” for a particular molecule that can be compared with reference spectra of known compounds, thereby aiding in the identification of unknowns and providing unambiguous confirmation of the identity of “known materials”.

High resolution FTIR spectrometry was used in order to determine the emissions of NH_3, N_2O, CH_4, and volatile organic compounds (VOC) at a commercial pig farm in Upper Austria using a straw flow system by Amon and co-workers (Amon et al., 2007). The latter ones used the same technology in another work to assess the effect of slurry treatment on CH_4, N_2O and NH_3 emissions during storage and after application of dairy cattle slurry (Amon et al., 2006)

Infrared gas analyser

An infrared gas analyser is an infrared spectroscope, a subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. Non dispersive infrared (NDIR) analyser measure the spectral absorption of a gas at one spectral band of the IR spectrum. The spectral dispersion of the absorption spectrum of the gas is not used.

The photoacoustic gas analyser (Fig.7) is included in this category. Photoacoustic spectroscopy is a widely recognised technique to measure trace gases at parts-per-million (ppm) or parts-per-billion (ppb) level using semi- conductor laser in the near infrared range. This technique is based on the generation of an acoustic wave in a gas excited by a modulated laser beam at a wavelength corresponding to a absorption line of the gas species, and on the detection of this sound using a sensitive microphone. Various sensors have been developed in the past decades in the field of atmospheric pollution monitoring, in the semiconductor industries, in medical applications and in life science applications.

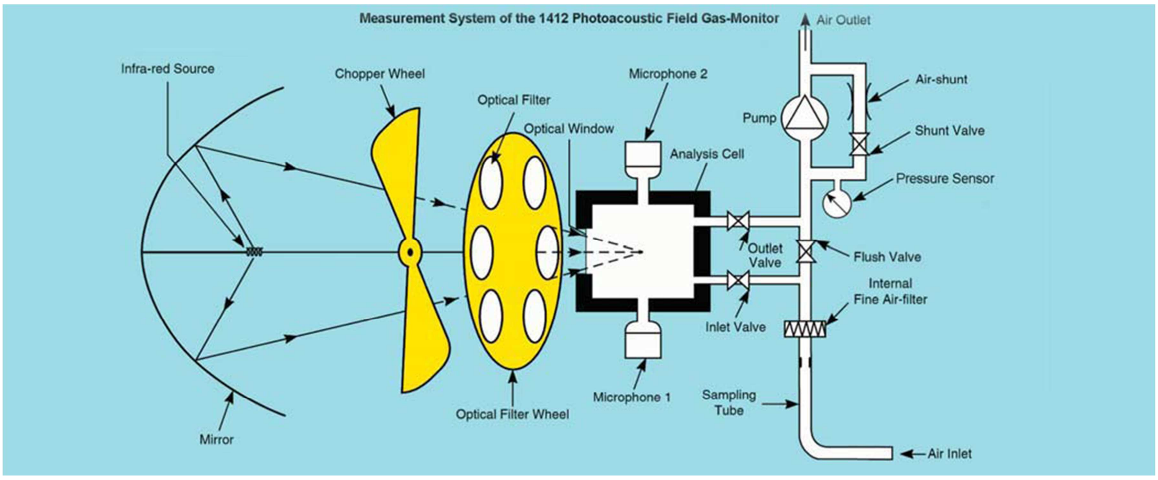


Figure 7 Scheme of a photoacoustic gas analyser.

The measurement cycle is the following:

1. The pump draws air from the sampling point through the air filter to flush out the “old” air in the measurement system and replace it with a “new” air sample. The pressure sensor is used to check that the pump sequence is elapsed successfully and to measure the actual air pressure.
2. The “new” air sample is hermetically sealed In the analyses cell by closing the inlet and outlet valves.
3. Light from an infrared light source is reflected off a mirror, passed through a mechanical chopper, which pulsates it, and then through one of the optical filters in the filter wheel.
4. The gas being monitored, causing the temperature of the gas to increase selectively absorbs the light transmitted by the optical filter. Because the light is pulsating, the gas temperature increases and decreases, causing an equivalent increase and decrease in the pressure of the gas (an acoustic signal) in the closed cell.
5. Two microphones mounted in the cell wall measure this acoustic signal, which is directly proportional to the concentration of the monitored gas present in the cell.
6. The filter wheel turns so that light is transmitted through the next optical filter, and the new signal is measured. The number of times this step is repeated is dependent on the number of gases being measured.
7. The response time is down to approx. 13 sec. for one gas or water vapour, or approx. 26 sec. if five gases and water vapour are measured.

This technique was used in many studies that deal with emission from animal storages. Some examples are: (Dinuccio et al, 2008), (Fangueiro et al., 2008), (Alluvione et al., 2010), (Guarino et al., 2007). The main advantages in using this technology are the following: possibility to obtain continuous measurements of four gases at the same time (NH_3, N_2O, CO_2, CH_4), rapid measurement time (≈ 2 min), portability. The gas analyser has a bult-in compensation for water and for potential cross-interference due to molecular relaxation between the other gases. However it was found (Chowdhury et al., 2014) that the software do not compensate fully for cross interference of CO_2 concentration on measured N_2O. Yamulki and Jarvis (1999) found that the main interferences came from water vapour. CO_2 also interfere with N_2O and CH_4 measurements. In particular they showed that there were not interference problems up to 100 and 40 ppm N_2O and CH_4, respectively.

Chemiluminescense analyser

Chemiluminescense NH_3 analysers involve an indirect measurement of NH_3 based on converting NH_3 to nitric oxide (NO) and then performing NO analyses with the chemiluminescense method. This technique requires two instrument modules: an NH_3 converter and NOx analyser.

This technique is not often used from measuring emissions from slurry stores. Although an example experience can be found in two works of Aneja (2001), where he measured NH_3 emission from anaerobic lagoons.

Laser spectroscopy

This technique utilizes laser for evaluation of gas concentration of the sample analysed.

All LGR analysers utilise a unique laser absorption technology called Off-Axis Integrated Cavity Output Spectroscopy. Unlike older laser-based methods, such as cavity ring down spectroscopy (CRDS), this approach utilizes true wavelength scanning to record fully resolved detailed absorption line shapes.

In brief, since the laser beam does not have to be resonantly coupled to the measurement cell (i.e. precise beam alignment is not critical), these Analysers are relatively inexpensive, simple to build, and inherently robust thermally and mechanically. In addition, since LGR's technology can record reliable absorption spectra over a far wider range of optical depths (absorbance values) compared with CRDS, LGR Analysers provide measurements over a much wider range of mixing ratios (gas concentrations). LGR Analysers display the entire absorption spectra to the user in real time allowing for immediate system diagnostics and performance validation.

The measurement range of a NH_3 LGR Analyser is 0.5-10000 ppb with a precision of 0.15 ppb. Anyhow because this technology is relatively new, its application on NH_3 emission measurement from animal slurries is still limited.

This instrument is relatively new and there is not any journal paper yet that consider its applications.

Figure 8 NH_3 LGR's analyser

2.6.2 Greenhouse gas emission

Laser spectroscopy

Los Gatos Research analyser are an exemple. The principle of functioning is the same of the NH_3 analysers. The measurements ranges are, 0.01 – 100 ppm, 200 – 20000 ppm, 7000 – 70000 ppm for CH_4, CO_2 and H_2O respectively. The precision is 2 ppb / 0.6 ppb, 300 ppb / 100 ppb, 200 ppm / 60 ppm for CH_4, CO_2 and H_2O respectively. Some of these analysers have also a portable version (Fig. 9).

Figure 9 Ultra-portable LGR's analyser

With IPad it is possible to interact with the instrument by VNC Lite application.

Concerned this instrument there already several journal papers that demonstrate its reliability in emission measurement in different application field (e.g. Farrel et al., 2013).

Gascromatography

N_2O, CH_4 and CO_2 are separated on two identical capillary columns and detected either by flame ionization (FID) (CO_2 and CH_4) or by electron capture (N_2O). CO_2 is converted to CH_4 after separation and prior to measurement. Working ranges: 2.0 –100 ppm CH_4, 0.3–40ppm N_2O, and 0.3–5000 ppm CO_2 and the limits of detection are 0.07, 0 and 2.4ppm, respectively.

- FID: the gas to analyse is brought in an oven where is burnt by hydrogen flame. The flame creates an ions flux, which increases when an organic molecule is burnt. A polarised voltage attracts the ions to the electrode positioned near the flame. The produced current is proportional to the amount of the burnt sample. The current produced is measured by an electrometer and converted in a digital form. On a display is possible to see the measurement. These types of detectors cannot measure the inorganic substances. This is the reason why in same systems there is a catalyst for CO_2 and CO measurement, which is constituted mainly by a Nichel bed, which reduces CO and CO_2 into CH_4, gas that can be detected by the FID.
- in the electron capture detector a radioisotope, commonly ^{63}Ni is deposited on a golden lamina end is used as electrons source. This emits β radiations, that are fats electrons, which ionise the transport gas, producing low electrons and positive ions that produce a specific value of electric current.

This technique is one of the most robust and reliable for measuring greenhouse gases. The main disadvantage is the impossibility to obtain measurement in continuous.

Many studies decided to use this technique for emission estimation from storage facilities: Loyon et al. (2007), Petersen et al. (2009), Massé et al. (2003), (Sanchez-Monedero et al., 2010) etc.

Infrared spectroscopy

CH_4, N_2O and CO_2 concentration can be measured also by a photoacustic technology based on infrared spectroscopy. More details have been already explained in the "Infrared spectroscopy" of Ammonia Section.

2.7 Ammonia release models

2.7.1 Introduction

Determining NH_3 emissions from agricultural facilities is critical to appropriately regulate emissions from livestock operations to protect the environment. Direct measurement of NH_3 fluxes from manure storage facilities, however, can be challenging, time consuming, and expensive (Liang et al., 2002).

The national NH_3 emission can be generated by commonly accepted methodology for the inventory of NH_3 emission. However two considerations suggest that a more dynamic, process-based approach will be increasingly necessary. Firstly, the atmospheric dispersion models used to assess the geographic distribution of NH_3 deposition require emissions estimates at a much higher temporal resolution. Secondly, abatement technique applied through changes in animal feeding or in animal housing will often modify the physical and the chemical nature of the manure that then passes through storage and is applied to land.

Since volatilization is governed by both manure characteristics and environmental or meteorological conditions, this onerous task has to be performed for each separate livestock operation because no two facilities will be similar in all respects. Process-based emission models offer an alternative, cost-effective approach for estimating NH_3 emissions from such systems, because process-based models generally only require values for key manure, environmental and meteorological parameters to effectively predict NH_3 volatilization rate for system in question.

Many models of NH_3 release from liquid manure, either in animal houses, in field applications or in constructed manure stores, have been published. Some of them are mechanistic ones, in which both physical understanding and quantitative description of NH_3 release are given. There also empirical NH_3 release models that describe simple statistical correlations of the measured data, these models can be useful in assessing the accuracy or application of mechanistic approach. Usually they also have the advantages of simplicity in structure and are easy to use in estimating the quantity of NH_3 released.

In Table 4 are summarized the models applied in this work.

Table 4 Brief description of the models considered in this thesis

Number	Model	Description	Application
1	Arogo et al., 1999	Mechanistic model (two film theory)	Liquid swine manure and aqueous solutions
2 - 3	Beija et al., 2006	Mechanistic model (two film theory)	Swine lagoon
4 - 5	Cortus et al., 2009	Mechanistic model (boundary layer theory)	Pig slurry pit
6 - 7	De Visscher et al., 2002	Mechanistic model (two film theory) and statistical model	Anaerobic swine lagoon
8	Harper and Sharpe, 1998	Statistical model	Anaerobic dairy waste lagoon
9	Sommer et al., 2006	Statistical empirical model	Slurry source
10	Sommer et al., 2013	Mechanistic model (two film theory)	Water
11	Teye et al., 2008	Mechanistic model (boundary layer theory)	Dairy building
12	Vaddella et al., 2013	Statistical model	Liquid dairy manure
13	Zhang et al., 2005	Mechanistic model (two film theory)	Liquid manure storage

2.7.2 Process involved in ammonia emission

Diffusion and convective mass transport are involved in the transport of NH_3 from animal manure to the free atmosphere. The transport of gas components can be divided into three closely related processes: gas component transport in the source to the surface air-manure boundary layer, gas transfer over the interface of the manure-air boundary layer and transfer from this interface to free air stream. The transfer over the manure-air interface to the atmosphere is referred to here as "release".

Transfer of gas components in the manure or in the air are strongly affected by the gas concentration gradient in the manure and in the air, because the diffusive nature is part of the transport. The gradient is affected by convection, which is related to natural or force stirring of the manure and air movement above the manure surface.

In conclusion three are the essential parameters for determining the NH_3 release: NH_3concentration in the liquid boundary layer, NH_3 concentration in the air boundary layer and the mass transfer coefficient.

For the interphase transport in multi component systems, several theories have been proposed. The two main theories are the "Two film Theory" and the "Boundary layer theory".

Two-film theory

The two film Theory was developed by Whitman in 1923 as reported by Welty et al. it's the most used theory for modelling NH_3 release. The theory has three principal assumptions:

- the rate of mass transfer between the two film is controlled by the rates of diffusion through the film on each side of the interface

- no resistance is offered to the transfer of the diffusing component across the interface
- The liquid phase below the film boundary layer is stirred and homogeneous and that the air above the air boundary layer is also mixed and homogeneous. At a given distance from the surface the concentration of molecules and ions is not significantly affected by the surface processes and a bulk composition is assumed.

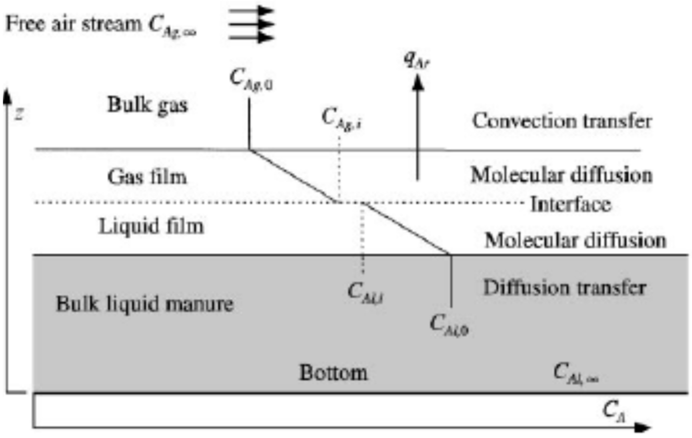


Figure 10 Two-film theory adopted in NH_3 release models Note: $q_{Ar,}$= flux of NH_3 release; z, vertical distance. Concentrations of NH_3 (C_A): $C_{Ag,\infty}$= gas phase in free stream; $C_{Ag,0}$ = gas phase on the immediate surface of gas film; $C_{Ag,I}$ = gas phase at the interface of two films; $C_{Al,I}$ = liquid phase at the interface of two films; $C_{Al,0}$ = liquid phase on the immediate surface of liquid film; $C_{Al,\infty}$= liquid phase at the bottom of the bulk manure. Source: Ni,1999

Fig. 10 illustrates the two-film model. The NH_3 concentrations in the gas phase $C_{Ag,I}$ and $C_{Ag,0}$ were sometimes expressed as partial pressure. The relationship of concentration and partial pressure is described by the ideal gas law. In the steady state, the flux of NH_3 transfer through the gas film is the same as through the liquid film. Since the movement through the liquid films is a molecular diffusion, it can be described by Fick's law diffusion, that describe the rate of diffusive transport of molecule or a species (A) through a stagnant phase of air or liquid phase. It describes the flux molcm^{-2}s^{-1}) through a layer of thickness Δ(cm)

$$F(A) = -D * \frac{d[A]}{dz} \qquad 4$$

$$F(A) = -\frac{D}{\Delta z} x([A]_2 - [A]_1) \qquad 5$$

Where [A] is in mol cm^{-3} and D is in cm^2 s^{-1}, and Δz (cm) is the thickness of the phase. The negative sign is because of the convection regarding the orientation of the z-axis (the component moves from the boundary with high concentration ([A_1]) to that with a low concentration ([A_2]) and thus [A_2]-[A_1] is negative). By multiplying by -1, the flux of components becomes positive, which is correct. Eqn. 5 shows that the flux increases with increasing the diffusivity coefficient and decreases with increasing the thickness of the layer through which the component A has to move. The diffusion coefficient is compound-specific and its magnitude depends mainly on the size of the molecule.

In most the models, the thickness of the gas and liquid films is not defined. However, as the name of "film" implies, their thickness should be very small compared with the thickness of bulk gas and bulk liquid. Therefore, concentrations gradients between the manure surface CG and free air stream should exist. The air film thickness is generally much larger (100 times) than the water film thickness (Sommer et al., 2013). In the NH_3 release models using the two-film theory, three steps of NH_3 mass transfer should be included. They are the convective form the surface of the gas film to the free air stream, the diffusion transfer across the two films, and the diffusion transfer inside the bulk manure. At the beginning of the release process, the convective transfer depletes the NH_3 from the surface of the gas film and creates a concentration gradient. This causes first the NH3 diffusion transfer across the two films and then the NH_3 diffusion transfer inside the bulk manure. The three steps of transfer make the structure of the NH_3 release model relatively complex. Moreover, the Nh3 concentrations at the interface of the two films are practically unmeasurable.

Boundary layer theory

This theory is describe by the Incropera and DeWitt (Ni, 1999): In a free air stream flows over a surface and concentration of NH_3 at the surface $C_{Ag,0}$ differ from that in the free air stream $C_{A,\infty}$ a concentration boundary layer will develop. It is the region of the fluid in which concentration gradients exist and its thickness is typically defined as the value of the vertical distance for which

$$\frac{CG-CA}{CG-CA\infty}= 0.99 \qquad 6$$

In the theory of boundary layer, conditions within the concentration boundary layer determine the convective mass transfer. In the NH_3 release models using the boundary layer theory, only two steps of NH_3 mass transfer are included: the convective transfer from the manure surface to the free air stream, and the diffusion transfer inside the bulk manure. Compared with the two-film theory, the boundary layer theory is simpler in structure and more clearly defined. It was used in the models of NH_3 release from applied fertilizer and stored slurries (Table 4).

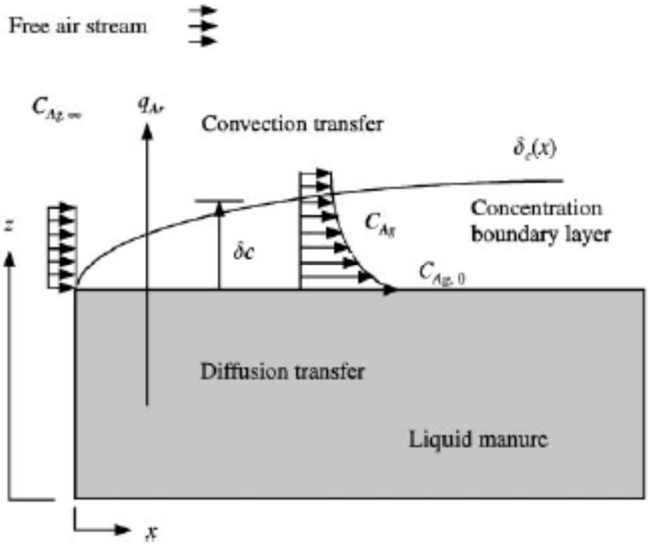


Figure 11 Concentration boundary layer theory adopted in NH_3. Note: S_c= thickness of concentration boundary layer; C_{Ag}= concentration of gaseous NH_3; $C_{Ag,\infty}$=, concentration of gaseous NH_3 in free air stream; $C_{Ag,0}$= concentration of gaseous NH_3 at liquid surface; q_{Ar} = flux of NH_3 release; x horizontal distance; z, vertical distance. Source: Ni,1999

Non dimensional number

In some models to include the influence of system geometry and other air, liquid manure properties in the mass transfer coefficient correlations, decided to use the dimensionless number approach.

An essential first step in the treatment of any convection problem is to determine whether the boundary layer is laminar or turbulent.

In the laminar boundary layer, the fluid flow is highly ordered and it is possible to identify streamlines along which fluid particles move. The highly ordered behaviour continues until a transition zone is reached, across which a conversion from laminar to turbulent conditions occurs. Conditions within the transition zone change with time, with the flow sometimes exhibiting laminar behaviour and sometimes exhibiting the characteristics of turbulent flow.

Flow in the fully turbulent boundary layer is, in general, highly irregular and is characterized by random, three-dimensional motion of relatively large parcels of fluid. Mixing within the boundary layer carries high-speed fluid toward the solid surface and transfers slower-moving fluid farther into the free stream.

The onset of turbulence depends on whether the triggering mechanisms are amplified or attenuated in the direction of fluid flow, which in turn depends on a dimensionless grouping of parameters called the *Reynolds number*

$$Re_x = \frac{\rho \mu_\infty x}{\mu} \tag{7}$$

It may be interpreted as the ratio of inertia to viscous forces in a region of characteristic dimension L. Inertia forces are associated with an increase in the momentum of a moving fluid.

In calculating boundary layer behaviour, it is frequently reasonable to assume that transition begins at some location x_c, This location is determined by the critical Reynolds number, $Re_{x,c}$. For flow over a flat plate, $Re_{x,c}$ is known to vary from approximately 10^5 to $3x\ 10^6$, depending on surface roughness and the turbulence level of the free stream. A representative value of

$$Re_{x,c} = \frac{\rho \mu_\infty x_c}{\mu} = 5 \times 10^5 \tag{8}$$

where, for a flat plate, the characteristic length is x, the distance from the leading edge.

The *Schmidt number,* which is defined by Equation…, provides a measure of the relative effectiveness of momentum and mass transport by diffusion in the velocity and concentration boundary layers, respectively. For convection mass transfer in laminar flows, it therefore determines the relative velocity and concentration

boundary layer thicknesses.

$$Re_L \times Sc = \frac{\nu}{\mathcal{D}_{AB}} \tag{9}$$

Sherwood number

$$Sh = f(x^*, Re_L, Sc) \tag{10}$$

This parameter is equal to the dimensionless concentration gradient at the surface, and it provides a measure of the convection mass transfer occurring at the surface.

2.7.3 Ammonia in the liquid phase: dissociation constant (k_d) determination

During the volatilization process, only free ammonia (NH_3(aq)) can be transported across the air-water interface and released into the atmosphere. In an aqueous solution an equilibrium exists between ammonium ion (NH_4^+) and NH_3(aq) . The equilibrium equations and NH_3 volatilization from solution can be represented by the following equations.

$$\mathrm{NH_4^+} \Leftrightarrow \mathrm{NH_{3(aq)}} + \mathrm{H^+}$$

$$\mathrm{NH_{3(aq)}} \Leftrightarrow \mathrm{NH_{3(g)}}$$

The equilibrium concentration of NH_3 species depends on the solution pH and temperature.

The NH_3(aq) fraction in solution increases with pH, and at any given pH the NH3(aq) fraction increases with temperature. Theoretically, volatilization should not occur below pH 7 because almost 100% of the NH_3in solution is in the NH_4^+ form. Another factor (discussed later) that may also affect the NH_4^+/NH_3 equilibrium is the ionic strength of the solution (Arogo et al., 2003).

There is no direct method to measure NH_3 (aq) concentration in solution. Usually, NH3 (aq) concentration is obtained by using the fraction (F) of total ammonium nitrogen (TAN =NH_4^++$NH_{3(aq)}$) that is $NH_{3(aq)}$, i.e.

$$F = \frac{[NH_{3(aq)}]}{[NH_4^+] + [NH_{3(aq)}]} = \frac{[NH_{3(aq)}]}{TAN}$$

$$[NH_{3(aq)}] = F \times TAN$$

Where - [NH_3 (aq)] is free NH_3 nitrogen, [NH_4^+] is ammonium nitrogen, and [H+] is hydrogen ion concentrations (moles/liter or kg/m^3) in solution. Based on the dissociation constant (K_d), the fraction F is given by

$$F = \frac{K_d}{K_d + 10^{-pH}}$$

Assuming the activity coefficient of all the species involved in the dissociation reaction to be equal to unity, the ammonium dissociation constant can be expressed as:

$$K_d = \frac{[NH_{3(aq)}][H^+]}{[NH_4^+]}$$

Usually, K_d is calculated as function of slurry temperature (T_s) as shown in Table 5.

Equation for K_d is only valid for very dilute aqueous solutions where ions behave independently and it can be assumed that their activity coefficients are unity (Zhang et al., 2005). However, in more concentrated solutions, like liquid animal manure, it is often necessary to account for the fact that in a chemical reaction a substance behaves as though its concentration were somewhat less than the actual. Thus, it may be necessary to adjust the dissociation factor with the activity coefficients for NH_4^+, NH_3(aq), and H^+. The activity coefficient of an ion is defined as the ratio between the apparent or active concentration of a substance to the analytical or actual concentration of the substance.

Generally, the activity coefficients decrease as the ionic strength of a solution increases (Zhang et al., 2005). Thus, the dissociation constant value for NH_4^+in solution with different total solids value is expected to be different from the value in deionized water. The lower the total value, the closer the k_d value will be to that in deionized water. It has been reported that the k_d value for ammonium in manure water is different from the value in water (Zhang et al., 1994; Liang et al. 2002). The k_d value in animal manure is 20-50% of the value in the water, depending on the characteristics of manure, such as solids content. Some authors (Hashimoto, 1971)reported that the value of NH_4^+dissociation constant in chicken manure with 3.5% to 8.5% TS was 17% the value in dilute anhydrous NH_3 solution. Zhang et al. (1994) reported that NH_4^+ dissociation constant in liquid swine manure with 1% TS was 20% the value in water. Liang et al. (2002) reported that ammonium k_d value for anaerobic swine lagoon liquid (TS = 0.25% and TAN =400 mg/L) to be 52% the value in deionized water at 25°C.

Table 5 Reported dissociation constant in ammonia release models.

Model	Dissociation constant (K_d o K_n)	Fraction of TAN in form of NH_3 (F o f)
Arogo et al. 1999	$\mathrm{K_d} = 10^{-\left(0.0897+\frac{2729}{(\mathrm{T_S}+273.15)}\right)}$	$\mathrm{F} = \frac{\mathrm{K_d}}{\mathrm{K_d} + 10^{-\mathrm{pH}}}$
Beija et al. 2006	$\mathrm{K_d} = 10^{-\left(0.0897+\frac{2729}{(\mathrm{T_S}+273.15)}\right)}$	$\mathrm{F} = \frac{\mathrm{K_d}}{\mathrm{K_d} + 10^{-\mathrm{pH}}}$
Cortus et al. 2009	$pH_E = pH + 1.1$ $K_d = 0.2 \times 10^{-\left(0.0897+\frac{2729}{T_{flm}}\right)}$	$f = -0.0444 \times TAN + 0.00105 \times pH$ $f = \frac{10^{pH_E}}{10^{pH_E} + \frac{1}{K_d}}$
De Visscher et al. 2002	$\mathrm{K_d} = 10^{-\left(0.0897+\frac{2729}{(\mathrm{T_S}+273.15)}\right)}$	$F_{corrected} = \frac{1}{1 + 10^{-pH}(1 + K_{ads})/K_d}$
Sommer et al. 2006	log K_N = -0.09018 -2729.92/T *(K)*	$[\mathrm{NH_3}]_{\mathrm{solution}} = \frac{[\mathrm{TAN}]}{1 + ([\mathrm{H_3O^+}]/K_N)}$
Sommer et al.2013	log K_N = -0.09018 -2729.92/T *(K)*	$[\mathrm{NH_3}]_{\mathrm{solution}} = \frac{[\mathrm{TAN}]}{1 + ([\mathrm{H_3O^+}]/K_N)}$
Teye et al. 2008	$K_d = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} = 0.2 \times 10^{-(0.0897+2729/T)}$ $= 0.16 \times 10^{-2729/T}$	$F = \frac{K_d \times 10^{\mathrm{pH}}}{K_d \times 10^{\mathrm{pH}} + 1}$
Vaddella et al. 2013	$\mathrm{K_d} = 10^{-\left(0.0897+\frac{2729}{\mathrm{T_S}+273.15}\right)}$	$\mathrm{F} = \frac{\mathrm{K_d}}{\mathrm{K_d} + 10^{-\mathrm{pH}}}$
Zhang et al. 2005	$\mathrm{K_d} = 10^{-\left(0.0897+\frac{2729}{\mathrm{T_S}+273.15}\right)}$	$\mathrm{F} = \frac{\mathrm{K_d}}{\mathrm{K_d} + 10^{-\mathrm{pH}}}$

2.7.4 Ammonia in the air boundary layer

The release of the dissolved NH_3 from the surface of the source to the air phase immediately above the liquid surface is driven by the difference in the atmospheric concentration of the gases and the concentration of the components in the surface liquid layer. The partitioning of the components between atmosphere and liquid is described by Henry's law. A high Henry law constant (K_H o H) indicates that the gas is soluble in the liquid and low constant that the gas is insoluble and has a large fraction in the gaseous phase. The Henry's law constant increases exponentially with temperature.

Henry's constant was expressed with different definition and different dimensions (Tab. 6). It can be concluded that the Henry's constant in NH_3 modelling are currently in a state of confusion and a standard Henry's constant needs to be established. In this context the non-dimensional form is more convenient for the calculation than others forms (Ni, 1999).

Table 6 Reported Henry's constant in NH_3 release models.

Model	Henry's constant	Dimension
Arogo et al. 1999	$H = 1384 \times 1.053^{(293-T)}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non dimensional
Beija et al. 2006	$\log H = -1.69 + \frac{1477.7}{273.15 + T}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non - dimensional
Cortus et al. 2009	$H = 1431 \times 1.053^{(293-T)}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non - dimensional
De Visscher et al. 2002	$H = \frac{2.395 \times 10^5}{T + 273.15} \times e^{(\frac{-4151}{Ts+273.15})}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non - dimensional
Rumburg et al. 2008	H= P_A/C_L	$\frac{P_A}{[NH_3\,]_L}$ = atm/(mol/l)
Sommer et al. 2006	$\log H = -1.69 + \frac{1477.7}{273.15 + T}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non dimensional
Sommer et al.2013	ln K_H = = $-160.559 + \frac{8621.06}{T+273.15} + 25.6767 * \ln(T + 273.15) - 0.035388 * (T + 273.15)$ H= K_H x 1 x 0.0821 x 298	$\frac{P_A}{[NH_3\,]_L}$ = atm/(mol/l)
Teye et al. 2008	$H = 4.169 \times 10^{-6} \times (273.15 + Ts) \times e^{\frac{4151}{(273.15+Ts)}}$ $\approx 4.169 \times 10^{-6} \times (273.15 + Ts) \times 10^{\frac{1800}{(Ts+273.15)}}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non dimensional
Zhang et al. 2005	$H = \frac{2.395 \times 10^5}{T + 273.15} \times e^{(\frac{-4151}{Ts+273.15})}$	$\frac{[NH_3]_l}{[NH_3]_G}$ Non dimensional

3 Aim of the research

This research is part of two projects one Italian (NER0) and one English (Defra project AC0114) which aim to give operational guidelines concerning the slurry management techniques in order to assess if they can be considered already possible mitigation techniques or if other options must be taken into account in order to limit the negative environmental impact. The activities carried out can be divided in two main groups:

1) *Experimental activity*
   a) Pilot scale experiments in controlled temperature conditions which aim to study comparatively the emission and the chemical evolution of treated and untreated slurries during one month storage. In particular it was evaluate how mechanical separation and anaerobic digestion affect NH_3 and greenhouse gas emissions from the storage. The experimental plan was designed in order to apply mechanical separation on untreated slurries and digestates and to consider different typologies of slurries, whose characteristics can be considered representative of the average for the region considered.

   In particular the methodology used enhanced the obtaining of potential nitrogen emissions which can be compared with the real nitrogen losses calculated from the chemical analyses.

   b) Pilot scale experiments in field conditions which aim to study the effect on NH_3 and greenhouse emissions of the following treatments and mitigation option:

      b.1) mechanical separation
      b.2) application of a coat of clay granules on slurry surface
      b.3) acidification with sulphuric acid

Experiments *a* and *b.1* took place at the experimental farm of Landriano (Italy). In particular a digestate and his respective separated fractions were stored for three months during two different seasons of the year in order to evaluate the effect of different climate conditions on emissions (precipitation, wind velocity, temperature). Furthermore the experimental set up enhanced the to give some operational information concerning the effect of disturbance actions on gaseous emissions.

Experiments (b) and (c) took place at Rothamsted Research Center (UK) under polytunnels. Emission factors were determined assessing only the impact of temperature.

Lastly the thesis work have concerned the assessment of various models found in literature which simulate the NH_3 emissions from storage. In particular for each experimental condition (field and laboratory) the best fitting models were chosen. Then calibration was carried out using the measured data during experiments.

2) Modelling activity
   The overall objective of this experiment was to evaluate the use of models to simulate ammonia emission rate from slurry storage suitable over a range of slurry chemical and physical properties, namely pH,
   temperature and concentration. The specific objectives to achieve the overall objective were:
   a) to assess the pre-existing models in literature
   b) to collect slurry composition and emission rate measurements from experimental activity into dataset
   c) to set a calibration procedure
   d) to evaluate the calibrated models

The idea of this activity is to have a model which evaluate NH_3emissions which can be correct with factors that consider the treatment applied (i.e. mechanical separation, anaerobic digestion, mitigation options) or the particular storage condition(i.e. climate conditions, crust presence). These specific coefficients are determined during the experimentations previously described.

This activity results very important in the order to evaluate the best available inventory technique for NH_3 emission from slurry stores. Coordination of model development is advisable, to pool knowledge, create synergies and guarantee good congruency among emission models.

4 Material and methods

4.1 Pilot scale experiments in controlled temperature conditions

The pilot scale experiments in controlled temperature conditions comprised 6 campaigns (Table 1) which took place in a room where temperature was set according to the annual average of maximum temperatures (17 ° C) in Pianura Padana. Each experiment lasted 32 days.

Table 1 Overview of the Experiments took place in temperature controlled conditions

Experiment	Treatment	Type of slurry	Abbreviation
1	Mechanical separation	Digestate (50 % cattle; 35 %pig; 5% poultry and cattle manure; 10 % other biomass)	P_UN
		Liquid fraction	P_LF ← P_TR
		Solid fraction	P_SF ←
2	Mechanical separation	Digestate (90 % cattle slurry; 10% corn silage)	C_UN
		Liquid fraction	C_LF ← C_TR
		Solid fraction	C_SF ←
3	Mechanical separation	Pig slurry	P_UN
		Liquid fraction	P_LF ← P_TR
		Solid fraction	P_SF ←
4	Mechanical separation	Cattle slurry	C_UN
		Liquid fraction	C_LF ← C_TR
		Solid fraction	C_SF ←
5	Anaerobic digestion	Cattle slurry	C_UN
		Digestate (100% cattle slurry)	C_TR
6	Anaerobic digestion	Pig slurry	P_UN
		Digestate (100% pig slurry)	P_TR

Design of pilot-scale storage facility

Each slurry was stored in duplicate (total of 6 vessels for each slurry) inside 35 L plastic open vessels (operative volume: 25 L, open surface 0.096 m^2) for a period of 32 days. The temperatures of the different fractions were recorded continuously using temperature sensors connected to a data-logger at 30-min intervals (HOBO U12, Onset Computer Corporation, Bourne, MA, USA).

Figure 1 Experimental set up

Slurry and storage management (Treatments)

In Table 1 it is possible to see which treatment was investigated in each experiment (Exp).

The aim of Exp. 1 and 2 was to study the effect of mechanical separation on emissions from codigested slurries. Thus two different digestates were investigated, one comprising pig and cattle slurries (P) and the other only cattle slurry (C):

- digestate P was derived from a cooperative biogas plant (1 MWe) located in Martinengo (BG), Italy, fed with 35% pig slurry, 50% cattle, 5% poultry and cattle manure, 10% other biomass (maize and sorghum silage, corn flour). Samples (60 L) were obtained from digested slurry (P_UN) and the liquid (P_LF) and solid fractions (P_SF) following mechanical separation (screw press);
- digestate C was derived from a farm installation (250 kWe) fed with 90 % cattle slurry and 10 % corn silage, located in Lodi Vecchio (LO), Italy. Samples (60 L) were taken of digested slurry (C_UN) and the liquid (C_LF) and solid fractions (C_SF) following mechanical separation (roller press).

For Exp. 3 and 4, which aim to investigate the effect of mechanical separation on emission from untreated slurries, one cattle and one pig slurry were chosen:

- P was derived from located in pig farm located in Guardamiglio (LO). Samples (60 L) were obtained from untreated slurry (P_UN) and the liquid (P_LF) and solid fractions (P_SF) following mechanical separation (screw press);
- C was derived from a dairy farm located in Brembio (Lodi). Samples (60 L) were taken of untreated slurry (C_UN) and the liquid (C_LF) and solid fractions (C_SF) following mechanical separation (roller press).

For Exp. 5 and 6, that aim to study the effect of anaerobic digestion on emissions from slurries the following slurries were chosen:

- digestate P was derived from a cooperative biogas plant (100 kWe) located in Treviglio (Bergamo) , Italy, fed with 100% pig slurry. Samples (60 L) were taken of untreated slurry (P_UN) and digestate (P_TR)
- digestate C was derived from a farm installation (100 kWe) fed with 100 % cattle slurry, located in Casale Cremasco (Cremona), Italy. Samples (60 L) were taken of untreated slurry (C_UN) and digested slurry (C_TR)

Gas Emission measurements

Gas emissions were measured twice a week using a dynamic chamber method (Dinuccio et al., 2008, Petersen et al.,2012) (Fig. 2). As in Petersen et al. (2012), on each sampling day the vessels were gently stirred with a mixer for about 1 minute and subsamples of one 1 L were transferred into 2 L plastic bottles (headspace: 1 L). An air flow of 1 L min^{-1} across the headspace was established for at least 30 min before gas sampling to reach a steady state (Dinuccio et al. 2008) and then emissions were measured over a period of 3 h. The air outlet was connected to two serial acids traps filled with 1% boric acid. The quantity of NH_3 trapped was determined by titration (Curtis et al., 1975).

An empty flask was inserted between the traps and the bottle, connected to a gas trace analyser (P-TGA) (1302 Photoacoustic gas-monitor, Innova AirTech Instruments, Denmark) for the determination of CH_4, CO_2 and N_2O concentrations. The instrument was run with corrections from cross-interferences between CO_2-H_2O and N_2O and between CO_2-H_2O and CH_4 (Yamulki & Jarvis, 1999, Chowdhury et al., 2014).

Fluxes were obtain with Eqn.2 of section 2.5.

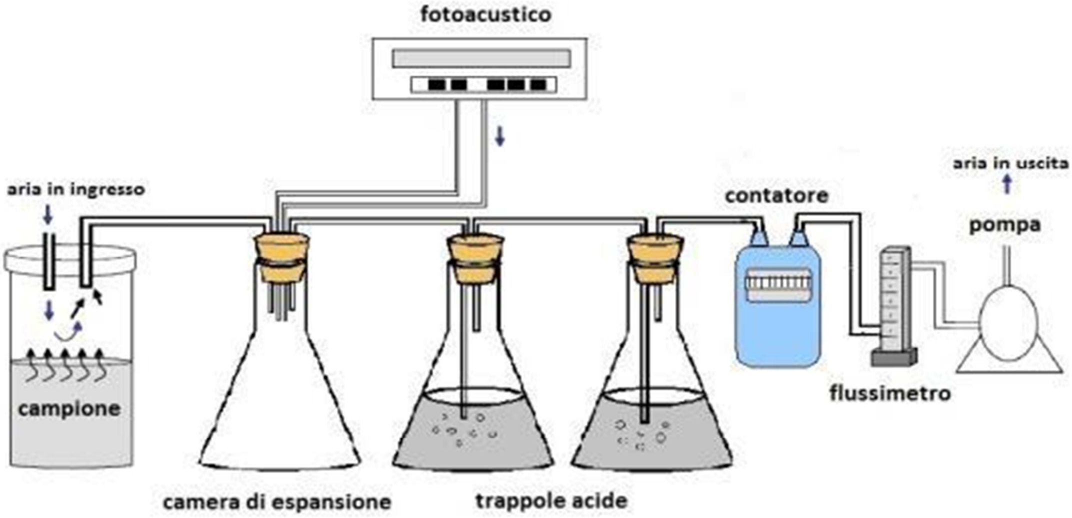


Figure 2 Scheme of gas sampling

In order to compare the emissions from the unseparated and the separated slurries, combined fluxes of the separated fractions were calculated using the following equation:

$F_{TR} = X_1 * F_{LF} + X_2 * F_{SF}$

Where F_{TR} is the sum of gas emissions from separated slurries, F_{LF} and F_{SF} are the fluxes for the liquid and solid fraction respectively, X_1 and X_2 are the mass separation efficiencies (%) of the mechanical separators used. The carbon emissions ($C\text{-}CH_4 + C\text{-}CO_2$) and the nitrogen emissions ($N\text{-}NH_3 + N\text{-}N_2O$) expressed in terms of g t^{-1} d^{-1} were then related to the initial TS and TAN contents, respectively.

To evaluate the emissions of GHGs in terms of CO_2 equivalents, conversion factors for 100 years' time horizon of 298 and 25 were used for N_2O and CH_4, respectively (IPPC, 2007).

Slurry analyses

The samples were analysed for total solid (TS), volatile solids (VS), total Kjeldhal nitrogen (TKN), total ammoniacal nitrogen (TAN) and pH, once a week and at the end of the investigation period, according to standard methods (APHA, 2005). All the chemical analyses data were adjusted taking into account the volume reduction caused by the evaporation during the storage period.

In order to compare the effect of treatment on slurry composition, differences in nitrogen loss were estimated from a mass balance of TAN and TKN analyses at the start and end of the storage period and expressed both as total losses and as a fraction of the TKN and TAN content at the beginning of the experiment. Losses from separated fractions were combined, considering the mass separation efficiency of the mechanical separators used. The total values obtained for the treated slurry (TR) are thus comparable with the unseparated digestates. The variation in TKN can be considered losses to air as in the storage environment the nitrification process is practically absent (Patni and Jui, 1991).

Also TAN variations can be considered losses, but in this case the concentration is also affected by the mineralisation processes and therefore can underestimate the effective emissions to air (Patni and Jui, 1991).

Statistics

Statistical data analyses were carried out with software package SAS (SAS 9.2, SAS Institute Inc., Cary, NC). Differences between treatments were assessed using a one way analyses of variance (ANOVA), followed by pair-wise comparisons the non-parametric Wilcoxon Test using PROC. UNIVARIATE in SAS. Significance levels of $P < 0.05$ (*) or $P < 0.01$ (**) have been used for statistical analyses. The treatments evaluated were mechanical separation and disturbance related to fluxes measurements and chemical analyses.

4.2 Pilot scale experiments in field condition

The pilot scale experiments comprised 7 campaigns (Table 2). Two took place at the Experimental farm of Landriano (Italy) and the other 5 at the North Wyke Research Center facilities (UK). The first two lasted 3 months whereas those ones placed at North Wyke lasted two months. In Exp.1 and 2 the emissions from anaerobically digested cattle slurry were studied during two different seasonal conditions, autumn-winter and spring-summer. Exp. 3, 4 and 7 studied the effect of clay granule layer on emission while 5 and 6 investigated the acidification effect. The timing of these was designed to give a good range of storage temperatures for each slurry type.

Table 2 Overview of Experiments took place in field conditions.

Experiment	Treatment	Type of slurry	Location	Period
1	Mechanical separation	Digestate	Landriano (PV) - Italy	1st November 2013 - 30th January 2014
2	Mechanical separation	Digestate	Landriano (PV) - Italy	8th May 2014 – 31st July 2014
3	Clay granules	Pig slurry	North Wyke - Devon - UK	10th April 2013 – 10th June 2013
4	Clay granules	Pig slurry	North Wyke - Devon - UK	21th June 2013 – 19th August 2013
5	Acidification	Cattle slurry	North Wyke - Devon - UK	27th September 2013- 25th November 2013
6	Acidification	Cattle slurry	North Wyke - Devon - UK	9th December 2013 – 3th February 2014
7	Clay granules	Pig slurry	North Wyke - Devon - UK	17th February 2014 – 24th April 2014

Design of pilot-scale storage facility

Landriano

The pilot-scale storage facility used in the experiment was situated at the experimental farm of the University of Milano (Landriano, Italy; 45°19'16.5"N, 9°15'56.4"E), in an open field 30 m from the nearest livestock building and storage. The pilot scale storage facility was comprised of 8 stainless steel cylindrical storage units (OscarInox 1000, ToscanaInox, Firenze, Italy) for liquid slurry and 4 heavy-duty PVC and polyester triple-layer side walls square containers with metal frame (Bestway s.r.l., Milano, Italy) for solid fraction. Each cylindrical storage unit was 1.25 m high, 1.02 m in diameter and had 1.02 m^3 total capacity (Fig. 3). Instead, metal frame square containers were 0.31 m high, 1.22 m per side, with a maximum storage capacity of 0.7 m3 of solid fraction. All 12 storage units were positioned above ground level and without lids or cover allowing rainfall and natural airflow over the slurry surface. An office container, located next to the storage units, contains equipment for regulation and monitoring of gas sampling.

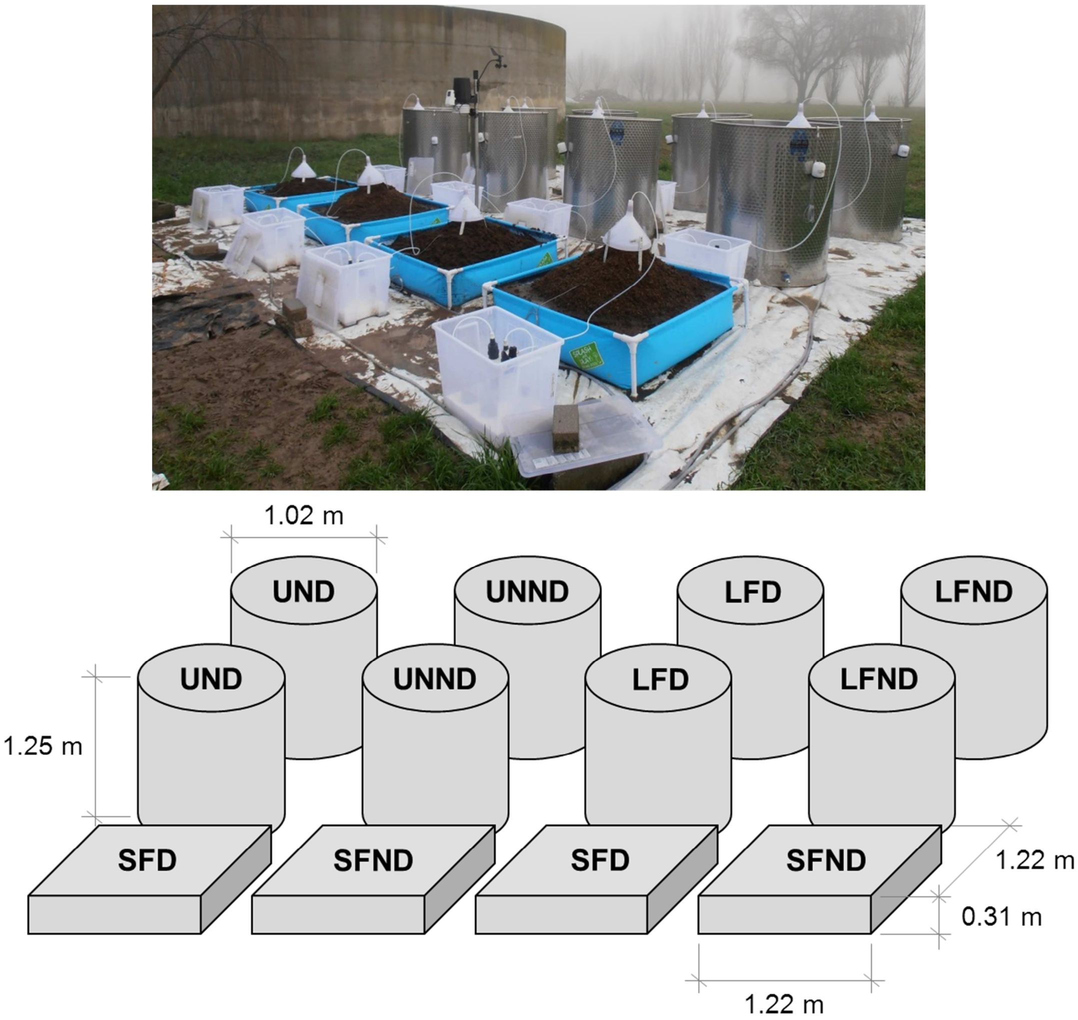


Figure 3 Pilot-scale storage, with 8 cylindrical storage units for liquid slurry and 4 square storage units for solid fraction. Anaerobically digested cattle slurry disturbed (UND) and undisturbed (UNND), liquid fraction disturbed (LFD) and undisturbed (LFND), and solid fraction disturbed (SFD) and undisturbed (SFND).

<u>North Wyke</u>

The measurements were conducted in one of the large polytunnels at the NW Polytunnel site (Fig.4). This excluded rainfall effects on storage and enables a greater contrast in storage temperatures over the year.

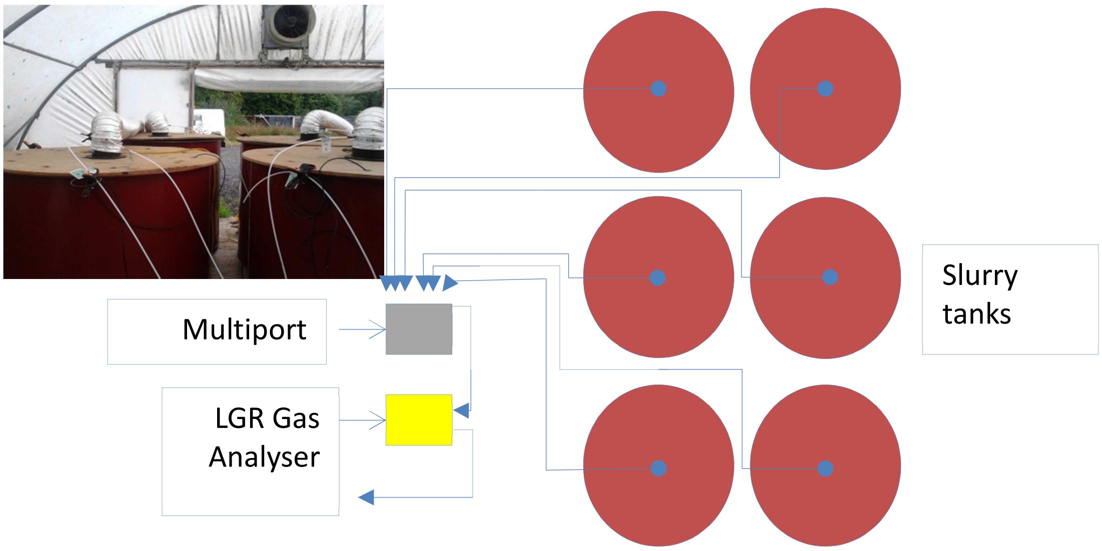


Figure 4 Schematic layout of slurry tanks, gas pipes and analyser

Slurry and storage management (Treatments)

Landriano

The slurry was collected from a biogas plant (250 kW) located in a lactating dairy cows farm (Lodi Vecchio, Italy) using sawdust as bedding material. The anaerobically codigested (**UN**) slurry (90 % cattle slurry, 10 % corn silage) was subjected to a mechanical separation with a roller presses generating liquid fraction (**LF**) and solid fraction (**SF**). Mechanical separation took place 24 h before the beginning of the storage experiment. Codigested slurry, liquid and solid fraction is transferred to the pilot-scale storage facility using conventional spreading equipment. At the start of each experiment the 8 cylindrical storage units were filled with liquid slurry (UN and LF) to a height of 0.95 m, corresponding to 0.8 m^3 each, while the 4 square containers were filled with SF to obtain a pyramidal pile (height of 1 m) corresponding to 250 kg each. For each type of fraction (UN, LF, and SF) were investigated disturbed and undisturbed (D and ND) treatment in duplicate (total of 12 containers). In the disturbed treatment, UN and LF were thoroughly stirred, with a mixer for about 6 minute, once a week to simulate filling and emptying situation in full-scale storage. Experiments were conducted in two different periods including autumn-winter season (AW) and spring-summer season (SS) within the years 2013 to 2014. The AW experimental period start from October 31, 2013 to January 30, 2014; and the SS period start from May 8 to July 31, 2014 for a period of 90 days.

North Wyke

Slurry was obtained from local commercial finishing pig and dairy farms from the under slat storage on the pig farm and the slurry pit reception area of the dairy farm to ensure that the slurry had not been previously stored for very long. The slurry was well mixed and then the 6 storage tanks were filled to a depth of approximately 0.8 m. A subsample of slurry was taken for analysis during the filling of each tank. Three tanks were randomly allocated as ‘controls’ and three as ‘treatment’ tanks to which the cover or acidification treatment were applied.

For the floating cover treatment, a layer of 2 cm diameter expanded clay granules was applied to the slurry surface to a depth of 7 cm. For the acidification treatment, 5 L of concentrated sulphuric acid was added to each tank during the filling process for Experiment 5. This proved to be too much, lowering the slurry pH dramatically to approximately 5 and causing excessive foaming during addition. For Experiment 6, 2.5 L were added to each tank.

Following tank filling and treatment addition, temperature probes were installed at approximately 20-30 cm slurry depth and tank lids fitted for commencement of measurements. At the end of the storage period, for Experiments 5-7 the slurry in each tank was thoroughly mixed and a subsample taken for analysis.

Temperature measurement and climate data

Landriano

Temperature in the slurry (UN, LF, and SF) was recorded every 30 minutes with temperature sensor (TMC6-HD, Onset Computer Corporation, Bourne, MA), located at 0.3 m beneath the surface and connected to a data logger (HOBO U12-006, Onset Computer Corporation, Bourne, MA), which is connected to a PC. Weather data (air temperature, air humidity, precipitation, wind speed and direction, and barometric pressure) were obtained from 2 stations (Vantage Pro2 Station, Davis Instruments Corp., California, USA), which were installed inside the storage facility, at a height of about 1.8 m above the floor (Fig.5). Climate data were recorded every 5 min over each storage period.

Figure 5 Vantage Pro2 Station for whether data collection

North Wyke

The temperature in the slurry was recorded every 5 minutes with 6 temperature sensors (CS-U-VL20-0, Grant Instruments (Cambridge) Ltd, Cambridgeshire, UK), located at 0.3 m beneath the slurry surface of each tank. Ambient air temperature was recorded every 5 minutes using 2 sensors (CS-U-VL20-0), Grant Instruments (Cambridge) Ltd, Cambridgeshire, UK), located 50cm above the ground within the polytunnel housing the experiments. These were connected to a data logger (Grant 2020 series squirrel data logger, Grant Instruments (Cambridge) Ltd, Cambridgeshire, UK), from which data was downloaded to a PC at the end of each experimental 70 day period.

Ammonia emission measurements

Landriano

Emissions of NH_3 were measured once every 2 weeks using a dynamic chamber method (Dinuccio et al., 2008, Petersen et al.,2012) from slurry surface of each storage. Measurement were performed in each storage period by using funnel systems (Balsari et al., 2007) floated on the slurry surface. The devices were placed at the centre of each storage unit. This system (Fig. 2) consists of a PVC funnel (Fig. 6), fixed on 4 PVC spherical ball float elements, covering 0.07065 m^2 of slurry surface, a two serial acids traps (Fig.6) filled with 1% boric acid solution, a vacuum pump, a volume meter and a flow meter. Airflow through the funnel system was approximately 9 l min^{-1}. NH_3 present in the sampled air is fixed in the boric acid trap and the quantity of NH_3 trapped was determined by titration (Curtis et al., 1985). NH3 fluxes were determined with Eqn.1 of section. 2.6.1

Where F is the flux expressed in terms of $mgm^{-2}h^{-1}$, mg_{in} are the mg of NH_3 captured during the functioning of the traps connected to the bottle containing the sample, mg_{out} are the mg of NH_3 captured from the trap of the blank, A is the bottle surface, T is the functioning time of the traps. The acid traps were measured over a period of 6 h.

Figure 6 Funnel systems placed on solid fraction (left) and slurry surface (centre) and acid traps (left)

North Wyke

NH_3 fluxes were measured twice a week. The equipment comprised 4 pump boxes (Fig. 7) associated tubing, power leads and transformer. Each bubbler unit has two sampling positions with two flasks filled with 100 ml of 0.02M Orthophosphoric acid (H_3PO_4). The traps were left at least one hour in function. Then samples were return to the Air Lab to calculate the NH_3 captured. Each trap subsamples the air flow coming out from the tanks with an air flow of ≈ $4lmin^{-1}$. The air flow inside the tank was estimated using an Airflow LCA6000 anemometer (Fig.8) that was placed at the end of ducting venting slurry tanks. The good fit was ensured using a funnel and preventing any air escaping. the air flow measurement was repeated 5 times.

The NH_3 content of the bubbler sample was determined using Aquakem 250 discrete photometric analyser. This technology is used for the determination of NH_4-N in raw and potable waters, including river water, rain water, waste water, surface and groundwater, and 0.1M boric acid, using a discrete photometric analyser. The limit of detection is 0.1 and the working range is 0.4 – 250 $mgNH_4$-N/litre. NH_3 is chlorinated with sodium dichloroisocyanurate to monochloramine, which reacts with salicylate to form a second intermediate, 5-aminosalicylate. Oxidative coupling of 5-aminosalicylate with salicylate forms an indophenol dye with an absorbance maximum at 660nm. Nitroprusside stabilises the monochloramine intermediate and also promotes the final oxidative coupling stage. The fluxes of NH_3 were calculated with Eqn.3 of Section 2.6.1.

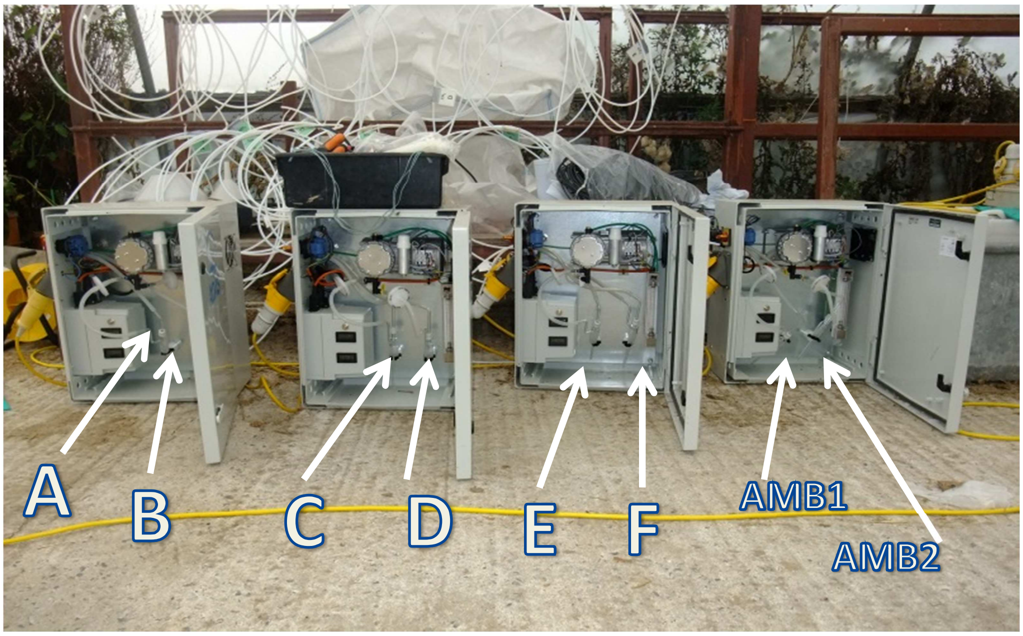


Figure 7 NH_3 **Bubbler order**

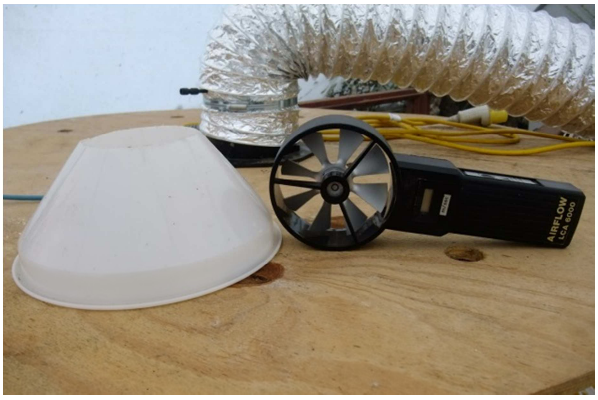


Figure 8 Cut off funnel and hand held anemometer

Greenhouse gas measurements

<u>Landriano</u>

Gas sampling for representative sampling of CH_4, CO_2, and N_2O emissions were collected from a subsample of the air using a funnel system as previously described. An empty flask was inserted between the traps and the funnel, connected to a gas trace analyser (P-TGA) (1302 Photoacoustic gas-monitor, Innova AirTech Instruments, Denmark) for the determination of CH_4, CO_2 and N_2O concentrations. The instrument was run with corrections from cross-interferences between CO_2-H_2O and N_2O and between CO_2-H_2O and CH_4 (Yamulki & Jarvis, 1999, Chowdhury et al., 2014).

Fluxes were obtained with Eqn.2 of section 2.6.2

Where F is the flux expressed in terms of $mgm^{-2}h^{-1}$, Q is the air flux expressed in m^3h^{-1} C_{in} is the concentration of the air above the slurry surface covered by the funnel, C_{out} is the concentration of the background air, A is the funnel surface.

North Wyke

CH_4 and CO_2 concentrations were measured using Los Gatos Research ultra-'portable greenhouse gas analyser (LGR UGGA) (Fig.9). A sampling point was placed along the pipe coming out from the tank.
The instrument and the presence of a multipoint sampler allow to do the gas measurements in continuous, as long as the instruments were available. The instrument was turned off only during the NH_3 sampling time (couple of hour, twice per week). In figure 4 and 5 it's possible have a view of different sides of LGR. With IPad we can interact with the instrument by VNC Lite application.

Fluxes were obtained with Eqn.2 of section 2.6.2

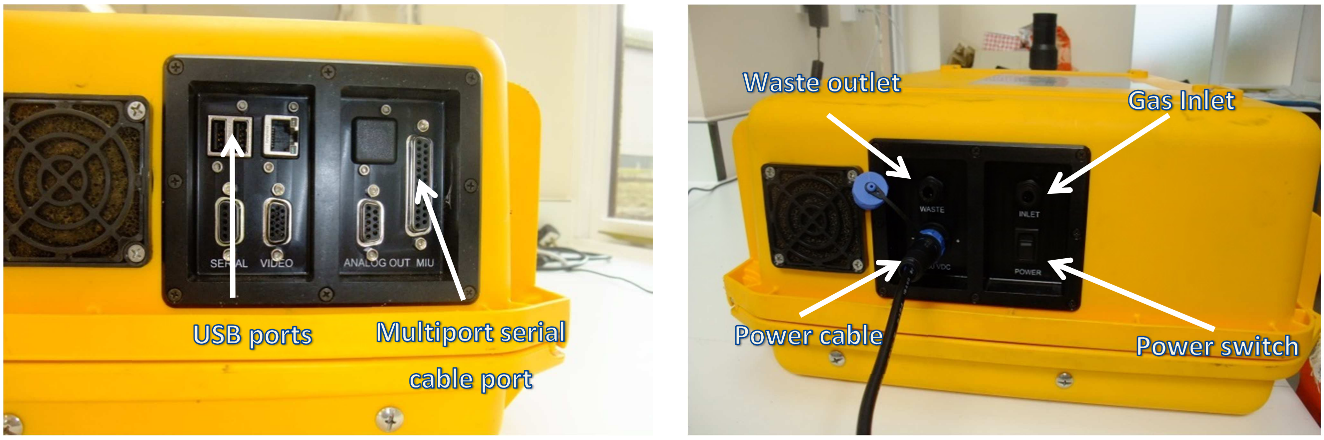


Figure 9 Los Gatos Research ultra-'portable greenhouse gas analyser. Details of the two sides.

N_2O concentration were measured using Perkin Elmer Clarus 580 Gas Chromatograph. In alternative also a Perkin Elmer Clarus 585 Gas Chromatograph. Twice a week for each tank 3 samples of air were taken (Fig. 10) and analysed. At the same time 6 ambient samples from randomly selected areas were taken as well. the sample were drawn with a syringe. Once the syringe was filled the air inside was injected into an appropriate vial which is returned to the laboratory for analysing.

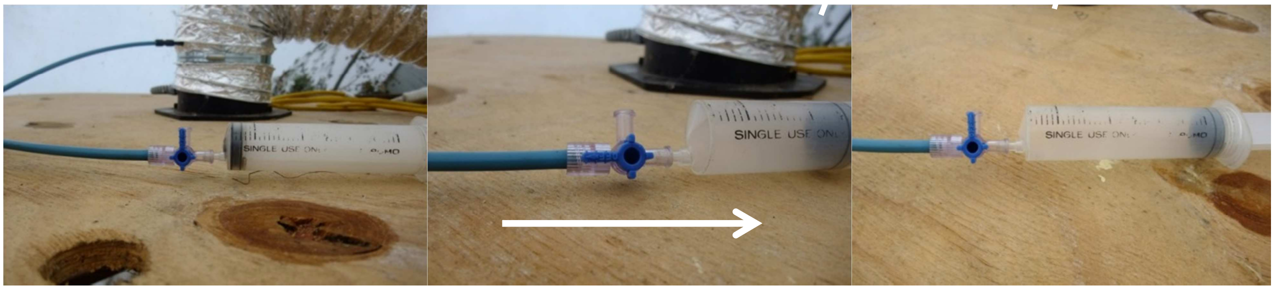


Fig 10 Procedure for gas chromatography sampling: 1. valve in open position 2. Venting the syringe, valve in closed position 3. Valve in open position and full syringe of sample

Slurry analyses and other measurements

Landriano

Slurry samples were taken at the beginning, at the finish, and once every 14 days of each storage period, for a total of 8 samples for each disturbed treatment (n=48) and 2 sample (start and end) for not disturbed treatment (n = 12). The slurry samples were analyzed for total solid (TS), volatile solids (VS), total Kjeldhal nitrogen (TKN), total ammoniacal nitrogen (TAN), pH, volatile fatty acids (VFAs), alkalinity (ALK), and total organic carbon (TOC) according to standard methods (APHA, 2005). Values of Phosphorus (P) and Potassium (K) are available just for the beginning of Exp.2.

All the chemical analyses data were adjusted taking into account the volume reduction and the volume increment caused by the evaporation and the rainfall during the storage period.

During each sampling day, after mixing of disturbed tanks and the activation of acid traps, some field measurements were done. These measurements concerned the following parameters:

- pH was measured at 2 cm depth and at 30 cm depth,
- slurry level for evaporation rate estimation
- pictures of the different slurries and manures for describing the status of the superficial layer: presence of absence of a crust.

This kind of observations further help in understanding the emission patterns resulting from flux measurements.

North Wyke

Slurry samples taken at the start and end of each storage period (at the start only for Experiments 3 and 4) were analysed for total solids and volatile solids content, total N, ammonium-N, pH. Total solids content was determined by measuring the mass loss after drying at 85 °C for 24 hours. Volatile solids content was determined by measuring the mass loss of a subsample of the total solids after further drying for 4 hours at 550 °C. Total N content was determined by Kjeldahl digestion. Ammonium-N was determined by automated colorimetry following extraction with 2M KCl. Potential CH_4 production was determined by incubating with inoculum at 37 °C using a purpose-designed laboratory system as described in the WP6 Task 1 report.

For Experiments 5 – 7, slurry pH was monitored twice per week throughout the storage period at the slurry surface and at a depth of 10 and 2 cm using a portable meter with pH probe. Pictures were also taken for monitoring the condition of the superficial layer.

Statistics

For Italian experiments statistical data analyses were carried out with software package SAS (SAS 9.2, SAS Institute Inc., Cary, NC). Differences between treatments were assessed using a one way analyses of variance (ANOVA), followed by pair-wise comparisons the non-parametric Wilcoxon Test using PROC. UNIVARIATE in SAS. Significance levels of $P < 0.05$ (*) or $P < 0.01$ (**) have been used for statistical analyses. The treatments evaluated were mechanical separation and disturbance related to fluxes measurements and chemical analyses.

For english experiments analysis of variance (Genstat 16.0, VSN International) was used to test for treatment effects within each experiment on cumulative gaseous emission over the storage period.

4.3 Models

This activity comprised three work steps:

1) Reproduction of models in literature and their application (see Section 4.3.1)
2) Model calibration (see Section 4.3.2)
3) Model evaluation (see Section 4.3.3)

4.3.1 Reproduction of models in literature and their application

The models evaluated are summarized in Table 4 in Section 2.7.1. The main characteristics and all the equations used for flux calculation are collected in Appendix 1.

The model selection was made in order to consider different type of models, afferent to the main theories. The major part were mechanistic models, while the remaining were statistical.

For a preliminary study of all the models was done using Excel in order to follow all the calculation steps that conduct to the flux. Very often, there were difficulties (especially for mechanistic models) to find all the Equations, necessary to run the model, in the same paper. However all the references are given in the Appendix 1.

4.3.2 Models calibration

The main steps of the calibration process were the following:

1) Model translation in Visual Basic codes

2) Dataset selection and characterisation

It was decided to divided all the measured data in 8 different dataset because different were the measurement conditions which are mainly related to environmental conditions. The measured data correspond to the input variables of the models (e.g. TAN, pH, temperature, humidity, air velocity) and to the measured fluxes. Dataset were built based on storage condition and pH measurement position: models hardly take into account the changes in slurry surface pH due to CO_2 emission from the slurry (Cortus et al., 2009). This is the reason why it was decided to test models with pH measured at 10 and at 2 cm depth. During the sampling operation, a pH gradient was observed in the superficial layer of the slurry. Because the variation sometimes is remarkable (> 0.5 point pH) and pH is one of the most influencing parameter on NH_3 emission determination, we decided to create two different dataset in order to evaluate which measurement position enable better simulations.

Below the main characteristics of each dataset are described:

- DATASET 1 represents the storage condition of the vessels stored in controlled temperature conditions. The main parameters that represent also the main input variables of the models are summarised in Table 3. pH measurement were at 10 cm depth. The measured data were derived from all the experiments that took place in controlled temperature conditions. With the data available it was possible to simulate 340 fluxes.
- DATASET 2 is equal to the prior one except for the pH measurement which were taken at 2 cm depth. With the data available 240 fluxes were simulated, a number that is inferior to that one obtained with the previous dataset: the experiments considered were only 3, 4, 5 and 6. In the first two the pH was only taken at 10 cm depth.

- DATASET 3 represents the conditions inside the bottle system. The main parameters are summarized in Table 3. For this condition only one pH value was used. After agitation in fact no gradient is observed. All experiments in controlled temperature condition were considered for a total number of simulated fluxes of 260.
- DATASET 4 represents the storage conditions of field Italian experiments (1 and 2), which were characterised by very variable climatic condition (Table 3). For dataset 4 pH was recorded at 2 cm depth. 168 fluxes were simulated.
- DATASET 5 differs from the prior one for pH measurement position which this time was taken at 10 cm depth. 168 fluxes were simulated.
- DATASET 6 collected all data from the experimental activity done at Rothamsted Research Centre: in this case regarding climatic conditions only temperature was variable, air velocity more or less remained stable by the time. pH is measured at 2 cm depth. The experiments considered were number 3, 4, 5. 102 fluxes were simulated. In Exp.5 data from slurries with clay granules cover were taken.
- DATASET 7 is equal to the prior except for pH, which was measured at 10 cm depth. The experiments were the same of dataset 6. 102 fluxes were simulated
- DATASET 8 collects all the data concerning solid fractions. Because all the models considered were developed for liquid slurries we decided to create a different dataset for solid fractions in order to evaluate if these kind of models can be used also for solid manures. 306 fluxes were simulated.

Table 3 Range of input variable parameters of the models

DATASET	pH	TAN (gkg^{-1})	AIR VELOCITY	T_AMB	T_SLURRY	TS (gkg^{-1})
1	6.3 - 8.5	3.3 – 0.6	0.05	16.3-18.9	12.4 - 21	1.75 - 13
2	6.25 – 8.6	2.8 – 0.6	0.05	16.3-18.9	12.4 - 21	1.75 - 13
3	6.3 – 8.45	3.3 – 0.6	0.002	16.3-18.9	12.4 - 21	1.75 - 13
4	7.4 – 8.4	2.4 – 1.3	0.2-0.4	- 0.5 - 26.6	1.6 – 30.4	3.22-8.28
5	7.4 – 8.35	2.4 – 1.3	0.2-0.4	- 0.5 - 26.6	1.6 – 30.4	3.22-8.28
6	4.1 – 7.8	0.7 – 3.8	0.025-0.04	2.3 – 14.6	3 – 14.1	5.22-8.1
7	4.1 – 7.8	0.7 – 3.8	0.025-0.04	2.3 – 14.6	3 – 14.1	5.22-8.1
8	7.5 – 9.1	0.1 - 2	0.002-0.4	- 0.5 - 26.6	0.5 – 32.2	7.83 – 28.4

In conclusion the datasets individuated represents 4 conditions:

- VESSEL SYSTEM: characterised by higher air velocity than BOTTLE SYSTEM. Its characteristics are more similar to a normal storage condition where slurry stay undisturbed for almost the entire period.
- BOTTLE SYSTEM were flux measurements are done after slurry agitation. It represents the potential emission of the sample at a certain temperature. It’s called potential because it was demonstrates that after agitation NH_3 volatise more easily thus a remarkable emission increment is always observed (Blanes Vidal et al., 2009).
- ITALIAN FIELD CONDITION: all the environmental conditions are variables: experiments run in these conditions are those ones more similar to normal storage condition.
- UK FIELD CONDITIONS: slurry are subjected only to temperature changes. Air velocity is usually lower than Italian experiments

Main limits for the 4 conditions investigated :

- VESSEL SYSTEMS: for these datasets no direct measurements was done thus the measured fluxes were derived from the chemical analyses, in particular from the TKN loss, calculated as the difference between initial and final concentration. Consequently an average flux was derived for the entire storage period and was adopted for all the sampling days. Consequently, during calibration, simulated data were compared always with same flux.
- BOTTLE SYSTEMS: all the measured fluxes were estimated using acid traps method. The system does not show particular limitations.
- ITALIAN FIELD CONDITIONS: all the measured fluxes were calculated using the funnel system in connection with acid traps were. The main limitations related to this dataset concerned two aspects: the methodology used that probably underestimate the absolute emissions and the many factors and conditions that in open field conditions can influence emission pattern, which are not taken into account for model development (e.g. rain, presence of a crust).
- UK FIELD CONDITIONS: for this condition Exp. 3-4-5 were used. All the measured fluxes calculated using acid traps. The biggest limitation related to this dataset was the availability of chemical characterisation during the storage period, thus the intermediate concentrations were derived by interpolation method using the initial and the final concentration.

3) Individuation of calibration parameters

For each model we individuated several parameters which are listed in Table 4. For each parameter we have a default value which is indicated by the author and a range within the parameter can vary.

Table 4 Calibration parameters with their relative abbreviations are listed: the default value indicated the value reported by authors. Min and max are the maximum and the minimum values of the calibration range individuated for each parameter.

id	Model	Parameter	Abbreviation	Default value	Min	Max
1	cortus	k	Ck_1	0.664	0.5	1
2	cortus	k	Ck_2	0.5	0.2	0.8
3	cortus	k	Ck_3	0.333	0.1	0.5
4	cortus	F	Cf_1	0.0444	0.01	0.08
5	cortus	F	Cf_2	0.00105	0.001	0.005
6	cortus	H	Ch_1	1431	1400	1500
7	sommer_2	log_kn	S2_kn1	0.09018	0.1	0.05
8	sommer_2	log_kn	S2_kn2	2729.92	2700	2800
9	sommer_2	K	S2_k1	89	85	95
10	beija_env	Kl	BE_kl	1	0.1	100
11	beija_env	Kd	BE_kd	0.0897	0.01	1
12	zhang	H	Z_h1	2.395	0.1	10
13	zhang	Kg	Z_kg1	5.317	0.1	10
14	zhang	Kg	Z_kg2	2.012	0.1	10
15	devisscherpro	Kh	DVP_kh	2.395	1	10
16	devisscherpro	Kg	DVP_kg1	18.568	0.1	200
17	devisscherpro	Kg	DVP_kg2	703.61	100	1000
18	devisscherstat	F	DVS_f1	50.33	0	100
19	devisscherstat	F	DVS_f2	2.9	1	100
20	devisscherstat	F	DVS_f3	0.3913	0.1	1
21	devisscherstat	F	DVS_f4	0.0132	0.01	0.1
22	devisscherstat	F	DVS_f5	4.8076	1	100
23	harp	F	H_f1	75.18	0	100

id	Model	Parameter	Abbreviation	Default value	Min	Max
24	harp	F	H_f2	3.91	1	100
25	harp	F	H_f3	0.4656	0.1	1
26	harp	F	H_f4	0.0127	0.01	0.1
27	harp	F	H_f5	7.5023	1	100
28	beija_lab	Kl	BL_Kl	1	0.1	100
29	beija_lab	Kd	BL_Kd	0.0897	0.01	1
30	teye	Kd	T_kd	0.16	0.1	1
31	teye	H	T_H	4.169	1	10
32	teye	Kgl	T_kgl1	0.821	0.1	1
33	teye	Kgl	T_kgl2	0.7	0.1	1
34	teye	Kgl	T_kgl3	0.5	0.1	1
35	teye	Kgl	T_kgl4	0.5	1	0.1
36	teye	Kgl	T_kgl5	0.67	0.1	1
37	cortus exp	pKe	CE_pKe	1.1	1	1.5
38	Cortus exp	ka	CE_ka	0.2	0.1	1
39	Cortus exp	k	CE_k1	50.1	10	100
40	Cortus exp	k	CE_k2	0.8	0.5	1
41	Cortus exp	k	CE_k3	1.4	1.5	1
42	Arogo	kallL	A_ka1	3.7	1	10
43	Arogo	kallL	A_ka2	0.1	0.05	0.15
44	Arogo	kallL	A_ka3	0.97	1	0.5
45	Sommer	logkn	S_kn1	0.09018	0.1	0.001
46	Sommer	logKn	S_kn2	2729.92	2800	2600
47	Sommer	kgTeye	S_kg1	0.821	0.1	1
48	Sommer	kgTeye	S_kg2	0.7	0.1	1
49	Sommer	kgTeye	S_kg3	0.5	0.1	1
50	Sommer	kgTeye	S_kg4	0.5	1	0.1
51	Sommer	kgTeye	S_kg5	0.67	0.1	1
52	Vaddella	kol	V_kol1	0.00000000001	0.0000001	0.00000000001
53	Vaddella	kol	V_kol2	9.7	9	10
54	Vaddella	kol	V_kol3	0.34	0.1	1
55	Vaddella	kol	V_kol4	8.02	4	10
56	Vaddella	kol	V_kol5	0.26	0.1	1

4) Calibration procedure

The calibration process was written using Visual Basic Software.

During the calibration process each parameter (p) can vary as described in the Equation below:

$p = p \pm p/x$
p = default value of the parameter
x= step
In this case step = 20

The calibration process was based on several loops of calculations. For every loop all the parameters of the model are varied in a positive and negative direction. At the end of each loop only the parameter that obtain a better results is varied. All the other parameters are maintained as before. The optimisation process has been based on the minimisation of the NMSE (Normal Mean Square Error).

5) End of calibration

At the end of calibration three tables of output are given:

1. Simulated fluxes: Measured fluxes and simulated fluxes calculated with the calibrated parameters can be observed for possible considerations. These results have been used to draw the graph presented in Appendix 2
2. Calibration parameters: here are reported the new values of the parameters optimised
3. Statistics table: all the statistics parameters (see the dedicated section) for model evaluations are listed with their relative value.

4.3.3 Model evaluation

As in Cortus et al. (2008) the indoor air quality standards prepared by ASTM (2003) were used as a guideline for evaluating model accuracy during the calibration process. General agreement between the predicted and observed values for each parameter was evaluated using the correlation coefficient (R), the line of regression (with slope b) and the normalised mean square error (NMSE). The bias between the predicted and observed values was evaluated based on fractional bias (FB: difference between predicted and observed values, divided by average of predicted and observed values), and the bias based on the variance (FS: difference between variances of predicted and observed values, divided by average of predicted and observed value variances). Table 5 describes the evaluation limits set out by ASTM (2003).

The Equations used to calculate the different parameters are listed below

FB = fractional bias

$$\text{FB} = \frac{(\overline{C}_o - \overline{C}_p)}{0.5*(\overline{C}_o + \overline{C}_p)}$$

FS = bias based on the variance of the concentration

$$\text{FS} = \frac{2*\sigma_p^2 - \sigma_o^2}{\sigma_p^2 + \sigma_o^2}$$

R = correlation coefficient

$$\text{R} = \frac{\overline{(C_o - \overline{C}_o)*(C_p - \overline{C}_p)}}{(\partial * C_p)*(\partial * C_o)}$$

NMSE = Normal Mean Square Error

$$\text{NMSE} = \frac{\overline{(C_o - C_p)^2}}{\overline{C}_o \overline{C}_p}$$

b = slope of regression line

$$\text{b} = \frac{n*(\sum x*y) - (\sum x)*(\sum y)}{n*(\sum x^2) - (\sum x)^2}$$

Table 5 Evaluation parameters and limits included in the Standard Guide Evaluation of Indoor Air Quality Models (ASTM, 2003)

Evaluation parameter	Abbreviation	Limits
Correlation coefficient	R	$R > 0.9$
Line of regression Slope	b	$0.75 < b < 1.25$
Normalised mean square error	NMSE	$NMSE < 0.5$
Bias based on the average modelled and measure values	FB	$-0.25 < FB < 0.25$
Bias based on the variance of the modelled and measured values	FS	$-0.5 < FS < 0.5$

5 Results and discussion

Results are organised in three section, two dedicated to the experimental activity and one for models.

Experiments in particular were organised in two main groups:

Pilot scale experiments in controlled temperature conditions (5.1)

Pilot scale experiments in field condition (5.2). These ones are then divided in three groups:

> Group A: experiments carried out at Landriano experimental farm, which considered the effect of mechanical separation (5.2.1)
> Group B: experiments carried out in Devon (UK), which investigated the effect of acidification (5.2.2)
> Group C: experiments carried in Devon (UK), which investigated the effect of clay granules cover (5.2.2)

Table 1 shows and summarises all the manures used in the experiments and the relative abbreviation or name with which they appear in the graphs

Table 1 Manure types and corresponding abbreviations

Manure type	Abbreviation
Cattle/Pig	C/P
Liquid fraction	LF
Solid fraction	SF
Digestate	UN/DIG
Untreated slurry	UN/control
Solid fraction + liquid fraction	TR
Not disturbed / disturbed	ND / D
Acidified slurry	Treatment
Slurry covered	Treatment

5.1 Pilot scale experiment in controlled temperature conditions

In all the experiments in controlled temperature conditions, the average temperature of the different fractions during storage was 16.13 ± 0.98 °C. Temperature inside the solid fractions remained stable as well showing, that non composting process took place inside the vessels.

5.1.1 Effect of mechanical separation on emissions from digestates

Slurry characteristics and changes during storage

The initial composition of each digestate and their separated fractions used in this storage experiment is presented in Table 2.

Table 2 Untreated slurries (P_UN, C_UN), liquid fractions (P_LF, C_LF) and solid fractions (P_SF, C_SF) compositions at the beginning of the storage period. Mean and Standard Deviations (in brackets) of replicates are given. NA: not available

	TS (g/kg)	VS (g/kg)	TKN (g/kg)	TAN (g/kg)	TAN/TKN %	pH
P_UN	5.09 (0.06)	3.63 (0.39)	3.11 (0.06)	1.95 (0.04)	63	8.02 (0.02)
P_LF	3.7 (0.03)	2.40 (0.01)	2.49 (0.01)	1.29 (0.02)	52	8.11 (0.01)
P_SF	22.68 (0.06)	20.17 (0.15)	5.66 (0.04)	2.03 (0.16)	36	NA
C_UN	6.26 (0.15)	4.59 (0.15)	3.49 (0.11)	1.66 (0.06)	48	8.24 (0.02)
C_LF	4.18 (0.06)	2.73 (0.04)	3.09 (0.08)	1.84 (0.01)	59	8.14 (0.02)
C_SF	14.9 (0.08)	12.73 (0.08)	4.56 (0.15)	1.84 (0.00)	40	8.91 (0.01)

The C_UN had higher TS contents than the P_UN, but this was not the case for their respective solid fractions samples. This can be explained by the different mass separation efficiencies of the two separators, 9% and 19% for P and respectively.

Fig. 1 shows the results from the analyses, made periodically during the storage period concerning the TS, VS, TAN, TKN contents and pH. In both digestates TS and VS tended to decrease slightly during the storage period, which may be explained by the biodegradation processes of the organic matter over this time (Patni & Jui, 1985).

Fig. 1 shows the TKN and the TAN concentrations over the duration of the storage period. In both cases, the TAN and TKN of the liquid effluents (UN and LF) showed a slow and constant reduction with time. Contrarily the solid fractions showed a more marked reduction. From the fourth week the TAN concentration of P_SF showed a marked decrease, from 1.47g/kg to 0.23 g/kg (Fig. 1). The C_SF displayed a similar trend after the second week when the TAN concentration decreased from 1.26 to 0.42 g/kg. Similar results were also obtained by Hansen et al. (2006), who reported significant reductions in TAN content of the solid fraction during storage. The volatilisation of NH_3, stimulated by the aerobic environment of the storage conditions due to the porosity of SF, may explain this observation. Part of this reduction might be also explained by N immobilisation, because of the high C/N ratio of solid fraction (Fangueiro et al., 2008).

Concerning the pH of slurries (Fig.1), an initial decrease was observed in all the samples. Considering all the data, pH variations were relatively limited with values between 7.8 and 8.2. On average, the cattle effluents had a higher pH than the pig effluents. During the last two weeks of storage the cattle effluents showed a pH reduction while that of the pig effluents increased.

An initial pH reduction was also reported by Moset et al. (2012) and Patni and Jui (1991): at the beginning when the storage vessels are filled, the degradation of the organic matter causes VFA production and thus a pH reduction. Another factor that can cause the same effect is the NH_3 emission. The subsequent pH increment, as reported by Blanes-Vidal et al.(2009), may be connected to two different processes: a reduction in VFA and the emission of CO_2. The latter is more volatile than NH_3 and has a lower resistance to transport through the gas phase boundary than NH_3. Thus during the storage period observed it seems that the pH varied, also if in a very limited range, due to the prevalence of one mechanism over the other.

This can explain why the pH decrease slightly in the first week when the production of VFA and NH_3 emissions might prevail the effect of CO_2 emission. From the second week the pH raises probably because the reduction of VFA. In any case, separation did not show any effect on pH trends.

From Table 3 it is possible to observe the effect of mechanical separation (considering both the liquid and solid fractions together) on nitrogen losses during the storage period calculated on chemical analyses basis.

Table 3 Mean and Standard Deviations (in brackets) of TKN and TAN losses during storage for separated and unseparated slurries.

	P_UN	**P_TR**	**Variation due to separation**
TKN loss (kg/t)	0.61 (0.05)	0.88 (0.01)	+45%
TKN loss /TKNin (%)	19.55 (1.25)	26.38 (0.10)	**+ 35%**
TAN loss (kg/t)	0.69 (0.06)	0.77 (0.03)	+13%
TAN loss/TANin (%)	**35.23 (2.44)**	**41.33 (0.40)**	**+ 17%**
	C_UN	**C_TR**	
TKN loss (kg/t)	0.49 (0.06)	0.88 (0.10)	+81%
TKN loss /TKNin (%)	13.96 (2.03)	26.00 (2.07)	**+ 86%**
TAN loss (kg/t)	0.33 (0.11)	0.78 (0.01)	+137%
TAN loss/TANin (%)	**19.82 (5.22)**	**42.74 (0.01)**	**+ 116%**

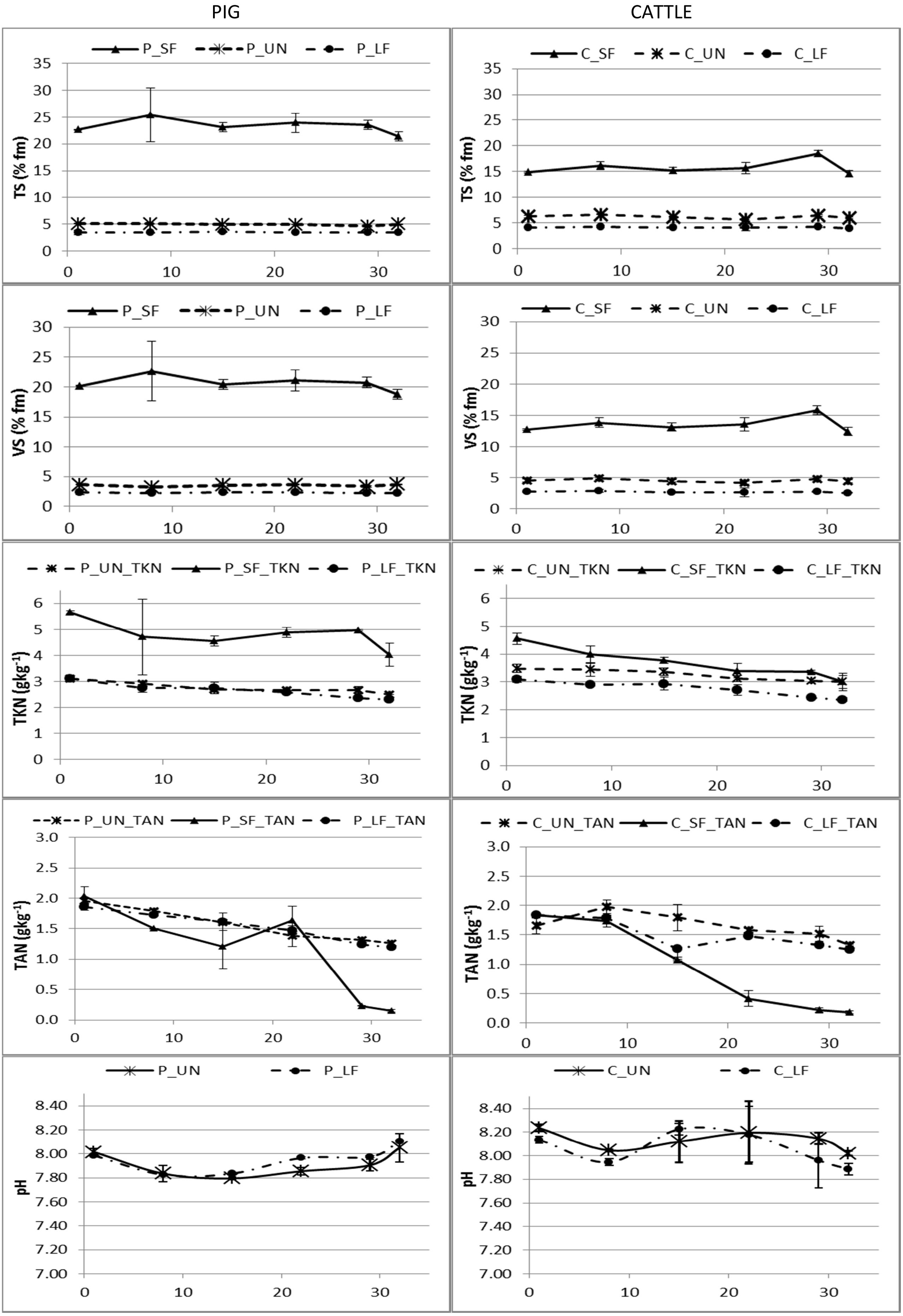


Figure 1 Chemical analyses of pig (left) and cattle (right) effluents resulted during storage period: Total Solids (TS), Volatile Solids(VS), Total Ammonia Nitrogen (TAN), Total Kjeldahl Nitrogen (TKN) and pH (fm = fresh manure). Error bars represent the standard deviaiton.

As expected, losses of TKN are higher than TAN losses (except for P_UN for which are similar) confirming that during the storage period some mineralisation of organic nitrogen occurred.

The combined nitrogen losses from the separated fractions resulted significantly higher than the respective unseparated digestates. During the storage period the P_TR and the C_TR lost 41% and 43%, respectively, of their initial TAN content while the P_UN and C_UN lost the 35% and 20% respectively (Table 3).

The separation treatment therefore affected the N losses, causing a 17% and a 116% increase of the losses referred to the initial TAN content for the P and C digestates, respectively. As in Fangueiro et al. 2008 these results are mainly due to the losses from the liquid fractions, usually characterized by the highest TAN/TKN ratio and lowest TS contents; Vaddella et al. (2013) found that the NH_3 mass transfer coefficient decreases with increasing TS concentration. These results are in accordance with other studies that report higher emission from the separated fractions during the storage (Fangueiro et al., 2008, Dinuccio et al., 2008).

These mechanisms can explain also the difference of losses between the P and C slurries. In fact, C_UN shows lower losses than P_UN that may be explained by the higher TS content and the lower TAN/TKN ratio. After separation, the two liquid fractions (P_LF and C_LF) have similar TS content and TAN/TKN ratio (Table 1) and also the losses resulted of the same level.

Ammonia and nitrous oxide emissions

Fig. 2 shows the NH_3 fluxes measured during the sampling days with acid traps. The unseparated slurries and the liquid fractions showed similar trend but with some difference between the two digestates: the P ones (P_UN and P_LF) show a gradual reduction during the storage period while the C ones show a pick at the end of the first week (C_UN and C_LF) after which a decreasing trend is observed. Both SFs showed a marked reduction of NH_3 flux (P_SF from 175 to 0 mg m^{-2} h^{-1} and C_SF from 300 to 20 mg m^{-2} h^{-1}) after the second week. This NH_3 emission pattern for the solid fractions was also reported by Hansen at al. (2006) who found the emission of NH_3 from uncovered material was high immediately after heap establishment; thereafter, the emission rate gradually declined to nearly zero within a few weeks of storage. In Chadwick et al. (2005) NH_3 emissions from cattle manure heaps lasted 3 weeks.

For P_UN and P_LF, good correlations (R_{UN}^2 = 0.74 *; R_{LF}^2 = 0.90 **) were found between the NH_3 emissions and TAN content. Thus when the TAN content decreased the NH_3 flux also decreased. Good correlations between NH_3 flux and TAN content were also found for the C_SF (R_{SF}^2 = 0.93 **) and C_UN (R_{UN}^2 = 0.83 **). Lastly, a good correlation was found between pH and NH_3 fluxes for C_UN (R^2 = 0.83**). These correlations underline the role of TAN concentration and pH in determining NH_3 emission especially in absence of a crust on slurry surface, or after slurry disturbances (for instance after mixing).

On average the fluxes from the cattle digestate were higher than those from pig digestate even though the TAN concentrations of the two digestates were not very different: this behaviour can be partly explained by the pH, which was higher for the cattle digestate (Fig. 1), favouring NH_3 emissions. The increase of the fluxes of C_UN and C_LF confirms the mineralisation of organic nitrogen during storage of these slurries, while this trend is shown only slightly by P_LF and is not observed by P_UN.

In this study the NH_3 emissions were higher than those reported by others authors (Fangueiro et al., 2008; Clemens et al., 2006.). These findings can be explained by the TAN/TKN ratios digestates, which are typically higher than those of raw slurries, and to the gas sampling method, that involved the mixing of the sample. Blanes-Vidal et al.(2012) have demonstrated that mixing operations cause an incremental increase in NH_3 emissions during the first hour after disturbance followed by a linear trend over the next three hours.

Regarding N_2O emissions, over the storage period (32 days) no fluxes were measured from any material until the beginning of the fourth week (Fig. 2), after which all the slurries showed an increasing trend. The highest fluxes were generated from the solid fractions (P_SF:13.21 day 25; C_SF: 4.26 day 32 mg N_2O m^{-2} h^{-1}).

Considering that the emissions of NH_3 have average values over 200 $mgm^{-2}h^{-1}$ of N-NH_3 it is evident that the predominant N emission was in form of NH_3, representing on average more than 99% of the measured N emissions.

Absent or very small N_2O fluxes from both C and P digestates in the first weeks of storage can be explained by the absence of a crust during the storage period (Berg et al. 2006; Sommer et al., 2000). The bulk of stored liquid slurries is anaerobic and therefore emissions of N_2O via nitrification and denitrification from slurry are insignificant. The higher emissions from the solid fractions might be explained by the aerobic condition of the superficial layer of the stored manure.

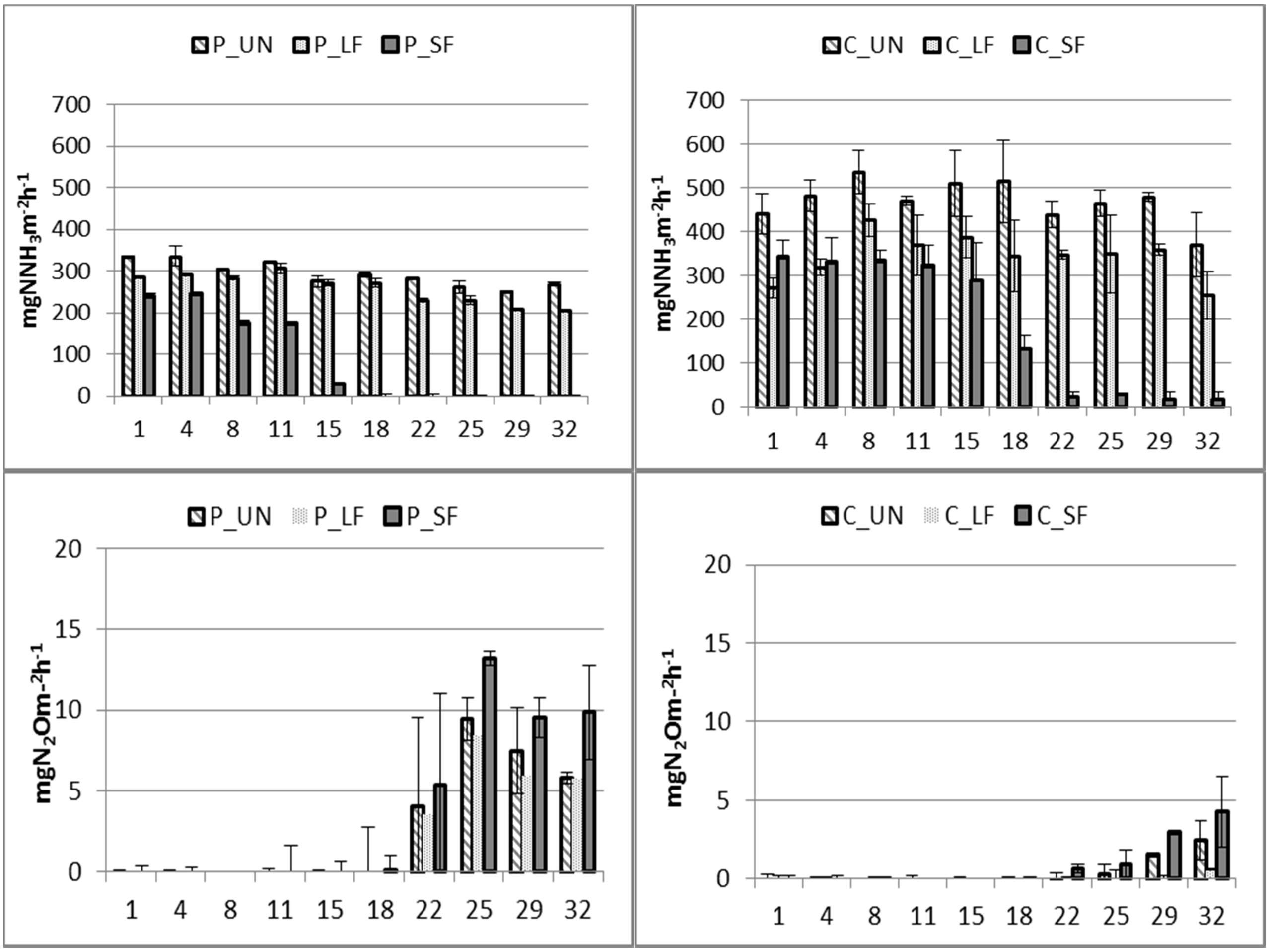


Figure 2 Net emission fluxes of NH_3 and N_2O ($mgm^{-2}h^{-1}$) from pig slurries (left) and from cattle slurries (right). Errors bars represent standard deviation of the means.

Methane and carbon dioxide emissions

CH_4 emission (Fig. 3) from both digested slurries was very low compared with others works that measured emissions from undigested slurries (Dinuccio et al., 2008, Moset at al., 2012, Petersen et al., 2012).For the pig effluents the emission rate peak occurred between the second and third week (maximum fluxes: 15-18 mg CH_4 m^{-2} h^{-1}). The highest average flux over the storage period was shown by the P_UN, (7.8 mg m^{-2} h^{-1}). For the C digestate, there was no CH_4 emission from C_SF, while C_UN and C_LF showed similar emission patterns with a slight increment during the last weeks.

Low CH_4 fluxes from stored digested slurries were also reported by Amon et al. (2006). In digestates the major part of the easily degradable matter had been already lost during the anaerobic digestion and for this reason they usually show a lower CH_4 flux than undigested slurries. Others factors that negatively influence CH_4 emissions are related to the storage condition (temperature, mixing operation). As in others studies (Moller et al., 2004; Dinuccio et al. 2008, Fangueiro et al., 2008) the amount of C lost via CO_2 emissions was higher than that lost via CH_4 emissions. The lowest CH_4 fluxes were from the C_SF, probably because no anaerobic sites were developed in the vessel.

The emissions of CO_2 showed high variability without clear trends (Fig. 3). On average, in both digestates, the solid fractions showed the higher fluxes of CO_2 (P_SF: 4529 ± 701 mg m^{-2} h^{-1} - C_SF: 4683 ± 423 mg m^{-2} h^{-1}) followed by the unseparated (P_UN: 3400 ± 106.90 mg m^{-2} h^{-1} - C_UN: 3138 ± 541.69 mg m^{-2} h^{-1}) and by the liquid fraction (P_LF: 2194 ± 410 mg m^{-2} h^{-1} - C_LF: 2545 ± 266 mg m^{-2} h^{-1}). Considering the low emissions of CH_4, CO_2 was the predominant carbon emission, accounting for 99 % of total C emission.

Results from the present study, in agreement with those of Fangueiro et al. (2008), showed that for each type of digestate, CO_2 emissions during storage are probably directly related to the carbon content of each fraction: the one characterized by the higher TS and the higher VS contents had the higher CO_2 emissions. The high CO_2 fluxes from the solid fractions can be partly explained also by the better oxygen diffusion through the solid fraction porosity, with subsequent degradation of organic compounds to CO_2. The declining CO_2 flux observed in C_SF is most likely due to the depletion of more easily digestible organic components in the biomass remained in the digestate after anaerobic digestion (Sommer et al., 2013).

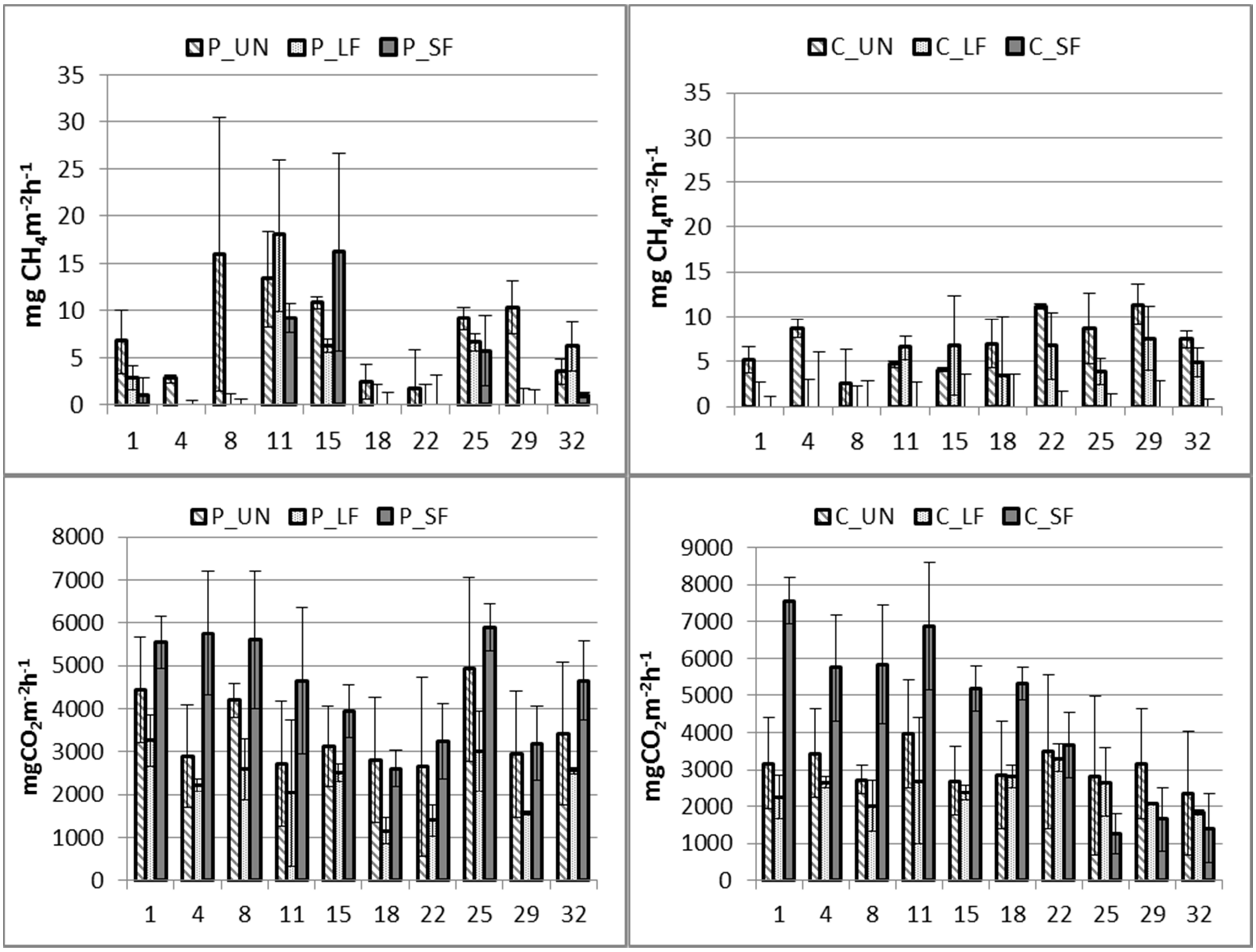


Figure 3 Net CH_4 and CO_2 emission fluxes (mgm^{-2}h^{-1}) from pig slurries (left) and from cattle slurries (right). Errors bars represent the standard deviation.

Effect of separation on emissions

Concerning the average NH_3 emissions, the separated fractions (Table 4) showed a significantly lower emission then unseparated slurries, with a 9% and 23% reduction for P and C, respectively. This result seems to be in contradiction with that obtained from chemical analyses. To understand this apparent discrepancy regarding nitrogen losses, it is important to considered the method by which the gas flux measurements were made, which involved premixing of the samples. Under these conditions, the apparent driving forces for emission were the N concentration and pH, and a daily loss of 3 – 5 % of initial TAN was observed. On the contrary, nitrogen losses estimated by mass balance were obtained by sampling the manure stored without mixing, which occurred only in a limited way on the sampling days. These conditions allowed stratification and formation of a superficial layer in the vessels with a higher resistance to NH_3 release and this effect appeared to be greater in the untreated digestates than in the separated fractions. Under these conditions, as estimated by mass balance, a daily N loss of 1-2% was observed, with lower losses from UN compared to TR.

mean NH_3 emissions from C effluents was higher than that from P ones; this is probably related to the higher pH and to the higher mineralisation rate of the organic N of C_UN and C_LF than the respective P matrices.

N_2O emissions were very low in both cases, especially for C effluents, and there was no significant effect of separation. Similarly CH_4 emissions were very low and significant differences were found only for the C effluents where the separation resulted in a 55% reduction ($P < 0.01$). For CO_2, the predominant C emission, separation had a significant effect only for the C slurries, resulting in a 24% increase ($P < 0.05$) in emission.

Under the studied experimental conditions, on daily basis, samples were characterized by 0.2 - 0.4% loss of initial TS and 4-6% loss of initial TAN , which mainly occurred by CO_2 and NH_3 emission, respectively. These rates showed that mixing operations which took place before gas sampling, as expected, can cause a high increase in N and C release. In terms of greenhouse gas emissions, expressed on CO_2 equivalent basis, no significant differences were found between the UN and the TR slurries. The pig effluents had the highest CO_2 equivalent emissions due to the higher N_2O emission.

Table 4 Mean values of emissions calculated on daily basis ($g\ t^{-1}\ d^{-1}$) for the unseparated and the two separated fractions of digestates. Mean and Standard Deviation (in brackets) are given.

	P_UN	**P_TR**	**Variation due to separation**	**Significance**
$N\text{-}NH_3$ ($gt^{-1}d^{-1}$)	60.12 (2.15)	54.71 (1.49)	-9%	*
N_2O ($gt^{-1}d^{-1}$)	0.52 (0.15)	0.61 (0.16)	19%	ns
CH_4 ($gt^{-1}d^{-1}$)	1.65 (0.99)	1.02 (0.45)	-38%	ns
CO_2 ($gt^{-1}d^{-1}$)	501.94 (211.33)	492.30 (41.35)	-2%	ns
$CH_4 + N_2O$ (CO_2 eq)	195.46 (69.97)	208.40 (58.11)	7%	ns
	C_UN	**C_TR**		
$N\text{-}NH_3$ ($gt^{-1}d^{-1}$)	96.26 (6.47)	74.04(5.63)	-23%	**
N_2O ($gt^{-1}d^{-1}$)	0.06 (0.02)	0.05 (0.01)	-6%	ns
CH_4 ($gt^{-1}d^{-1}$)	1.47 (0.27)	0.67 (0.32)	-55%	**
CO_2 ($gt^{-1}d^{-1}$)	652.28 (112.57)	805.86 (59.81)	24%	*

*** and ** mean significant differences with $P < 0.05$ and $P < 0.01$ respectively, ns = not significant**

5.1.2 Effect of mechanical separation on emissions from livestock slurries

From Table 5 it is possible to observe the initial chemical characteristics of the slurries used in Exp. 3 and 4. As expected pig slurries are characterised by the lower TS content than cattle ones, but by the higher nitrogen content. TAN/TKN ratio is much higher for P_LF and P_UN than cattle ones. Another big difference concerns pH: expect the SFs, which reported a very similar pH (about 8.3), the pig liquid slurries are characterised by one more point pH. The mass efficiencies of the separators used were 10% and 1% for cattle and pig respectively. This can explained the very similar values of TAN, TS and pH of P_LF and P_UN especially.

Table 5 Untreated slurries (P_UN, C_UN), liquid fractions (P_LF, C_LF) and solid fractions (P_SF, C_SF) compositions at the beginning of the storage period. Mean and Standard Deviations (in brackets) of replicates are given.

Slurry Type	TS (gkg^{-1})	VS (gkg^{-1})	TKN (gkg^{-1})	TAN (gkg^{-1})	TAN/TKN %	pH
P_UN	1.64 (0.02)	1.02 (0.00)	3.23 (0.04)	2.09 (0.01)	64.7	7.88 (0.02)
P_LF	1.62 (0.04)	0.92 (0.05)	2.78 (0.02)	2.12 (0.01)	76.3	7.88 (0.01)
P_SF	32.63 (0.2)	27.63 (0.17)	6.82 (0.02)	1.56 (.05)	22.9	8.36 (0.04)
C_UN	4.31 (0.17)	3.63 (0.12)	1.60 (0.0)	0.71 (0.11)	44.2	6.82 (0.01)
C_LF	2.39 (0.08)	1.91 (0.10)	1.25 (0.03)	0.77 (0.04)	61.7	6.97 (0.02)
C_SF	22.49 (0.72)	20.47 (0.62)	2.33 (0.06)	0.40 (0.01)	17.0	8.28 (0.13)

In Fig.4 it is possible to observe the trends of the different chemical parameters (TS, VS, TAN, TKN, pH) over the time of storage.

C_LF and C_UN show very stable trends for either TS, VS, TAN and TKN meaning that low carbon and nitrogen losses occurred during storage. Clearer trends are shown by the C_SF with a slight decrement of VS content and a remarkable TAN loss during the last week, which however is not very evident if TKN is considered. The results contained in Table 6 confirm that nitrogen losses were practically absent from cattle slurries: differences between the initial and the final concentration were not found. The main reasons may be two: the low pH of C_LF and C_UN that remained stable between 6.8 and 6.4, and the development of crust during the days when the mixing operation did not occur. Instead, for pig slurries nitrogen losses were much more consistent. P_UN and P_TR during one month storage lost 47 and 44 % of their initial TKN: in this case mechanical separation caused a 19% reduction of nitrogen loss ($P < 0.05$). Also in Dinuccio 2008 the combined emissions measured from storage of the liquid and solid fraction resulted in reduced nitrogen losses. Probably this result is related to the low content of solids which tend to deposit on the vessel bottom. This avoid the crust formation thus untreated slurries characterised by the higher TAN concentration emit more. Concerning carbon losses P_UN and P_TR lost 26 and 22% of their initial VS content respectively. Mechanical separation resulted in a significant increment ($P < 0.01$) of carbon losses probably related to the presence of solid fraction rich in carbon.

Table 6 Mean and Standard Deviations (in brackets) of TKN, TAN, TS and VS losses during storage for separated and unseparated slurries.

	C_UN	**C_TR**	**Variation due to separation (%)**	**P_UN**	**P_TR**	**Variation due to separation (%)**
TKN loss (kg/t)	n.f.	0.044 (0.01)	500 (**)	1.51 (0.09)	1.22 (0.05)	**-19.2 (*)**
TKN loss /TKNin (%)	n.f.	3.22 (0.75)		46.9 (2.1)	43.76 (1.6)	
TAN loss (kg/t)	n.f.	0.15 (0.06)	(ns)	1.02 (0.02)	1.02 (0.03)	(ns)
TAN loss/TANin (%)	n.f.	20.46 (7.39)		48.99 (1.37)	48.33 (1.52)	
TS loss	0.095 (0.24)	0.38 (0.10)	(ns)	0.15 (0.07)	0.25 (0.14)	66.7 (**)
TS loss/Tsin (%)	2.09 (5.42)	8.53 (2.31)		9.0 (4.08)	12.9 (7.12)	
SV loss	0.14 (0.11)	0.37 (0.1)	(ns)	0.26 (0.03)	0.27 (0.09)	3.8 (**)
SV loss/SVin	3.64 (2.99)	9.85 (2.53)		26.20 (2.63)	22.31 (7.03)	

*** and ** mean significant differences with $P < 0.05$ and $P < 0.01$ respectively, ns = not significant. n.f.= not found.**

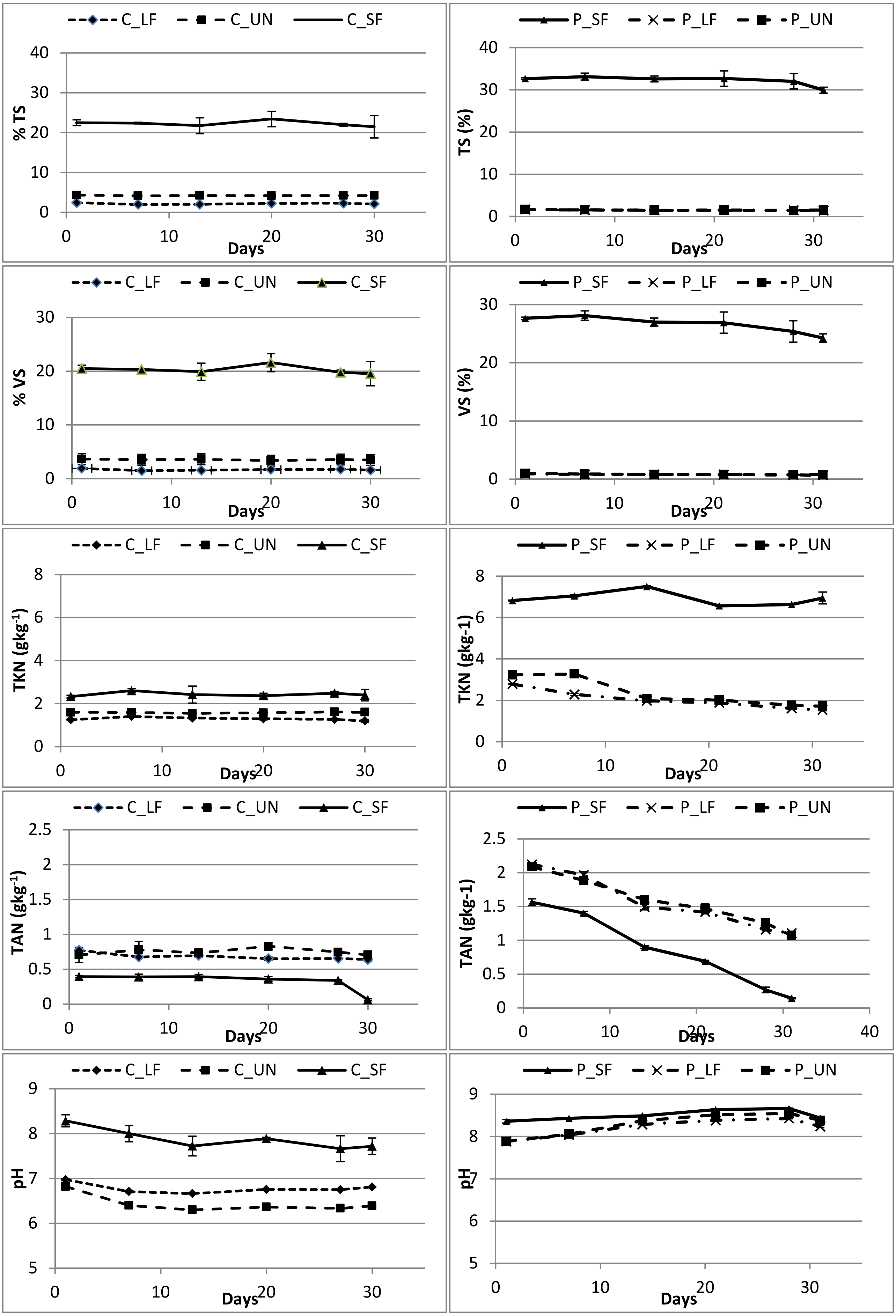


Figure 4 Chemical analyses of pig (left) and cattle (right) effluents resulted during storage period: Total Solids (TS), Volatile Solids(VS), Total Ammonia Nitrogen (TAN), Total Kjeldahl Nitrogen (TKN) and pH (fm = fresh manure). Error bars represent the standard deviation.

Ammonia and nitrous oxide emissions

On average NH_3 emissions from pig slurries were higher than those from cattle ones (Fig.5). This result may be mainly explained by the higher pH, the higher TAN and TAN/TKN ratio values of pig slurries. On average P_UN, P_LF and P_SF emitted 383.5, 396.1 and 21.42 $mgm^{-2}h^{-1}$ respectively.

C_LF reported a 33.4% emission increment compared with C_UN. In the other experiments, after agitation, typically the contrary was observed: untreated slurries emit more than liquid fraction. The possible reason may be related to the much higher TAN/TKN ratio reported by the C_LF (62% vs 44%) and by the lower TS content. On average C_LF and C_UN emitted 74.84 and 56.08 $mgm^{-2}h^{-1}$ respectively.

In both experiments N_2O represents less than 99% of total nitrogen losses. In the case of pig slurries the reason is also related to the low contribute of solid fraction in terms of mass efficiency of the separator. As in the other experiments the highest fluxes were reported by the solid fractions. In particular P_SF reported a peak of 32.8 $mgm^{-2}h^{-1}$, which is the highest observed for all experiments carried out. For the first time in the vessels containing the solid fraction an increment of temperature was observed during the second and the third week (Fig. 6), meaning that a composting process started. The P_SF unlike the other solid fractions analysed was characterised by very small particles that probably enhanced the compaction instauring suitable conditions for composting.

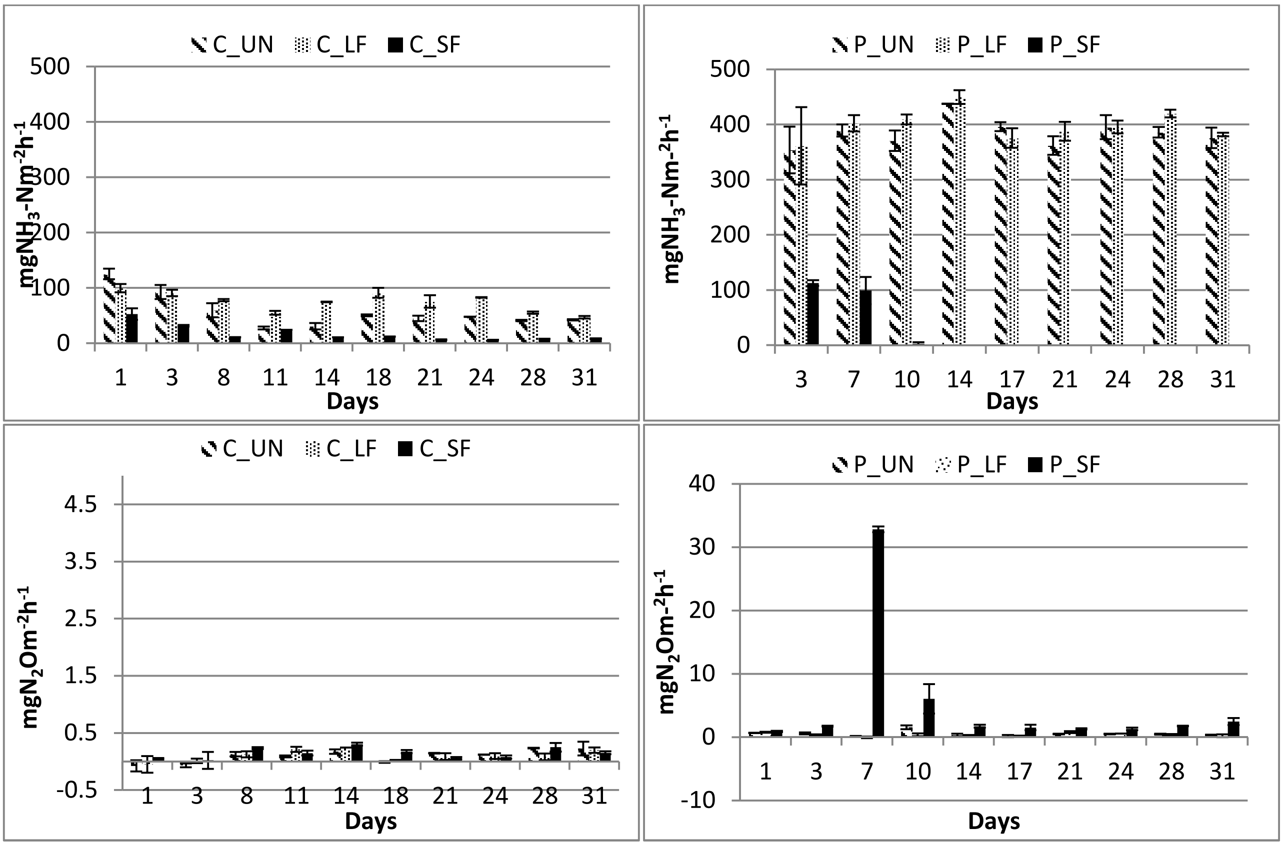


Figure 5 Net emission fluxes of NH_3 and N_2O ($mgm^{-2}h^{-1}$) from pig slurries (left) and from cattle slurries (right). Errors bars represent Standard Deviation.

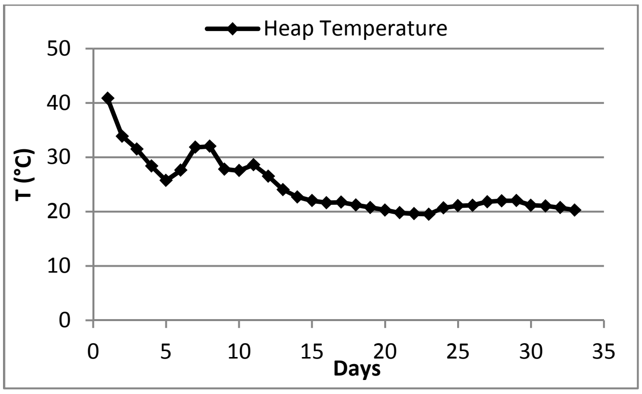


Figure 6 Temperature recorded during the storage of P_SF

Methane and carbon dioxide emissions

Fig. 7 describes CO_2 and CH_4 fluxes recorded during the sampling days. Despite the higher content of VS cattle slurries had very low CH_4 fluxes. Contrary P_UN and P_LF were on average characterized by 60.78 and 59.47 $mgm^{-2}h^{-1}$ of CH_4 emission. Usually organic matter contained in pig slurry is easier to degrade, this is also the reason why pig slurry has an higher biogas potential than cattle slurry (Schievano et al., 2009). Another reason can be related to the presence of an inoculum of methanogenic bacteria inside the storage tank where pig slurry was sampled. Because the separator draws the material contained in this tank, P_LF is inoculated as well. The decreasing trends for CH_4 and CO_2 emissions can be related to the availability of easy degradable organic matter and to the slurry temperature: when slurries were transferred into the vessels they were about 24-25° C of temperature, which slowly decreased until aligning to ambient temperature (after two days). These two factors may have promoted the degradation process with CO_2 production, which like in other experiment seems to be strictly correlated to the TS content: with average fluxes of 6214 and 4550 $mgm^{-2}h^{-1}$, C_SF and P_SF respectively have reported the highest CO_2 emissions.

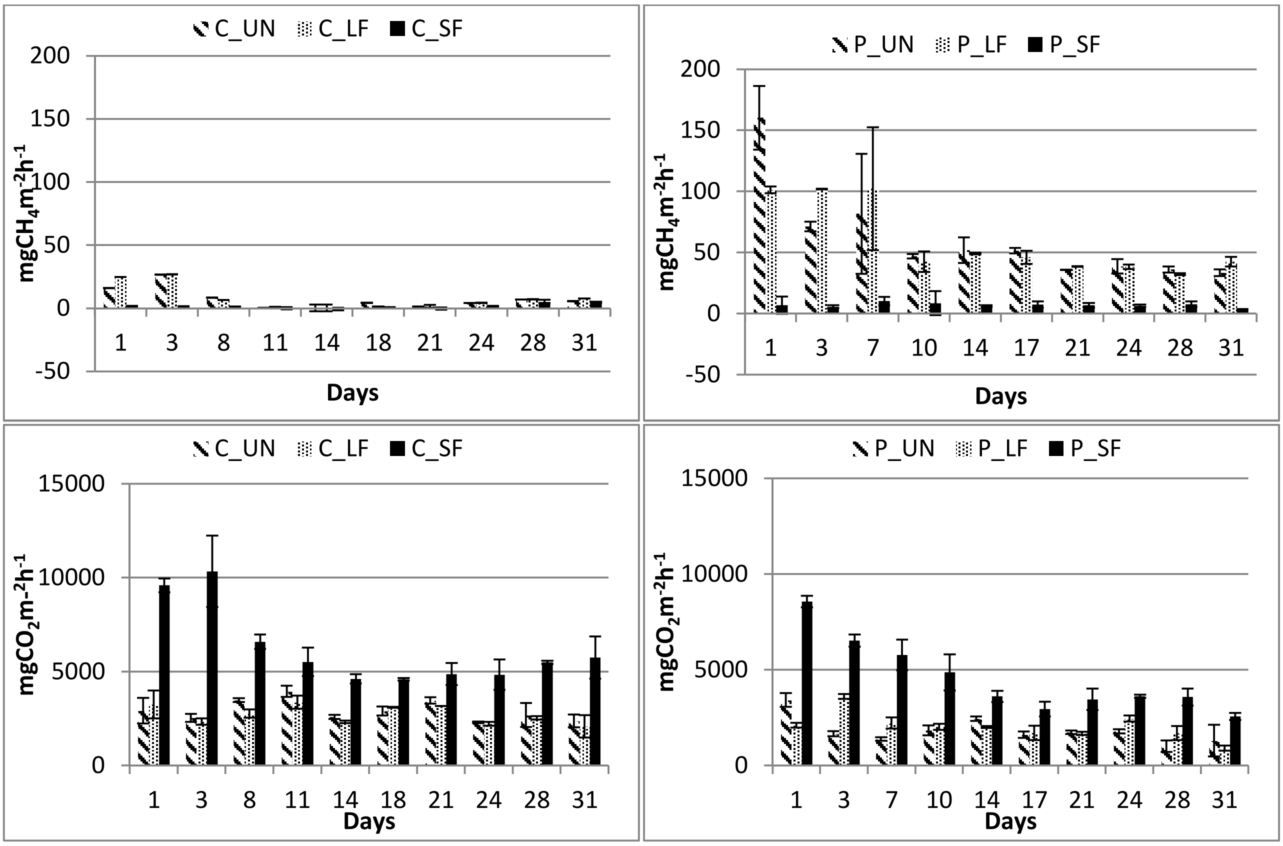


Figure7 Net CH_4 and CO_2 emission fluxes ($mgm^{-2}h^{-1}$) from pig slurries (left) and from cattle slurries (right). Errors bars represent the Standard Deviation.

Effect of mechanical separation

In Table 7 the main effects of mechanical separation on measured fluxes are summarised. Considering pig slurries no significant differences were found between unseparated and separated slurries. This result may be mainly explained by the very low mass efficiency, thus the presence of the solid fraction weighted very low in the overall assessment of the effect of mechanical separation. Consequently the chemical characteristics of P_LF and P_UN were similar enough to determine as much similar emission patterns. Concerning cattle slurries no significant difference was found between C_UN and C_TR expect for CO_2 emission. As previously described this difference is related to the presence of the C_SF. In terms of CO_2 equivalent it can be pointed out that pig slurries emit 7 times more than cattle slurries and this is mainly cause by the higher CH_4 emissions. Also the potential NH_3 emission from pig slurries were 7 times higher. iI this case the pH TAN and TAN/TKN ratio were the key factors.

Table 7 Mean values of emissions calculated on daily basis (gt^{-1} d-^{1}) for the unseparated (P_UN and C_UN) and the two separated slurries (P_TR and C_TR)). Mean and Standard Deviation (in brackets) are given.

	P_UN	**P_TR**	**Variation due to separation**	**Significance**
N-NH_3 (gt^{-1}d^{-1})	79.69 (1.92)	81.88 (2.87)	2.75	†
N_2O (gt^{-1}d^{-1})	0.11 (0.021)	0.09 (0.01)	-20.6	ns
CH_4 (gt^{-1}d^{-1})	12.63 (2.08)	12.25 (1.28)	-3	ns
CO_2 (gt^{-1}d^{-1})	378.4 (9.11)	429.19 (2.99)	13.42	ns
CH_4 + N_2O (CO_2 eq)	348.23 (45.73)	332.01 (33.45)	-4.66	**ns**
	C_UN	C_TR		
N-NH_3 (gt^{-1}d^{-1})	10.46 (0.39)	9.72 (0.40)	-7.07	ns
N_2O (gt^{-1}d^{-1})	0.01 (0.00)	0.02 (0.00)	14.3	ns
CH_4 (gt^{-1}d^{-1})	1.54 (0.04)	1.56 (0.01)	1.3	ns
CO_2 (gt^{-1}d^{-1})	606.33 (35.70)	830.87 (6.97)	37	**
CH_4 + N_2O (CO_2 eq)	42.77 (0.51)	43.88 (0.01)	2.6	ns

*** , **and † mean significant differences with *$P < 0.05$, $P < 0.01$, $P < 0.1$* respectively, ns = not significant**

5.1.3 Effect of anaerobic digestion on emissions from raw livestock slurries

Slurry characteristics and changes during storage

In these experiments to study in deep the effect of mixing four vessels were added. Thus there were in total 8 vessels: four vessels containing the two replicates of untreated slurry and the two replicates of digestate which were agitated when the flux sampling day occurred as in the previous experiments, and four left undisturbed (two untreated slurries and two digestates) for the entire period of storage. The latter were sampled only for chemical analyses at the beginning and at the end of the experiment. Table 8 shows the initial chemical characteristics of the slurries used in Exp. 5 and 6. First of all it is possible to notice that pig slurries are much more diluted than cattle. The differences between P_DIG_ND and the P_DIG_D are suspicious because the vessels were filled with same slurry sample: a sampling error may be occurred. Concerning TS, VS and TKN pig slurries and cattle ones are comparable. Instead TAN is higher in pig slurries like TAN/TKN ratio that resulted included between 74 - 79%. In both experiments, as expected, TAN and pH increased in digestates.

Table 8 Untreated not disturbed and disturbed slurries (P_UN_ND, P_UN_D, C_UN_ND, C_UN_D), disturbed and not disturbed digestates (P_DIG_ND, PIG_DIG_D, C_DIG_ND, C_DIG_D) compositions at the beginning of the storage period. Mean and Standard Deviations (in brackets) of replicates are given.

	TS (g/kg)	VS (g/kg)	TKN (g/kg)	TAN (g/kg)	TAN/TKN %	pH
P_UN_D	2.80 (0.04)	1.46 (0.05)	2.98 (0.04)	2.35 (0.01)	78.69	7.14 (0.01)
P_UN_ND	2.80 (0.03)	1.48 (0.06)	3.09 (0.04)	2.37 (0.03)	76.70	7.14 (0.0)
PIG_DIG_D	2.91(0.19)	1.31 (0.11)	3.65 (0.05)	2.70 (0.07)	74.07	7.97 (0.01)
P_DIG_ND	2.40 (0.2)	1.00 (0.11)	3.49 (0.07)	2.65 (0.03)	75.93	7.96 (0.00)
C_UN_D	11.33 (0.48)	9.53 (0.4)	3.58 (0.01)	1.30 (0.04)	36.31	6.75 (0.03)
C_UN_ND	11.00 (0.12)	9.31 (0.08)	3.73 (0.05)	1.40 (0.05)	37.45	6.74 (0.01)
C_DIG_D	7.66 (0.35)	5.91 (0.4)	3.76 (0.06)	2.02 (0.05)	53.59	7.95 (0.03)
C_DIG_ND	7.79 (0.15)	5.98 (0.15)	3.82 (0.03)	2.13 (0.05)	55.70	7.96 (0.02)

In Fig. 8 it is possible to observe the chemical analyses evolution during the storage period. Concerning TS and VS the decreasing trends are much more evident for cattle slurries. During the storage period C slurries lost between 0.9 - 2.3 of their initial TS content in contrast with the pig ones which lost between 0.2 - 0.8. (Table 9). Except for P_DIG the highest carbon losses were reported by the disturbed slurries. In particular the differences between disturbed and undisturbed are very accentuated in the case of cattle slurries: compering TS losses of C_UN_D and C_DIG_D with those of C_UN_ND and C_DIG_ND an 87% and 55% increments were observed.

Concerning TAN and TKN trends both slurries typologies show clear reducing trends. As expected digestates lost more TKN than their relative untreated slurries. C_DIG_D and C_DIG_ND reported a 13 % ($P = 0.08$) and 46 % ($P < 0.05$) increment. For pig slurries anaerobic digestion caused a 35- 40 % increment of nitrogen losses (Table 10), even if this difference was statistically significant only for disturbed slurries ($P < 0.05$). In general TKN losses were always higher than TAN losses, meaning that some mineralization process has occurred during the storage period (Patni and Jui, 1985). Considering carbon losses in general lower emissions were observed from the digestates: this result may be explained by the lower TS content and by the lower degradable organic matter content of C_DIG and P_DIG. Concerning the effect of disturbance from Table 10 it can be pointed out that, unexpectedly, pig slurries ND reported higher nitrogen losses. This result may be explained by the following reasons: the crust absence and slight differences of the climatic conditions considering different parts of the the room were vessels were stored.

On average pig slurries lost more nitrogen than cattle ones: on average the latter showed lower pH and a lower TAN/TKN ratio, two key factors for NH_3 emission determination.

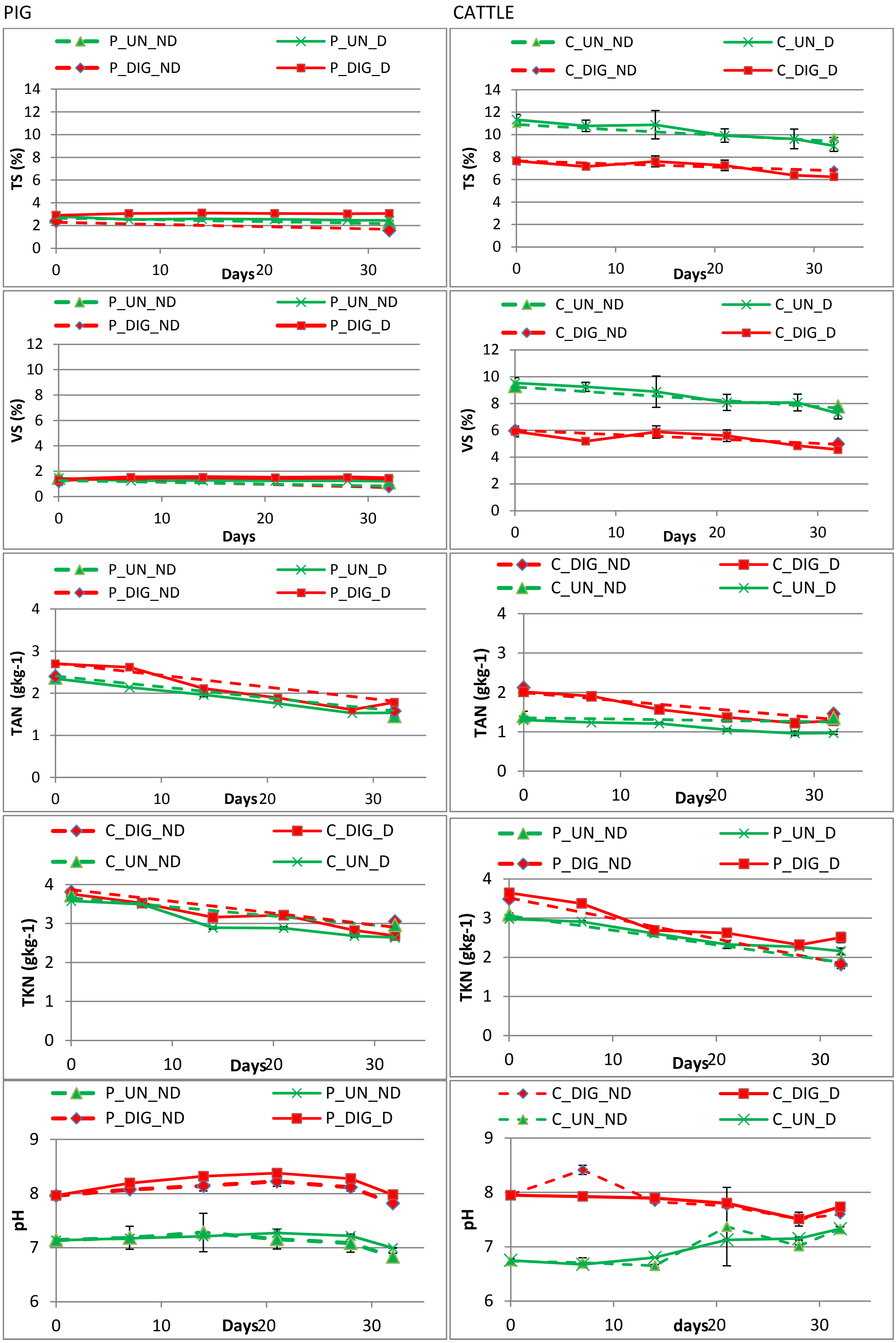


Figure 8 Chemical analyses of slurries resulted during storage period: Total Solid (TS), Volatile Solids (VS), Total Ammonia Nitrogen (TAN), Total Kjeldahl Nitrogen (TKN), Volatile Fatty Acid (VFA) and pH. Data are expressed on a fresh weight basis.

Table 9 Mean and Standard Deviations (in brackets) of TKN ,TAN, TS, VS losses of untreated and digested slurries during storage in disturbed and undisturbed condition. Standard Deviation are given in brackets.

	P_UN		P_DIG		C_UN		C_DIG	
	D	ND	D	ND	D	ND	D	ND
TKN loss (kgt^{-1})	1.07 (0.0)	1.24 (0.2)	1.44 (0.1)	1.74 (0.0)	0.94 (0.0)	0.77 (0.1)	1.07 (0.1)	0.76 (0.0)
TKN loss /TKNin (%)	35.77 (1.9)	40.26 (5.0)	39.56 (2.5)	49.79 (2.0)	26.25 (0.4)	20.46 (1.7)	28.54 (1.4)	19.89 (0.9)
TAN loss (kg/t)	0.98 (0.1)	0.97 (0.1)	1.13 (0.1)	0.98 (0.1)	0.33 (0.0)	0.04 (0.1)	0.73 (0.0)	0.66 (0.0)
TAN loss/TANin (%)	41.92 (2.7)	40.96 (3.1)	41.89 (1.6)	36.90 (3.5)	25.42 (0.2)	2.60 (5.7)	36.36 (0.1)	31.16 (0.2)
TS loss	0.63 (0.0)	0.56 (0.0)	0.21 (0.2)	0.87 (0.2)	2.33 (1.0)	1.24 (0.1)	1.41 (0.4)	0.91 (0.2)
TS loss/Tsin (%)	22.32 (0.7)	19.93 (0.2)	6.98 (6.6)	36.21 (4.6)	20.40 (7.7)	11.28 (1.0)	18.32 (3.9)	11.64 (2.6)
SV loss	0.61 (0.0)	0.61 (0.0)	0.30 (0.1)	0.50 (0.1)	2.26 (0.8)	1.53 (0.1)	1.36 (0.5)	0.99 (0.2)
SV loss/SVin (%)	41.60 (0.3)	41.42 (0.5)	22.41 (8.3)	49.21 (6.6)	23.54 (7.6)	16.44 (0.5)	22.75 (6.5)	16.52 (3.4)

Table 10 Mechanical separation and disturbance effect.

	P_UN Variation (%) due to disturbance	**P_DIG Variation (%) due to disturbance**	**P_D Variation (%) due to an. digest**	**P_ND Variation (%) due to an. digest**	**C_UN Variation (%) due to disturbance**	**C_DIG Variation (%) due to disturbance**	**C_D Variation (%) due to an. digest**	**C_ND Variation (%) due to an. digest**
TKN loss	-13.7 (ns)	-17.2 (†)	+34.6 (*)	+ 40.3 (ns)	+23.7 (*)	+ 40.8 (ns)	+ 13.8 (†)	+ 46.7 (*)
TAN loss	+ 1.0 (ns)	+ 15.3 (ns)	+ 15.3 (*)	+ 1.0(*)	+ 725.1 (ns)	+ 10.6 (**)	+ 121.1 (*)	+ 1500 (ns)
TS loss	+ 12 (ns)	- 75.8 (*)	- 66.6 (†)	+ 55.3 (*)	+ 87.9 (ns)	+ 54.9 (ns)	- 39.5 (**)	-26.6 (**)
SV loss	0 (ns)	- 40.0 (*)	-103.0 (ns)	-18.0 (**)	+ 47.7 (ns)	+ 37.4 (ns)	- 39.8 (**)	- 35.2 (**)

Levels of significance are given in brackets. * and ** mean significant differences with $P < 0.05$ and $P < 0.01$ respectively, ns = not significant

Ammonia emission

Fig. 9 shows NH_3 and N_2O fluxes measured during Exp. 5 and 6.

As expected digestates were always characterised by higher fluxes (P_DIG: 477.06 mgm^{-2}h^{-1}; C_DIG: 336.39 mgm^{-2}h^{-1}) than their relative untreated slurries (P_UN: 210.79 mgm^{-2}h^{-1}; C_UN 147.73 mgm^{-2}h^{-1}). This is in accordance with that found observing the chemical analyses (Table 9). Comparing the two typologies of slurries the pig ones showed more stable trends, although the TAN concentration was reducing over the time. P_DIG started to report NH_3 emission reduction only during the last week in correspondence with pH reduction. C_UN and C_DIG showed opposite trends that reflect the pH trends. At the end of the storage period C_DIG and C_UN had similar NH_3 emission with an average flux of 225 mgm^{-2}h^{-2}. The pH increment can be explained by CO_2 stripping process, that probably was higher for C_UN slurries, as it can be seen by the CO_2 fluxes (Fig. 15) and by the major TS and the VS losses (Table 9) .

NH_3 emission in both Experiments represented more than 99% of N emissions. N_2O emissions from P slurries are practically absent. Some remarkable N_2O fluxes were observed by the cattle slurries, in particular by the C_UN, which reports a pick of 2.34 mgm^{-2}h^{-1}. Probably the development of a crust, which did not occurred in the case of P slurries, favours the instauration of suitable condition for nitrification and denitrification process.

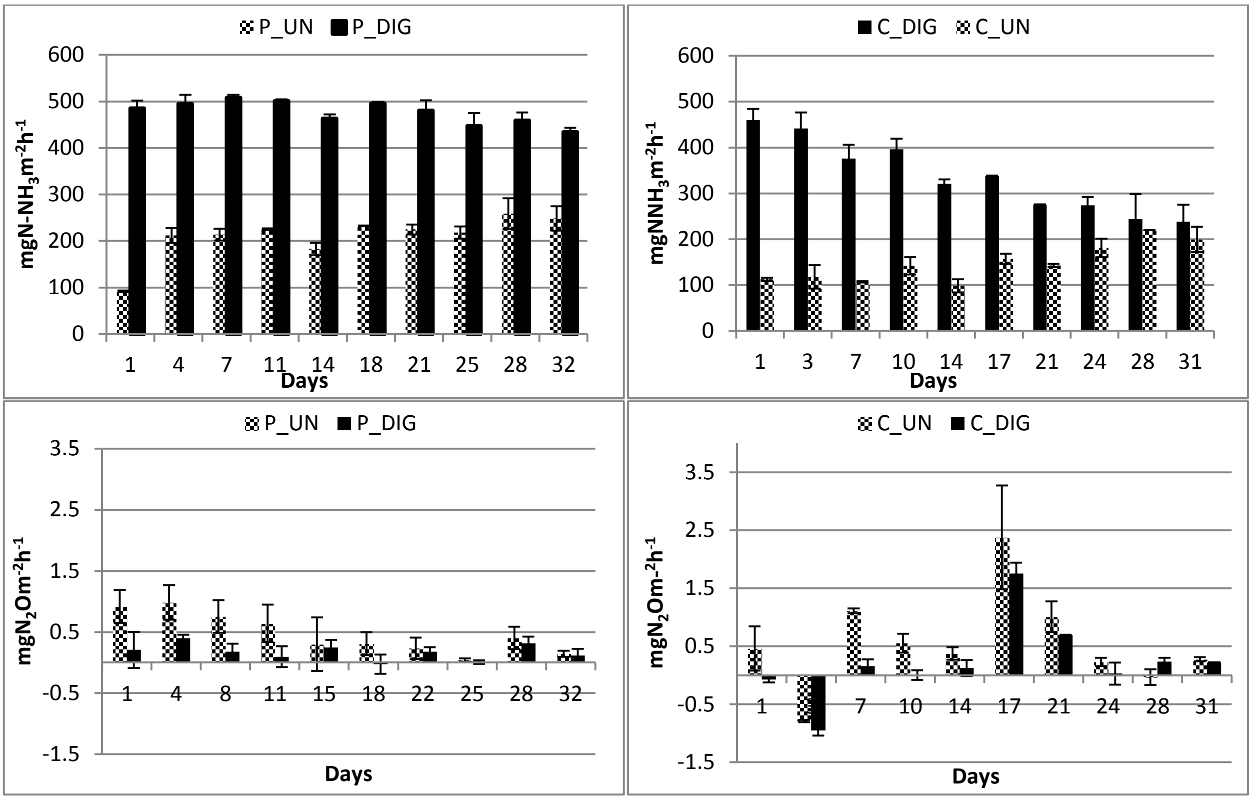


Figure 9 Net emission fluxes of NH_3 and N_2O ($mgm^{-2}h^{-1}$) from pig slurries (left) and from cattle slurries (right). Errors bars represent the standard deviation.

Methane and carbon dioxide emission

On average the P_DIG fluxes (39.5 $mgm^{-2}h^{-1}$) were higher than those of P_UN (23.7 $mgm^{-2}h^{-1}$). This result was not expected as the anaerobic digestion should cause a CH_4 emissions reduction. Probably the hydraulic retention time (HRT) of the biogas plant was not sufficiently long to enable a complete degradation of the organic compounds, which continued during the storage phase producing more CH_4 emissions. However pig CH_4 emissions were lower than cattle slurries denoting a general low level of easy degradable organic matter of the pig slurries. On daily average the fluxes measured were 48.7 and 21.8 $mgm^{-2}h^{-1}$ for C_UN and C_DIG respectively. In this case anaerobic digestion resulted in a 50% reduction of CH_4 emission.

The peak reported by C_UN during 1st (274 $mg^{-2}h^{-1}$) and 28th day (175) of storage (Fig. 10) characterized by high variability can be explained by the bubble release model for CH_4, thus suddenly an increment of CH_4 concentration was observed but only for one of the replicates.

CO_2 emissions are the main C emissions, accounting for more than 95% of carbon losses. As observed in the previous experiments the highest CO_2 fluxes were reported by slurries characterised by the highest solids content. Because the TS contents of P_UN and P_DIG were very similar also the CO_2 emission did not report significant differences (P_DIG: 1341.5 $mgm^{-2}h^{-1}$; P_UN: 1527.9) (Table 11). The lowest fluxes are always observed in the middle of the storage period, when probably a slowdown of the degradation processes occurred.

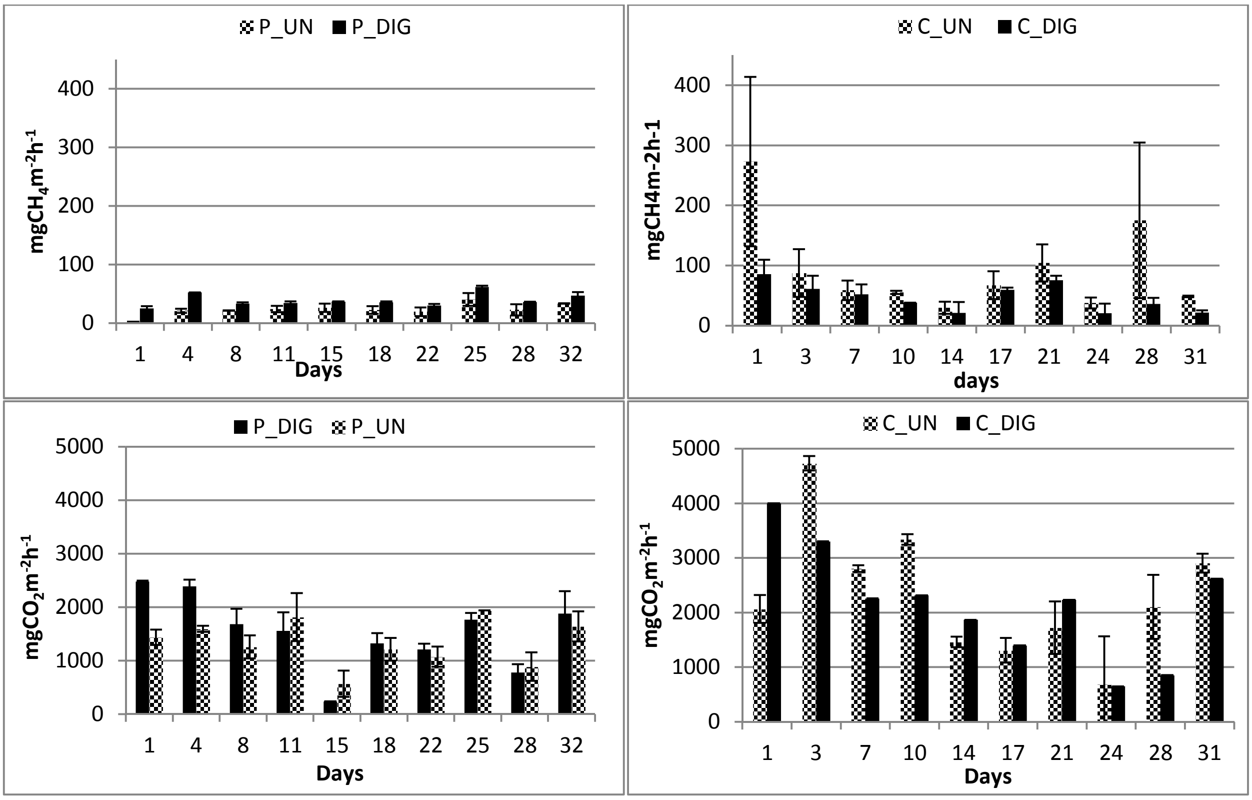


Figure 10 Net CH_4 and CO_2 emission fluxes (mgm^{-2}h^{-1}) from pig slurries (left) and from cattle slurries (right). Errors bars represent standard deviation.

Effect of anaerobic digestion and disturbance

Table 11 shows the main results of Exp. 5 and 6. Overall anaerobic digestion caused an increment of NH_3 potential emissions up to 127 %. This result was confirmed also by the chemical analyses. Crust formation may limit nitrogen losses (Misselbrook et al., 2005) . Comparing the N losses obtained by the chemical analyses from ND samples and the potential loss observed from the agitated sample it's possible to point out that, on daily average, the disturbance can cause 2.4 % up to 4% loss of the initial TAN, while its absence can halved these losses. Concerning N_2O anaerobic digestion caused a significant emission reduction ($P < 0.01$). This result can be related to the conditions of the slurry superficial layer and to the lower content in organic N. On CO_2 eq basis the anaerobic digestion had different effect considering the two experiments. The C_DIG reported a 50% reduction of CO_2 eq emission, where only the 5.5% is represented by N_2O. This is in accordance with other studies (Amon et al., 2006; Clemens et al., 2006), which observed that during anaerobic digestion process, organic matter present in the alimentation mixture is degraded in CO_2 and CH_4, which are captured in the biogas reactor, thus their release during the storage phase is very limited. Instead in Exp. 6 a significant increment of CO_{2eq} emissions was found ($P < 0.01$) for P_DIG. This result allowed to conclude that, if the HRT of the biogas plant is not well calculated as a function of the alimentation mixture, this treatment may have a negative impact, not only related to the incremented NH_3 emissions, but also concerning the emissions of CH_4 which resulted in a 41.3% increment of CO_2 eq emissions, of which 95% is represented by CH_4 emissions.

Table 11 Mean values of emissions calculated on daily basis (g t^{-1} d^{-1}) for the untreated and the digestates. Mean and Standard Deviation (in brackets) are given.

	P_UN	P_DIG	Variation due to anaerobic digestion (%)	Significance
N-NH_3 ($gt^{-1}d^{-1}$)	47.66 (2.03)	103.00 (0.77)	115.40	**
N_2O ($gt^{-1}d^{-1}$)	0.10 (0.05)	0.08 (0.02)	-20.00	**
CH_4 ($gt^{-1}d^{-1}$)	4.92 (1.04)	8.20 (0.19)	66.10	**
CO_2 ($gt^{-1}d^{-1}$)	278.80 (30.94)	317.52 (19.48)	13.89	ns
CH_4 + N_2O (CO_2 eq)	152.40 (39.52)	215.40 (10.7)	41.33	**
	C_UN	C_DIG		
N-NH_3 ($gt^{-1}d^{-1}$)	30.70 (1.98)	69.91 (3.11)	127.70	**
N_2O ($gt^{-1}d^{-1}$)	0.12 (0.01)	0.05 (0.01)	-58.30	**
CH_4 ($gt^{-1}d^{-1}$)	19.47 (1.08)	9.81 (2.35)	-49.60	*
CO_2 ($gt^{-1}d^{-1}$)	480.55 (12.51)	446.37 (53.25)	-7.11	ns
CH_4 + N_2O (CO2 eq)	521.20 (28.55)	258.76 (61.55)	-50.30	**

* and ** mean significant differences with $P < 0.05$ and $P < 0.01$ respectively, ns = not significant

5.2 Pilot experiments in field condition

5.2.1 Effect of mechanical separation (Group A)

Table 12 reassumes the two pilot experiments in field conditions at the experimental farm of Landriano.

Table 12 Pilot experiments in field conditions

Experiment	Matrix	Time
1	Digestate + liquid fraction + solid fraction	1st November 2013 - 30th January 2014
2	Digestate + liquid fraction + solid fraction	8th May 2014 – 31st July 2014

Slurry temperature

The temperature profiles throughout the storage duration differed across the Experiments (Fig. 11). For Experiment 1, temperature shows a decrease trend in particular during the first month and half, after which temperature is relatively stable between 3 and 7 °C until the final 90 d. On average the slurries temperature are higher than ambient air. Solid fraction reported the highest temperature during the first month. A pick of 39°C was observed during the first week; the start of a composting activity may explain this phenomena. Anyhow the conditions inside the heap were not suitable to complete the composting process thus, after the peak the temperature started to decrease. Solid fractions reported also the highest variability especially in the second experiment. The position of the probe may explain this observation: in late spring-summer conditions stratification is more accentuated: the superficial layer is drier and his temperature is more closed to ambient temperature (average: 21.4 ± 0.4). Going deeply inside the heap the humidity increases and the temperature as well. Anyhow also in Exp. 2 the storage conditions did not allow the instauration of composting processes. Temperatures of disturbed slurries and the relative undisturbed did not show significant differ, meaning that crust formation had an insignificant effect on bulk temperature. Furthermore from the graphs it is possible to note that both seasons were characterised by abundant precipitations. A total of 350 and 285 mm of rain were recorded since the beginning of Exp 1 and 2 respectively. In particular, the summer season recorded an average daily temperature lower than the average temperatures relative to the geographic zone where experiments took place. This factors have to be taken account in emissions analyses.

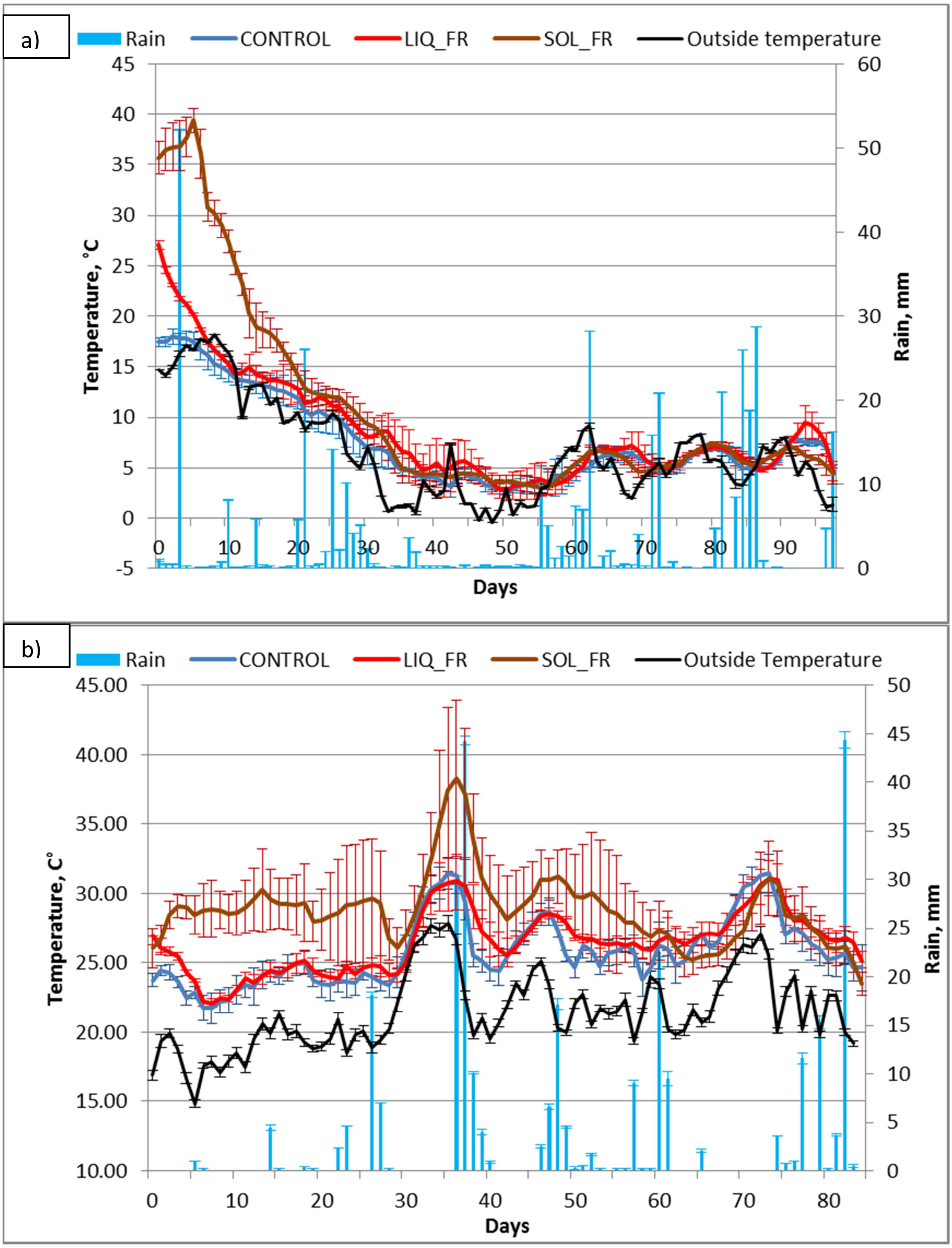


Figure 11 Slurry and ambient air temperatures and rain amount for Experiment 1(a) and Experiment 2 (b). Error bars show ± SD.

Slurries characteristic and changes during storage

In Table 13 the initial chemical compositions of slurries and manures used are shown.

The slurries used were representative in terms of total solids content, total nitrogen and ammoniacal nitrogen content of typical digestate obtained from Italian dairy farm (Schievano et al., 2009).

Table 13 Untreated slurries (P_UN, C_UN), liquid fractions (P_LF, C_LF) and solid fractions (P_SF, C_SF) compositions at the beginning of the storage period. Mean and Standard Deviations (in brackets) of replicates are given. Percentages are referred to fresh manure weight

	Sample	**pH**	**ST (%)**	**SV (%)**	**TAN (gl^{-1})**	**TKN**	**TAN/TKN**	**VFA (mg$_{CH3COOH}$ l^{-1})**	**Total alkalinity**	**Ratio VFA/Alk**	**TOC (%)**	**P (gl^{-1})**	**K (gl^{-1})**
EXP 1	UN_D	8.01 (0.01)	6.58 (0.22)	4.88 (0.19)	1.96 (0.16)	3.55 (0.07)	0.55 (0.06)	622 (301)	14131 (513)	0.025 (0.01)	6.44 (0.03)		
	LF_D	8.29 (0.02)	5.16 (0.04)	3.64 (0.04)	2.17 (0.27)	3.35 (0.07)	0.65 (0.07)	905.5 (305)	14242.5 (328)	0.045 (0.02)	5.16 (0.04)		
	SF_D	8.88 (0.05)	16.72 (0.13)	14.54 (0.1)	0.38 (0.07)	3.4 (0.14)	0.11 (0.02)	372.5 (120)	6220.5 (1189)	0.145 (0.02)	16.72 (0.13)		
	UN_ND	8.07 (0.08)	6.05 (0.52)	4.49 (0.36)	1.93 (0.11)	3.7 (0.14)	0.52 (0.01)	601 (204)	13985.5 (308)	0.03 (0.0)	6.21 (0.74)		
	LF_ND	8.26 (0.00)	5.08 (0.01)	3.57 (0.03)	1.99 (0.01)	3.4 (0..00)	0.59 (0.00)	1081 (557)	14584.5 (194)	0.04 (0.01)	5.08 (0.01)		
	SF_ND	8.89 (0.06)	17.02 (0.37)	14.84 (0.38)	0.40 (0.01)	3.7 (0.28)	0.11 (0.01)	464 (8)	7786.5 (2092)	0.15 (0.11)	17.02 (0.37)		
EXP 2	UN_D	8.47 (0.04)	6.295 (0.04)	4.54 (0.02)	2.14 (0.03)	3.855 (0.06)	0.55 (0.00)	768.2 (7.35)	11522 (939)	0.07 (0.01)	2.45 (0.07)	2.77 (0.13)	0.67 (0.01)
	LF_D	8.51 (0.04)	5.01 (0.13)	3.32 (0.06)	2.08 (0.03)	3.685 (0.05)	0.56 (0.02)	974.605 (60.72)	12465 (213)	0.18 (0.04)	1.94 (0.01)	2.61 (0.27)	0.66 (0.02)
	SF_D	9.10 (0.01)	16.185 (0.04)	13.77 (0.12)	1.33 (0.06)	4.255 (0.01)	0.31 (0.01)	159.77 (3.64)	3955 (487)	0.015 (0.00)	6.62 (0.2)	2.85 (0.17)	0.91 (0.07)
	UN_ND	8.46 (0.08)	6.325 (0.05)	4.54 (0.02)	2.135 (0.01)	3.905 (0.01)	0.55 (0.00)	774.26 (11.79)	9878 (1431)	0.06 (0.00)	2.72 (0.08)	2.37 (0.05)	0.73 (0.02)
	LF_ND	8.42 (0.03)	5.205 (0.53)	3.28 (0.63)	2.08 (0.02)	3.675 (0.02)	0.57 (0.01)	913.78 (39.29)	11063 (1892)	0.09 (0.01)	1.82 (0.37)	2.41 (0.15)	0.68 (0.02)
	SF_ND	9.1 (0.01)	15.42 (0.57)	13.10 (0.38)	1.59 (0.06)	4.56 (0.06)	0.35 (0.01)	162.025 (181.31)	5450 (1530)	0.04 (0.04)	6.62 (0.31)	2.63 (0.02)	0.91 (0.11)

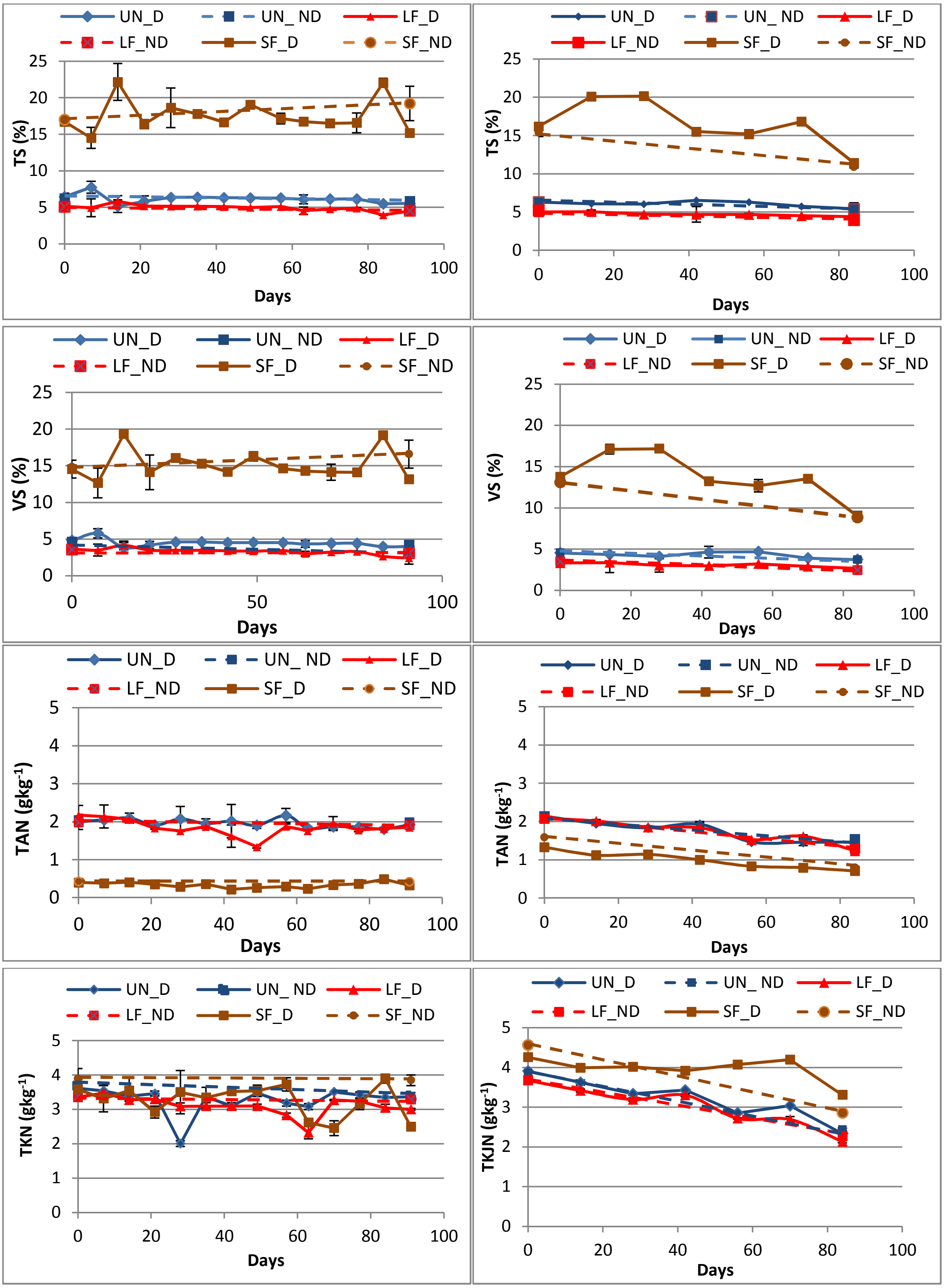
As the manure used was drawn from the same farm the slurry characteristics vary only slightly in the two experiments. Mechanical separation leads to a solid fraction (SF) rich in phosphorous (P) and organic matter (VS), and to a liquid fraction which is rich in soluble nitrogen (N). The total solids were between 6.5-6.05 %, 5.2-5.08 %, 17.02-15.42% for UN, LF, SF, respectively. Also for the other parameters a low variability was observed. On average UN, LF, SF contain 2.04 ± 0.11, 2.08 ± 0.07, 0.92 ± 0.63 gkg^{-1} of TAN and 3.75 ± 0.16, 3.53 ± 0.18, 3.98 ± 0.52 of TKN.

The liquid fractions are always characterised by the highest TAN/TKN ratio: 0.59 ± 0.04 against 0.54 ± 0.016 and 0.22 ± 0.13 of UN and SF.

Concerning pH the highest values were recorded during Exp.2: the UN slurries varied between 8 and 8.5 while LF and SF showed values included between 8.3 - 8.5 and 8.9 - 9.1 respectively. VFA are concentrated in the liquid fractions with values include between 905 and 1080.

Figure 12 shows the chemical analyses trends during storage period. During Exp. 1 TS, VS and TOC tended to remain stable meaning that the climate conditions did not promote carbon emission. TKN and TAN showed a slight decrease during days meaning that small nitrogen losses probably took place. VFA losses patterns are similar in both experiments. It seems that during the first month of storage there is a VFA production followed by a consumption until stabilisation. Furthermore it seems that climate conditions did not affect VFA generation and degradation. This assumption can be partly confirmed by pH trends: in both experiments during the first month a decreasing pattern was observed after which the tendency was the opposite except for SF of Exp. 2. The initial pH reduction was also reported by other authors (Moset et al., 2012, Patni and Jui, 1991): at the beginning when tanks are filled, the degradation of organic matter causes VFA production and thus a pH reduction. Then oxidation of VFA may cause the pH of the slurry to increase because part of the acids are removed (Paul and Beauchamp 1989). When VFA decrease the importance of HCO_3^-/CO_3^{--} buffer system increases and thus the emission of CO_2 provokes pH increment. Anyhow the pH variations after the first month were very limited: the average pH values of LF_D, SF_D,UN_D were 7.99, 8.55, and 7.85 in the Exp.1 and 7.75, 8.36, and 7.70 in the Exp.2. The lower pH values recorded during Exp. 2 may be also explained by the higher carbon and nitrogen losses, both of which affect pH. In particular the NH_3 loss effect is pH reduction which is summed with VFA production effect. Instead CO_2 emission together with VFA oxidation has the opposite effect.

Exp. 2 shows clearer trends especially for TKN and TAN: warm condition have promoted N losses for all the slurries and manures considered. Solid fractions part of their TAN contents. The volume used and their compaction did not enhance the complete volatilization of NH_3 present in the manures stored.


UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
TS (%)
0
5
10
15
20
25
0
20
40
60
80
100
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
TS (%)
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
VS (%)
0
50
100
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
VS (%)
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
TAN (gkg-1)
0
1
2
3
4
5
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
TAN (gkg-1)
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
TKN (gkg-1)
Days
UN_D
UN_ ND
LF_D
LF_ND
SF_D
SF_ND
TKJN (gkg-1)
Days

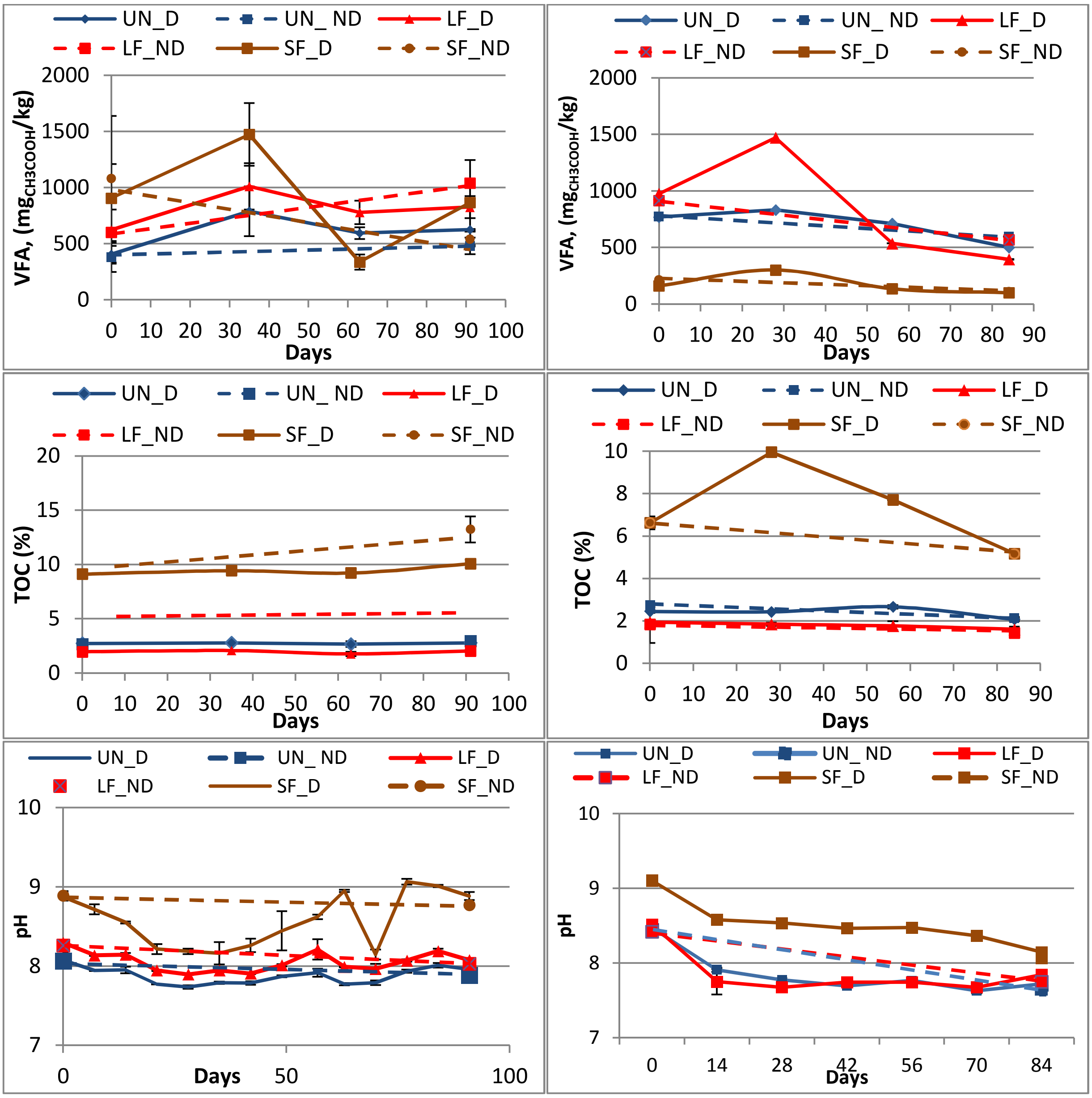


Figure 9 Chemical analyses of slurries and manures resulted during the storage period of Exp.1 (left) and Exp.2 (right): Total Solid (TS), Volatile Solids (VS), Total Ammonia Nitrogen (TAN), Total Kjeldahl Nitrogen (TKN), Volatile Fatty Acid (VFA) and pH. Data are expressed on a fresh weight basis.

Nitrogen and carbon losses

From Table 14 and 15 it is possible to observe the effect of mechanical separation on nitrogen and carbon losses during storage. During Exp. 1 no significant differences were found between the separated and unseparated slurries except for TAN concentration ($P < 0.01$). Also disturbance had not significant effect. Nitrogen losses were limited: on average unseparated slurries and separated slurries (D and ND) lost 7.2 % and 7.5 % of their initial TKN content.

Table 14 Mean and Standard Deviations (in brackets) of TKN, TAN, TS, VS, TOC losses during storage of Exp.1 for separated and unseparated slurries.

	UN_D	**UN_ ND**	LF_D	LF_ND	SF_D	SF_ND	**TR_D**	**TR_ND**	**Variation due separation**	
									D	**ND**
TKN loss (kg/t)	**0.24**** **(0.00)**	**0.28** **(0.10)**	0.35 * (0.08)	0.09* (0.03)	1.09** (0.17)	0.09 (0.07)	**0.42**** **(0.05)**	**0.09** **(0.03)**	**73% †**	**-67%**
TKN loss/TKN in (%)	**6.77** **(0.02)**	**7.71** **(2.20)**	10.42 (2.10)	2.80 (0.78)	30.25 (3.55)	2.3 (1.7)	**12.59** **(1.55)**	**2.81** **(1)**	**86%**	**-64%**
TAN loss (kg/t)	**0.13 t** **(0.05)**	**0.06** **(0.02)**	0.13 † (0.03)	0.07 (0.00)	0.08 (0.00)	0.00 (0.01)	**0.12** **(0.03)**	**0.07** **(0.00)**	**-4%****	**6%****
TAN loss/TAN in (%)	**6.20%** **(2.29)**	**3.07 (0.67)**	6.40 (1.53)	3.73 (0.03)	19.46 (2.48)	1.10 (2.03)	**6.30** **(1.15)**	**3.37** **(0.04)**	**2%**	**10%**
TS loss (%)	**0.90**** **(0.08)**	**0.37** **(0.84)**	0.66** (0.06)	0.53* (0.13)	1.52* (0.45)	-2.18 (1.99)	**0.75**** **(0.01)**	**0.26** **(0.08)**	**-17%**	**-30%**
TS loss/Tsin (%)	**13.97** **(1.17)**	**5.19** **(12.89)**	12.80 (1.07)	10.42 (2.58)	9.10 (2.64)	12.69 (11.39)	**13.48** **(0.04)**	**4.41** **(1.29)**	**-4%**	**-15%**
VS loss (%)	**0.80**** **(0.09)**	**0.40** **(0.58)**	1.23 (0.79)	0.53* (0.05)	1.41* (0.41)	-1.73 (1.65)	**1.25** **(0.75)**	**0.31 †** **(0.12)**	**56%**	**-23%**
VS loss/Vsin (%)	**16.73** **(1.78)**	**7.99** **(11.62)**	33.87 (22.05)	14.90 (1.61)	9.71 (2.71)	11.56 (10.88)	**31.41** **(19.22)**	**7.25** **(2.68)**	**88%**	**-9%**
TOC loss (%)	**-0.06** **(0.07)**	**-0.30** **(0.31)**	-0.08 (0.06)	-0.08 (0.16)	-0.96 (0.50)	-4.18 (1.04)	**-0.17** **(0.00)**	**-0.49** **(0.04)**	**nf**	**nf**
TOC loss/TOCin (%)	**-2.20** **(2.59)**	**-12.35** **(13.42)**	-4.10 (2.88)	-4.21 (8.57)	-10.58 (5.63)	-46.13 (10.64)	**-6.05** **(0.08)**	**-16.82** **(1.60)**	**nf**	**nf**

*** , ** and † mean significant differences with *$P < 0.05$*, *$P < 0.01$* and *$P < 0.10$* respectively. nf = not found**

Table 15 Mean and Standard Deviations (in brackets) of TKN, TAN, TS, VS, TOC losses during storage of Exp.2 for separated and unseparated slurries. Data are expressed on a fresh weight basis.

	UN_D	**UN_ ND**	LF_D	LF_ND	SF_D	SF_ND	**TR_D**	**TR_ND**	**Variation due separation**	
									D	**ND**
TKN loss (kg/t)	1.57** (0.01)	1.42** (0.09)	1.54** (0.05)	1.41** (0.09)	0.95** (0.09)	1.71** (0.04)	1.48** (0.04)	1.44** (0.09)	- 6**	+ 2**
TKN loss/TKN in (%)	40 (0)	37 (2)	42 (1)	38 (2)	22 (2)	37 (0)	40 (2)	38 (4)	- 2	+ 4
TAN loss (kg/t)	0.68** (0.06)	0.59** (0.01)	0.85** (0.05)	0.78** (0.06)	0.62** (0.09)	0.29** (0.72)	0.78** (0.03)	0.77** (0.05)	+ 15**	+ 30 †
TAN loss/TAN in (%)	32 (2	28 (0)	41 (3)	38 (2)	47 (4)	19 (45)	41 (1)	39 (2)	+ 31	+ 40
TS loss (%)	0.87* (0.09	0.90† (0.25)	0.60 (0.39)	1.24 t (0.41)	4.76* (0.83)	4.52** (0.62)	0.98* (0.41)	1.19 † (0.40)	+ 13	+ 33
TS loss/Tsin (%)	14 (1)	14 (4)	12 (8)	24 (5)	29 (5)	29 (3)	17 (6)	25 6)	+ 25	+ 78
VS loss (%)	0.82** (0.05)	0.84* (0.23)	0.65* (0.15)	1.04 t (0.32)	4.76** (0.68)	4.26** (0.31)	1.00** (0.16)	1.01* (0.29)	+ 22	+ 20
VS loss/Vsin (%)	18 (1)	19 (5)	19 (4)	29 (6)	35 (5)	32 (1)	23 (3)	29 (6)	+ 28	+ 64
TOC loss (%)	0.38 (0.15)	0.38 (0.15)	0.34 (0.14)	0.40 (0.33)	1.45 (0.2)	1.47 (0.4)	0.45 (0.14)	0.51 (0.33)	+ 18	+ 34
TOC loss/TOCin (%)	15.5% (5.8)	15.5% (5.0)	17.4% (6.9)	20.4% (13.7)	21.8% (2.3)	22.0% (5.1)	21.9% (7.7)	23.6% (14.9)	+ 41	+ 52

*** , ** and † mean significant differences with $P < 0.05$, $P < 0.01$ and $P <0. 10$ respectively.**

Much higher were the nitrogen losses from the slurries examined in Exp 2: disturbed slurries lost up to 40% of their initial TKN while the undisturbed 38-37% of their initial TKN. As expected, TKN losses were higher than TAN losses confirming that during storage period some mineralisation of organic nitrogen occurred (Patni and Juice, 1985). On average the mechanical separation had a significant effect on TAN (for D slurries P < 0.001, for ND P = 0.08) and TKN losses (for D and ND slurries $P < 0.001$) from both disturbed and not disturbed slurries. Concerning carbon losses any significant difference was found between treatments. In terms of TS and VS, the losses in Exp. 2 were similar for both UN slurries (D and ND) with a 14% loss of their initial TS, while losses from separated slurries ranged between 17 and 25 % of their initial TS. Furthermore observing the two Tables together it can be pointed out that TS and VS losses of ND slurries were quite similar during the two seasons while losses from UN_ND and TR_ND showed a 143% and 358% increment increased passing from cold to warm condition. Probably this can be explained by the presence of a very diluted superficial layer inside the slurry tanks (Fig.13) Disturbance had a significant effect only considering the TKN losses of treated slurries of Exp.2. In this case a 3% increasing of TKN loss was observed. This result underline the potential effect that slurry management operations can have on nitrogen losses especially during warm conditions.

Figure 10 Pictures representing a typical condition of slurry treatments during Exp.1 : A1D = UN_D ; A1ND = UN_ND B1D = LF_D ; B1ND = LF_ND ; C1D = SF_D ; C1ND = SF_ND

Figure 11 Pictures representing a typical condition of slurry treatments during Exp.1 : A1D = UN_D ; A1ND = UN_ND B1D = LF_D ; B1ND = LF_ND ; C1D = SF_D ; C1ND = SF_ND

Ammonia emissions

Figure 15 shows NH_3 emissions during the two field experiments. First of all it can be pointed out that fluxes recorded during the summer experiment were much higher than those recorded during the cold season. During the latter the average temperature was 6.5°C and the highest temperatures values were observed during the first month: this may explain the decreasing trend of emissions during the storage period. In both experiments the solid fraction show remarkable fluxes only during the first sampling. This can be related to the condition of the heap and to the climate conditions during sampling (Fig.13 - 14): presence of an ice layer ,very low temperature, very abundant precipitations, very dry condition of the heap surface etc.

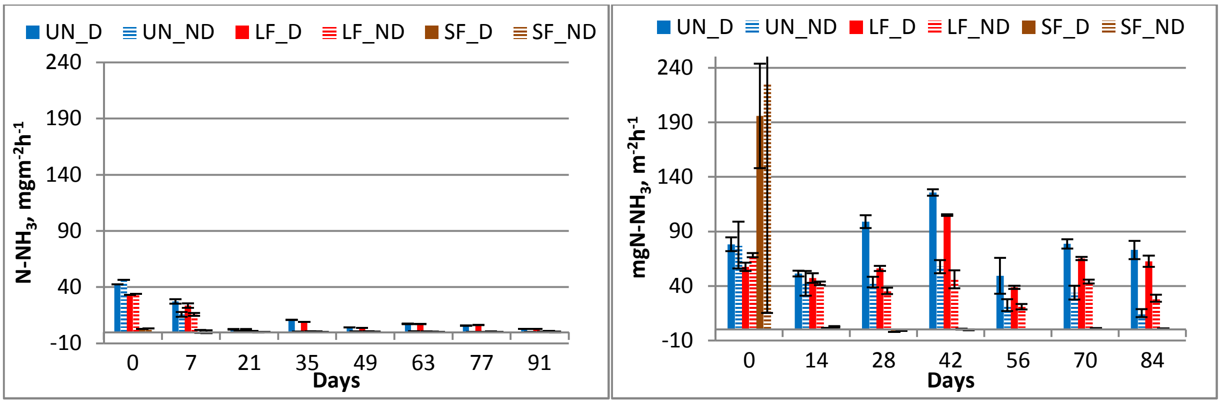


Figure 12 Net emission fluxes of NH_3 (mgm^{-2}h^{-1}) measured during Exp.1 (left) and Exp.2 (right). Errors bars represent standard deviation.

Nitrous oxide emissions

Fig. 16 shows the N_2O fluxes measured during sampling days. In cold conditions emissions were in practice absent from untreated and liquid slurries. Contrary solid manure showed remarkable fluxes during the 49th (SF_D: 8.03 ± 6.04 mgm^{-2}h^{-1}) and the 77th day (SF_ND: 12.99 ± 3.6 mgm^{-2}h^{-1}) of experiment. Also in the second experiment some fluxes were observed from the solid fractions with a peak during the 14th day of storage (SF_ND: 16.91 ± 9.73, SF_D: 11.1 ± 0.14 mgm^{-2}h^{-1}). After the first month no flux was detected. Fluxes from solid fractions were found also in others studies (Hansen et al., 2006), that showed mechanical separation may cause higher N_2O emissions: mix of aerobic and anaerobic conditions in the heap promotes N_2O production. Slurries stores, remain mainly anaerobic thus nitrification process are practically absent (Chadwick et al., 2011). The N_2O fluxes observed from the UN_ND during Exp.2 may be explained by the crust presence. Recent studies have shown as increasing DM content of the slurry may promote N_2O emissions, in particular stored slurry with a natural crust may be a source of N_2O emissions (Chadwick at al. 2011). Unseparated digestates showed a thicker crust than liquid fractions. The crust characteristics of untreated digestate could have provided aerobic conditions and hence nitrification with N_2O generation.

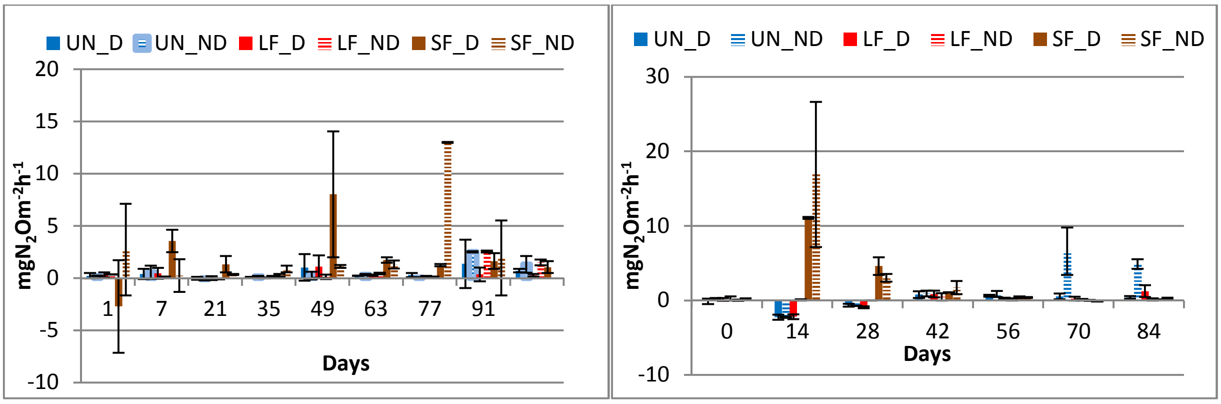


Figure 13 Net emission fluxes of N_2O (mgm^{-2}h^{-1}) measured during Exp.1 (left) and Exp.2 (right). Errors bars represent standard deviation.

Methane emissions

The cold conditions of the first experiment did not promote methanogenesis (Fig. 17). The average fluxes were 4.4 ± 6.9, 3.3± 5.7, 5.5 ± 11.4 mgm^{-2}h^{-1} for UN, LF and SF respectively.

CH_4 production is low at temperature < 15°C. Lots of studies found positive correlation between CH_4 emissions and temperature (Massè et al. 2003, VanderZaag 2010, Clemens et al. 2006).

Warm conditions coincided with higher emissions, which on average were 70.7, 38.6, 4.5 mgm^{-2}h^{-1} for UN, LF and SF respectively.

Solid fractions always showed negligible CH_4 fluxes, expect for the last day of sampling of Exp.1. Presumably these emissions are function of heap anaerobic conditions, temperature and heap compaction. In other studies solid manures stores have shown to be a source of CH_4 emission but, in these studies it is not very evident.

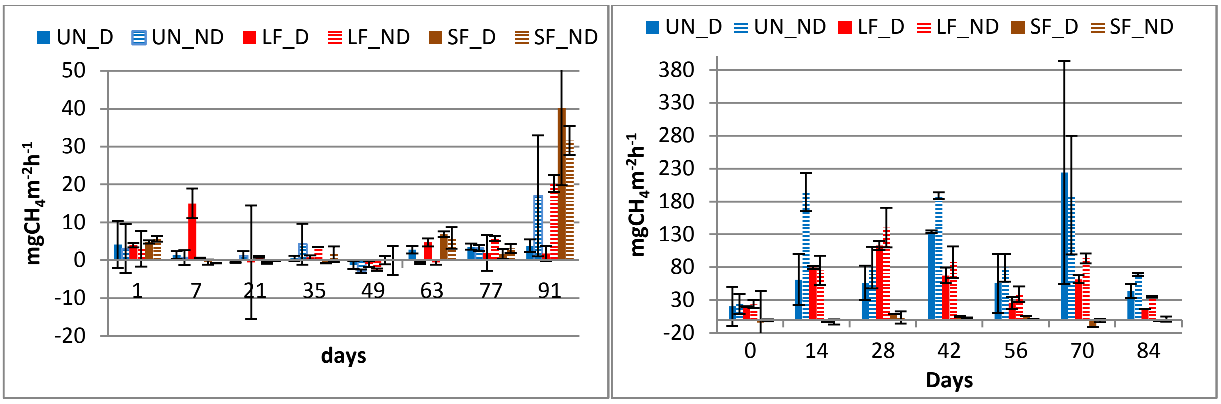


Figure 14 Net emission fluxes of CH_4 (mgm^{-2}h^{-1}) measured during Exp.1 (left) and Exp.2 (right). Errors bars represent standard deviation.

Carbon dioxide emissions

Figure 18 shows CO_2 emissions during storage. CO_2 showed high variability without clear trends. On average the CO_2 fluxes measured during the first experiment were 487.2 ± 459.1, 354.8 ± 333.0, 545.3 ± 610.2 mgm^{-2}h^{-1} for UN, LF, SF, while for the Exp.2 were 635.6 ± 391.8, 541.2 ± 327.2, 787.25 ± 460.4 mgm^{-2}h^{-1}. In both experiments CO_2 emission was the predominant carbon emission, accounting for 99- 90% of total carbon emission. As in experiments in controlled temperature conditions, CO_2 emissions show a probable relation with carbon content: the one characterized by the higher TS and the higher VS contents had the higher CO_2 emissions.

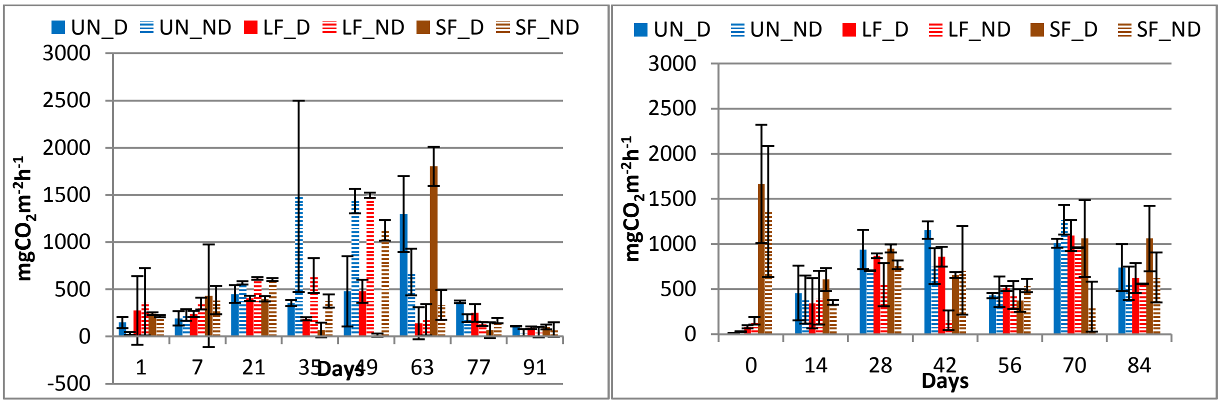


Figure 15 Net emission fluxes of CO_2 ($mgm^{-2}h^{-1}$) measured during Exp.1 (left) and Exp.2 (right). Errors bars represent standard deviation.

Effect of mechanical separation, disturbance and season.

Mechanical separation had a significant effect only in Exp.1 ($P < 0.05$) considering the disturbed slurries (Table 16). Thus after mixing separated slurries emitted 18% less than unseparated slurries. This result confirms what was found in controlled temperature experiment: after disturbance NH_3 emissions is correlated with TAN concentration: the unseparated slurry has always the highest TAN concentration and consequently it reports the highest NH_3 emission.

Disturbance had significant effect in both experiments ($P < 0.01$). In all cases it causes an increment on NH_3 emission. The differences between undisturbed and disturbed tanks were slighter in cold conditions for two main reasons: low temperature and absence of a crust. Sometimes, after rain or snow a very diluted layer was observed on the surfaces of liquid slurries (Fig. 13). Other times an ice crust was developed during night (Fig.13). These observations may explain the practically absent emissions from undisturbed slurries. In warm conditions the development of a crust (Fig. 14) effectively reduced the emissions from undisturbed slurries during sampling. In this season the average emissions for disturbed slurries were 2.14 and 1.86 $gt^{-2}d^{-1}$ for UN and TR slurries respectively. 106 % and 25 % NH_3 emission reductions were achieved by UN_ND and TR_ND.

Concerning **N_2O** emissions mechanical separation had caused a significant increment on N_2O emission ($P < 0.001$ expect for D slurries of Exp.1 for which $P = 0.052$) (Table 16), underling the role of the solid fraction for N_2O production.

Disturbance had significant effect only in the case of UN slurries of Exp.2: UN_D slurries showed a 460 % reduction of N_2O emissions compared with the UN_ND. This result highlights the importance of the condition of the superficial layer of stores in favouring or not the N2O production.

In Exp. 1 **CH_4** emissions were not significantly affected by disturbance and mechanical separation. Contrary in Exp. 2 the mechanical separation had a significant effect ($P < 0.001$) in case of disturbed slurries: on average the separated ones (UN_D: 2.45 ; UN_ND: 1.47 $gt^{-1}d^{-1}$) showed a 39 % emission reduction than unseparated ones. Other studies showed a contrary effect (Chadwick et al, 2011) demonstrating that it's difficult to say if slurry separation increases or decreases CH_4 emissions since it depends mainly on the storage conditions and the characteristics of slurry fractions obtained. Wood et al. (2012) has found a linear increment as a function of TS considering liquid dairy slurries: availability of degradable C was the main factor in regulating total CH_4 emissions.

Table 16 Mean values of emissions calculated on daily basis (gt^{-1} d-^{1}) for the unseparated (C_UN) and the separated slurries (C_TR) stored in disturbed (D) and undisturbed conditions (ND). Mean and Standard Deviation (in brackets) are given.

					Variation due to separation (%)	
Exp.1	**C_UN_D**	**C_UN_ND**	**C_TR_D**	**C_TR_ND**	**D**	**ND**
N-NH$_3$ (gt^{-1}d^{-1})	0.27 (0.03)	0.125 (0.00)	0.22 (0.01)	0.1 (0.01)	-18.5*	-20.0
N$_2$O (gt^{-1}d^{-1})	0.011 (0.00)	0.013 (0.00)	0.021 (0.00)	0.025 (0.00)	90.9 †	92.3 *
CH$_4$ (gt^{-1}d^{-1})	0.08 (0.08)	0.13 (0.10)	0.06 (0.02)	0.065 (0.07)	-25.0	-50.0
CO$_2$ (gt^{-1}d^{-1})	9.21 (1.69)	13.12 (1.11)	9.74 (1.73)	13.85 (0.38)	5.8	5.6
CH$_4$ + N$_2$O (CO$_2$ eq)	5.19 (2.15)	6.94 (2.39)	7.74 (0.09)	8.96 (2.42)	49.1	29.1
Exp.2	**C_UN_D**	**C_UN_ND**	**C_TR_D**	**C_TR_ND**		
N-NH$_3$ (gt^{-1}d^{-1})	2.14 (0.11)	1.08 (0.17)	1.86 (0.12)	1.4 (0.5)	-13.1	29.6
N$_2$O (gt^{-1}d^{-1})	0.01 (0.006)	0.051 (0.02)	0.051 (0.37)	0.055 (0.01)	457**	6.6**
CH$_4$ (gt^{-1}d^{-1})	2.45 (1.16)	3.27 (0.71)	1.47 (0.06)	1.85 (0.1)	-39.9**	-43.4
CO$_2$ (gt^{-1}d^{-1})	21.04 (3.37)	18.35 (1.21)	31.65 (1.18)	23.87 (0.12)	50.5**	30.1
CH$_4$ + N$_2$O (CO$_2$eq)	64.32 (30.7)	97.28 (23.01)	52.13 (1.89)	62.84 (9.61)	-19.0**	-35.4

*** , ** and † mean significant differences with $P < 0.05$, $P < 0.01$ and $P <0. 10$ respectively.**

In Exp.2 also disturbance had significant effect on the measured fluxes ($P < 0.05$ and $P = 0.06$ for UN and TR slurries respectively): the undisturbed slurries in average showed higher emission (Table 16): crust formation may enhance methanogenic activity and act as sink of CH$_4$ (Wood et al., 2012). At the same time it was found that mild agitation of slurry can increase CH$_4$ emissions, as dissolved gas and bubbles are released (VanderZaag et al., 2010). The sum of the two contrary effects may explain the results obtained. In other experiments crust reduced CH$_4$ emissions due to slower transport into surface or oxidation in the crust (Misselbrook et al., 2005).

Concerning **CO$_2$** emissions mechanical separation had a significant effect only for disturbed slurries of Exp. 2. In this case emission from separated slurries was 50% higher than that from unseparated. This is probably related to the presence of a solid fraction rich in carbon and characterized by high CO$_2$ emissions. This was not observed in Exp. 1 and reason may be related to the very wet conditions of the heap and to the low temperatures. Disturbance had a significant effect on separated slurries of Exp. 2., causing a 32 % increment of CO$_2$ emissions (Table 16). CO$_2$ is a gas strongly influenced by agitation (Blanes Vidal et al., 2009) and it is characterized by a high Henry's constant thus the transport to atmosphere is controlled by the liquid phase: breaking the crust during slurry mixing increases evidently CO$_2$ emission.

Lastly from Table 16 it is evident the effect of season on emission determination. This is particularly evident for NH3, CO$_2$ and CH$_4$ emission. In terms of CO$_2$ equivalent on average the warm season caused an emission almost 10 times higher.

In conclusion the results obtained underline the importance of adopting mitigation techniques especially during the warm season where the major part of emissions occurred. Management operations that involve slurry disturbance must be carefully planned in order to limit the emission, particularly those of NH_3 and CO_2. The adoption of mechanical separation has many advantages concerned manure handling but should be carefully considered for environmental impact if any mitigation option is adopted. In particular it was observed an increment of NH_3 and N_2O emission.

5.2.2 Effect of slurry acidification and clay granules (Group B and C)

Initial slurry characteristics

The slurries used in the experiments were representative in terms of total solids content, total nitrogen and ammoniacal nitrogen content of typical slurries from UK dairy and finishing pig production systems (Table 17).

pH was recorded from the third week of Exp.3. On average pH recorded from slurries non acidified were included between 7.05 - 7.60. As it can be noticed from Fig. 19 acidified slurries of Exp. 3 reported a pH value lower than 4.5 that tends to be stable for all the storage period. In Exp.4 the pH increased by the time. In this experiment the amount of acid used was inferior to that of Exp.3 and reflects the commercial recommendation. At the end of storage period acidified slurries have almost the same pH value of control slurries. In all treatments a pH gradient was observed in the first ten cm of the slurry superficial layer: typically the pH measured a 2 cm is higher than that one measured at 10cm. This gradient is mainly related to CO_2 emission. CO_2 volatise very easily and because in solution it is in equilibrium with the acid form, in the first cm a lower concentration of carbonic acid is observed and thus a higher pH is also measured.

Table 17 Slurries chemical characterisation at the beginning and at the end of the storage period. All the percentage are referred to fresh manure. NA, not available; Values in parentheses are standard deviation of the mean (n = 3).

	%TS	%VS	N-NH_4 (gkg^{-1})	Ntot (gkg^{-1})	N-NH_4/Ntot	pH
1. Pig – control START	7.81 (0.23)	6.12 (0.18)	2.65 (0.08)	6.25 (0.38)	42.33	NA
1. Pig – covered START	8.40 (0.47)	6.76 (0.65)	3.01 (0.34)	6.39 (0.51)	47.33	NA
1. Pig – control END	NA	NA	NA	NA	NA	NA
1. Pig – covered END	NA	NA	NA	NA	NA	NA
2. Pig – control START	6.22 (0.09)	4.97 (0.08)	3.03 (0.29)	5.7 (0.0)	53.15	NA
2. Pig – covered START	6.12 (0.20)	4.83 (0.63)	2.80 (0.09)	5.74 (0.00)	48.78	NA
2. Pig – control END	NA	NA	NA	NA	NA	NA
2. Pig – covered END	NA	NA	NA	NA	NA	NA
3. Cattle - control START	6.33 (0.05)	4.86 (0.08)	0.73 (0.03)	5.01 (0.07)	14.57	7.12 (0.01)
3. Cattle - acidified START	6.91 (1.04)	5.02 (0.90)	0.95 (0.15)	5.26 (0.08)	18.06	5.08 (0.36)
3. Cattle - control END	5.56 (0.40)	4.11 (0.33)	0.94 (0.04)	2. 54	37.00	7.09 (0.03)
3. Cattle - acidified END	7.15 (0.16)	5.05 (0.12)	1.11 (0.02)	2. 44	45.49	4.27 (0.12)
4. Cattle - control START	5.40 (0.14)	4.30 (0.12)	0.77 (0.03)	2.55 (0)	30.20	7.34 (0.27)
4. Cattle - acidified START	5.44 (0.01)	4.35 (0.00)	0.79 (0.02)	2.43 (0.2)	32.51	5.54 (0.15)
4. Cattle - control END	5.28 (0.06)	4.16 (0.05)	0.90 (0.04)	2.59 (0)	34.75	7.20 (0.16)
4. Cattle - acidified END	5.53 (0.12)	4.26 (0.02)	0.85 (0.18)	2.6 (0.1)	32.69	7.06 (0.17)
5. Pig – control START	6.14 (0.09)	4.93 (0.08)	3.76 (0.01)	5.60 (0.01)	67.56	7.61 (0.31)
5. Pig – covered START	6.16 (0.04)	4.97 (0.07)	3.63 (0.03)	5.71 (0.1)	66.66	7.17 (0.07)
5. Pig – control END	6.02 (0.66)	3.53 (0.48)	3.42 (0.05)	NA	NA	7.06 (0.04)
5. Pig – covered END	4.68 (0.65)	4.82 (0.60)	3.30 (0.09)	NA	NA	7.06 (0.13)

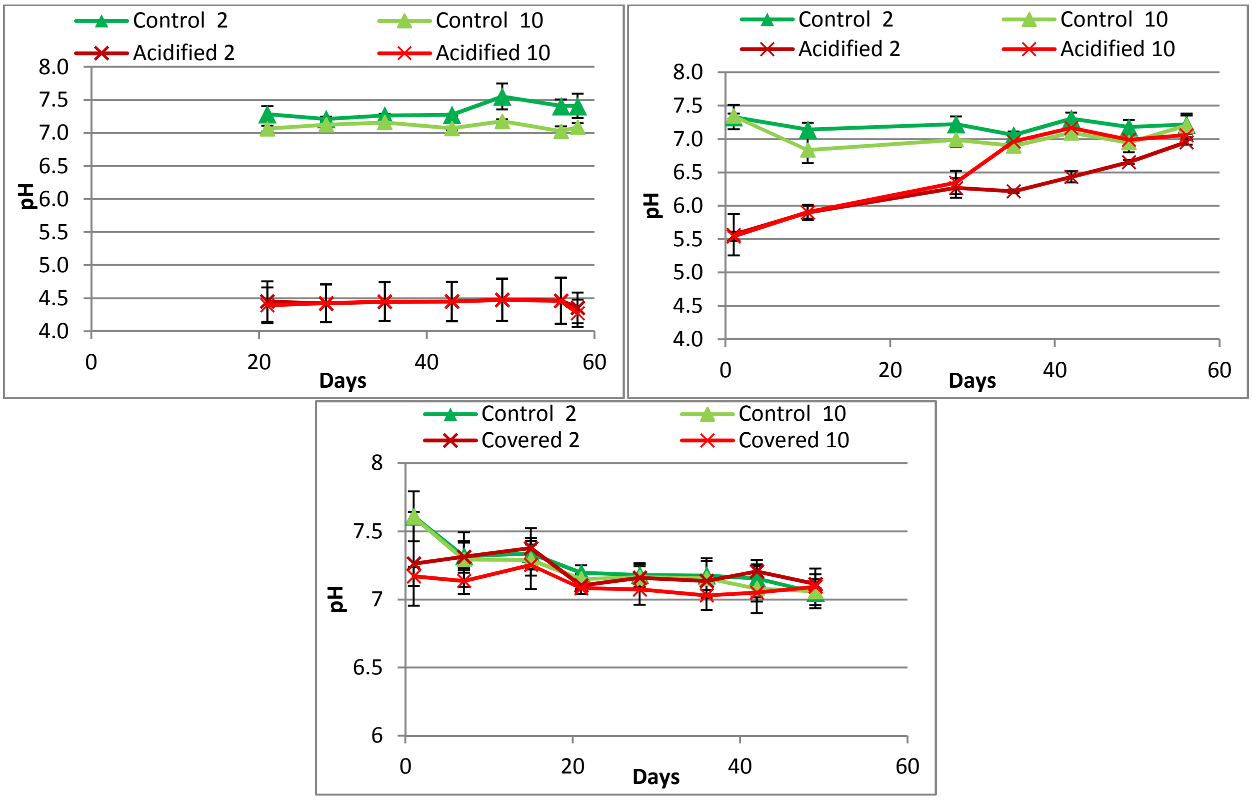


Figure 19 Ph recorded during Exp.3-4-5 (left-right-centre). PH was measured at 2 and at 10 cm. Error bars represent standard deviation.

Slurry temperature

The temperature profiles throughout the storage duration differed across the Experiments (Fig. 20). For Experiment 1, temperature was relatively stable between 10 and 15 °C until the final 15 d of storage when there was a rise in temperature. For Experiment 2, temperature started at about 15 °C , rose to 20-25 °C and then declined again. For Experiment 3, temperature declined throughout the storage period from an initial 15 °C to a final temperature approaching 0 °C.

Exp. 4 and 5 showed the most stable temperature profile, remaining between 5 and 10 °C throughout the storage period. The diurnal variation in slurry temperature was much less than that for ambient air temperature, as would be expected. The clay granule floating cover treatment resulted in a higher slurry temperature and also further reduced diurnal variation when compared with the control slurry (Fig. 20- 1,2 and 5). There was no significant difference between ambient air, control slurry and the acidified slurry temperatures in Experiment 3 and 4 (Fig. 20- 3 and 4).

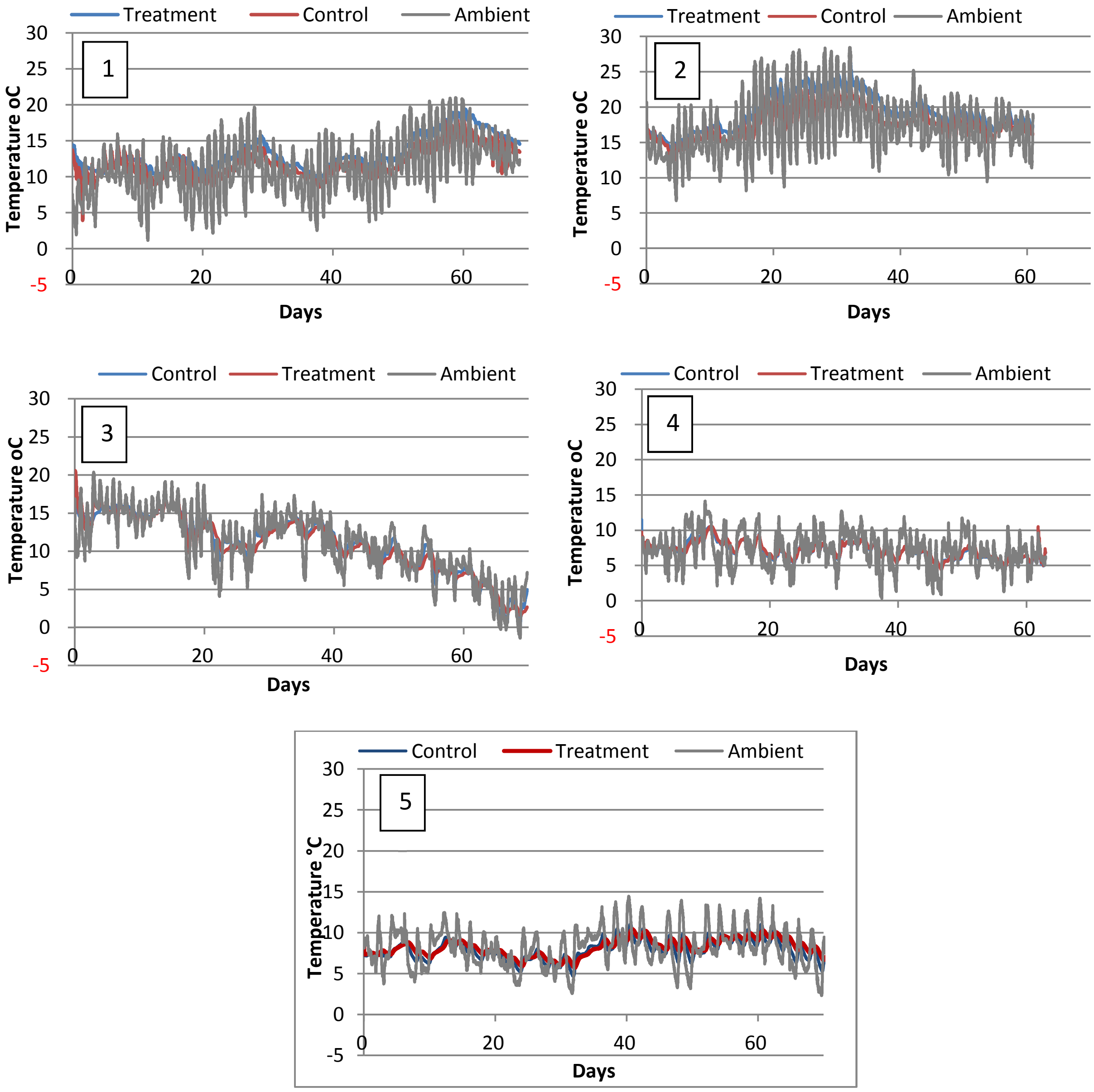


Figure 20 Slurry and ambient air temperatures for Experiment 1, Experiment 2, Experiment 3, Experiment 4, Experiment 5.

Ammonia emissions

NH_3 emissions from the control pig slurry stores (Experiments 1,2 and 5) were in the range 100 -1200 mg NH_3-N m^{-2} h^{-1} (Fig. 21), and changes in emission rate correlated well with temperature changes. Covering the slurry with a layer of floating clay granules significantly reduced the emission rate throughout the measurement period. Emission rates from the control cattle slurry stores were very much lower, in the range 100 - 25 mg NH_3-N m^{-2} h^{-1} (Fig. 21). Acidification significantly reduced the emission rate; in Experiment 3 the slurry pH remained below 5 throughout the measurement period (Fig. 19) and the emission rate from the acidified treatment remained at or below zero throughout. In Experiment 4, where less acid was added, pH started at 5.5 but increased over the storage period (Fig. 19). NH_3 emission from this treatment increased as the pH value increased until day 30 and then remained at a rate just below that of the control treatment.

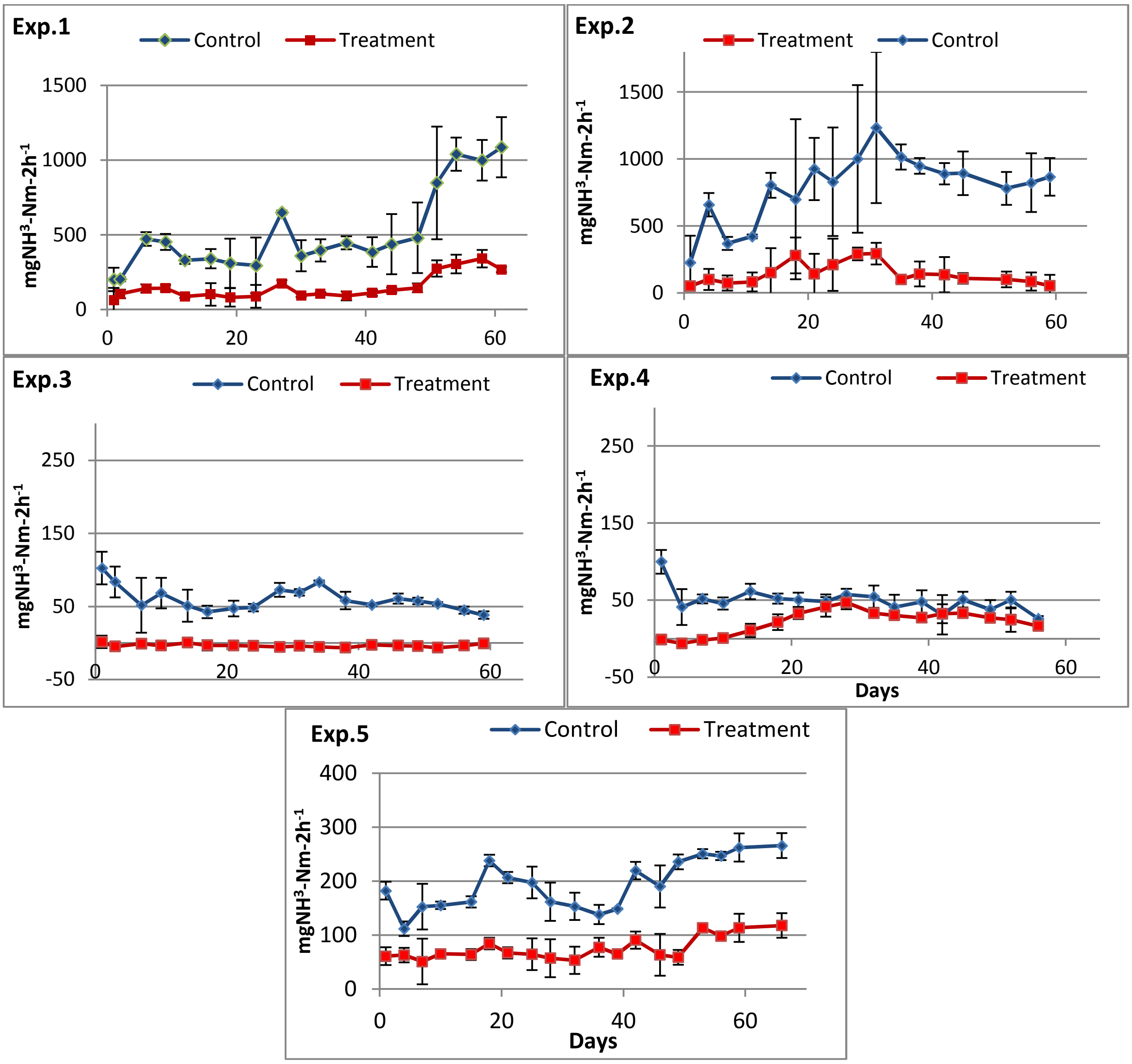


Figure 21 Net NH_3 fluxes flux during the slurry storage experiments (error bars show standard deviation of the mean)

Table 18 Cumulative NH_3 emissions. Standard deviation are given in brackets

Expt.	g NH_3-N m^{-3}			Emission as % initial slurry total N		Emission as % initial slurry TAN	
	Control	Treatment	*P*	Control	Treatment	Control	Treatment
1	790 (80)	234 (21)	*< 0.05*	7.9	3.6	30	13
2	1214 (94)	207 (37)	*< 0.001*	21	3.6	40	7.4
3	115 (4)	0.5 (0.2)	*< 0.001*	2.3	0.01	15.7	0.05
4	73 (7)	34 (1)	*< 0.05*	3.1	1.54	10.2	4.7
5	384 (8)	148 (1)	*< 0.05*	6.87	2.61	10.21	4.08

Values in parentheses are standard errors of the mean (n = 3)

Cumulative NH_3 emissions were greater from the pig slurries than the cattle slurries both in absolute terms and as a percentage of the initial slurry N content (Table 18). Losses expressed as a percentage of initial total ammoniacal N (TAN) content for the pig slurry are high compared with the current UK emission factor for slurry tanks of 13%, but comparable with the currently-used value for slurry lagoons of 52% (Misselbrook et al., 2013), perhaps reflecting the relatively low depth to surface area ratio of the stores used in this experiment in comparison to slurry stores on commercial farms.

Covering of pig slurry with the floating layer of clay granules gave a significant reduction in emission of 70, 83 and 62% for Experiments 1, 2, and 5 respectively. These reduction efficiencies are at the high end of the range reported in the literature (e.g. Horning et al. 1999; Guarino et al., 2006; Portejoie et al., 2003; VanderZaag et al., 2008). Acidification of cattle slurry gave 100% reduction in emission where slurry pH remained below 5 and c. 50% reduction in emission where the pH was only kept below 6.0 for the first 20 d of storage.

Methane emissions

The daily CH_4 flux for each experiment is shown in Fig. 22. In Experiments 1,2 and 5 CH_4 emissions from the pig slurry varied between 40 and 1500 mg m^{-2} h^{-1}, similar to those reported by Rodhe et al. (2012). There was a distinct diurnal pattern of CH_4 flux for these experiments (data not shown), correlating well with the diurnal temperature variation. Variation in measured flux between replicates was high on some occasions (shown by large error bars in Fig. 22), which may be due to the episodic release of CH_4 through ebullition events. There is some evidence of a positive relationship with temperature, with the increase in CH_4 flux towards the end of Experiment 1 and the increase in flux in the middle period of Experiment 2 both associated with increases in temperature. However, this does not explain the initial higher flux and subsequent decline in Experiment 1 during a period of relatively stable temperature. There is some evidence of greater flux from the floating clay granule treatment (although not consistently throughout the storage period), which may be associated with the slightly higher temperature of this treatment in both experiments, or may be due to the cover producing more anaerobic conditions in that treatment.

Daily CH_4 fluxes from the cattle slurry in Experiments 3 and 4 were very much lower than those from the pig slurry in Experiments 1 and 2, despite the mean ambient temperatures being similar for Experiments 1 and 3. Maximum emission rates observed higher than 90 mg CH_4 m^{-2} h^{-1} and there was no strong correlation between slurry temperature and emission rate. Sommer et al. (2000) also reported relatively low emission rates from stored cattle slurry (0 – 22 g CH_4 m^{-3} d^{-1}), and Wood et al. (2012) reported a lag of 50 – 70 d before the onset of increased CH_4 fluxes from stored cattle slurry which they thought might have been associated with the time required for the establishment of sufficient methanogenic population. This is less likely to be the case in our study where slurry was taken from a reception pit in which methanogenic bacteria would be expected to be present; however, we cannot rule out the possibility that fluxes from the cattle slurry storage may have increased in subsequent weeks. Acidification effectively stopped CH_4 emissions after the first few days of storage (Fig. 22). Exp. 5 shows lower emissions than Exp.2 and 3. This result is probably related to the lower temperatures that characterised the storage between: it was demonstrated that with the temperatures lower than 15°C, methanogenesis is not stimulated with consequently very low CH4 production (VanderZaag et al., 2011).

There was no significant effect of the floating clay granule cover on cumulative CH_4 emissions from pig slurry in either Experiment 1, 2, 5 (Table 19). The literature evidence is diversified for the effect of floating covers on CH_4 emissions. Petersen et al. (2005) demonstrated methanotrophic activity within crusts forming on slurry stores and hypothesised that this might be an effective CH_4 emission reduction measure. However, more recent evidence suggests that crusts or floating covers may be ineffective in this respect as the majority of CH_4 emissions occur as ebullition events which either by-pass any crust or cover or pass through it at too high a rate for effective methanotrophic activity to occur (Petersen et al., 2013). Sommer et al. (2000) reported a 40% reduction in emissions from stored cattle slurry with either a crust, straw or clay granules cover. Wulf et al. (2002) reported increases in CH_4 emission with straw covering and suggested that this was because of the addition of easily degradable carbon in the straw to the slurry. Rodhe et al. (2012) reported no significant effect of straw cover, but a 40% reduction with a floating plastic cover. Guarino et al. (2006) reported no significant effect of floating cover materials on CH_4 emissions when used on pig slurry storage, but did report a significant 32 and 16% reduction in CH_4 emissions for wood chip and expanded clay, respectively, when used on cattle slurry storage. Successful mitigation though the use of floating covers most likely depends therefore on the establishment of an active methanotroph population within the cover matrix. This may not have occurred in our current study which was of relatively limited duration.

There was a significant effect of acidification on cumulative CH_4 emissions from cattle slurry, with emission reductions of 91 and 86% from Experiments 3 and 4, respectively. This agrees well with Petersen et al. (2012) who reported emission reductions of between 67 and 87% when acidifying cattle slurry to pH 5.5.

Table 19 Cumulative methane emissions. Standard Deviation are given in brackets.

Expt.	g CH_4 m^{-3}			g CH_4 kg^{-1} VS		
	Control	Treatment	*P*	Control	Treatment	*P*
1	1175 (91)	1244 (81)	*ns*	19.3 (1.8)	18.6 (1.9)	*ns*
2	1265 (73)	1374 (12)	*ns*	25.5 (1.7)	27.4 (2.2)	*ns*
3	39.6 (1.7)	3.5 (0.2)	*<0.001*	0.82 (0.04)	0.07 (0.01)	*<0.001*
4	73.4 (5.6)	10.6 (1.3)	*<0.001*	1.77 (0.14)	0.25 (0.03)	*<0.001*
5	165 (5.57)	168 (9.8)	*ns*	3.34 (0.05)	3.39 (0.21)	*ns*

Values in parentheses are standard deviation of the mean (n = 3)

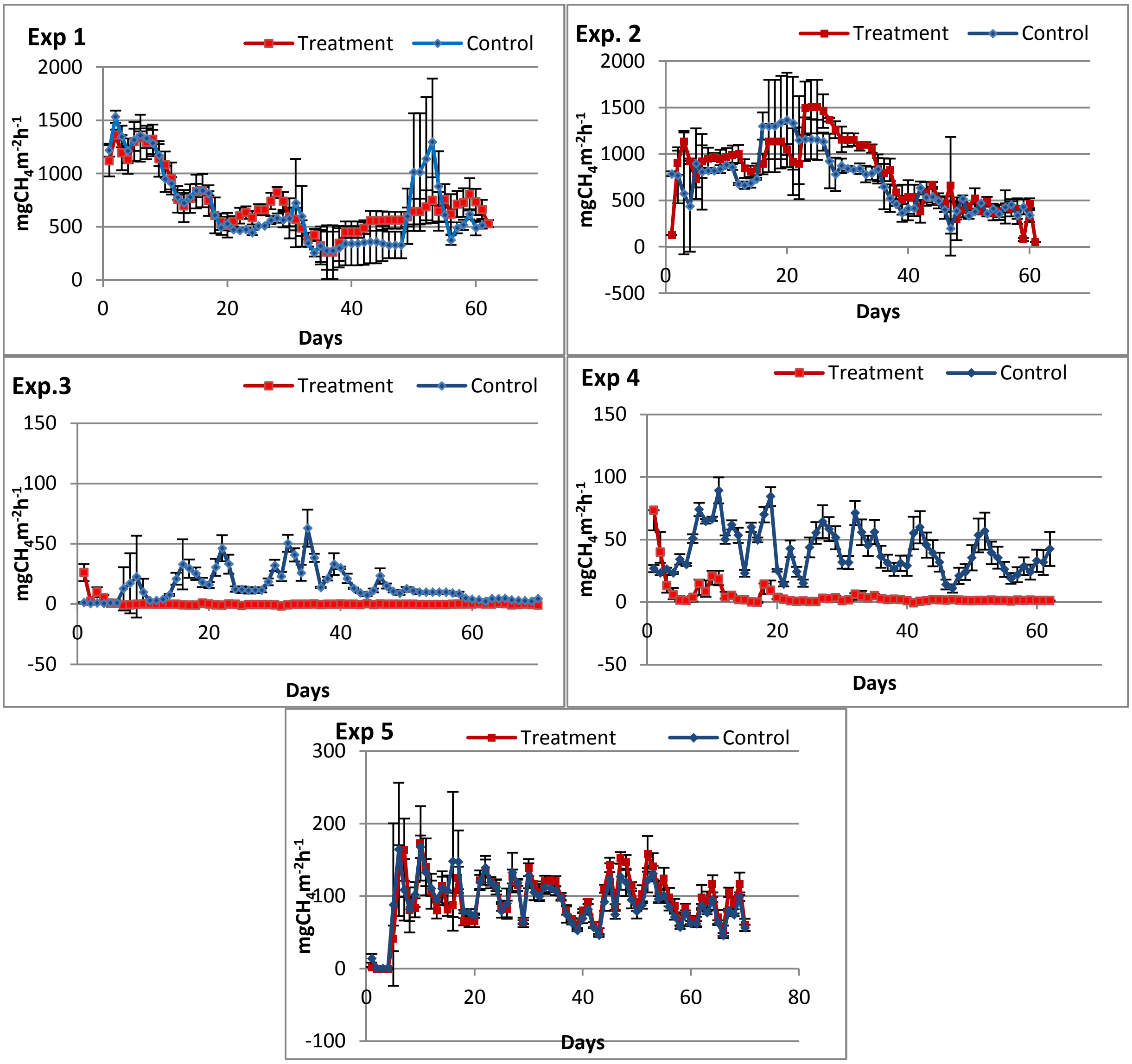


Figure 22 Daily CH_4 flux during the slurry storage experiments (error bars show standard deviation of the mean)

Carbon dioxide emissions

CO_2 fluxes also showed some correlation with temperature for Experiments 1, 2 and 5 (Fig. 23). Emissions peaked at c. 12490 mg CO_2 m^{-2} d^{-1} for the floating clay granule treatment in Experiment 2, associated with the temperature peak for that experiment. Emission rates were lower from the clay granule covering treatment throughout Experiment 1 and 5 and for all the second half of Experiment 2, suggesting that the increased anaerobicity of the slurry from the covering was more influential on emission rate than the small increase in slurry temperature.

For the cattle slurry (Experiments 3 and 4, Fig. 23), there was a large initial peak emission which declined rapidly. Subsequent emission rates were in the range 400 – 1000 mg CO_2 m^{-2} h^{-1}. With the exception of lower emissions from the acidified slurry for a few days following the initial high peak event, there were no significant differences in fluxes between treatments. These results are in accordance with those of Fangueiro et al. 2013, who observed an intense CO2 emission immediately after the acidification of LDM with 2.8% of total initial C released during the first hour after acidification. In this case the initial high emission rate of CO2 on addition of acid to the slurry may not have been fully captured in the measurements, as there was some delay between filling of the slurry tanks, acid addition, lid installation and the commencement of measurements.

Also clay granules covers have effectively reduced CO_2 emissions.

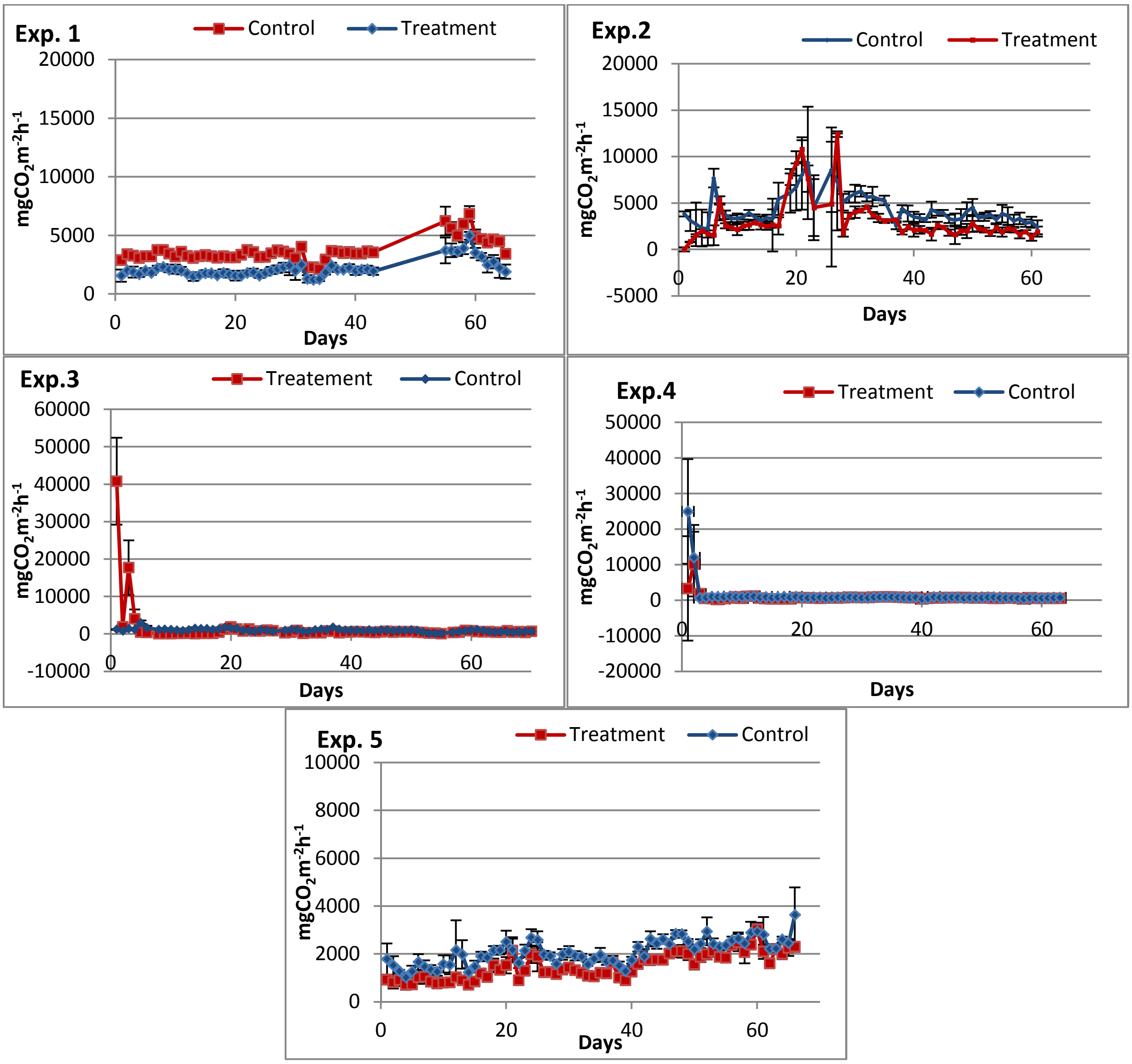


Figure 23 Daily CO_2 flux during the slurry storage experiments (error bars show standard deviation of the mean)

Cumulative CO_2 emissions over the 2-month storage period were of a similar order of magnitude for the cattle and pig slurries (Table 20). Carbon loss was greater in the form of CO_2 than CH_4 from all control slurries, by an order of x2 for the pig slurries, but by an order of x10-x20 for the cattle slurries. Covering of pig slurry with layer of floating clay granules gave a significant emission reduction, of 40 and 27% for Experiments 1 and 2, respectively. Acidification of the cattle slurry resulted in a significant 82% increase in emission in Experiment 3, but a significant 37% decrease in Experiment 4.

Table 20 Cumulative carbon dioxide emissions. Standard deviation are given in brackets.

Expt.	g CO_2 m^{-3}			g CO_2 kg^{-1} VS		
	Control	Treatment	*P*	Control	Treatment	*P*
1	6350 (115)	3793 (320)	*< 0.05*	104 (1.8)	56.7 (1.9)	*< 0.05*
2	7545 (578)	5543 (123)	*< 0.05*	151 (12)	109 (2.4)	*< 0.05*
3	2535 (114)	4604 (342)	*<0.05*	52.2 (2.2)	94.4 (14.6)	*< 0.05*
4	2498 (325)	1562 (81)	*< 0.05*	57.9 (7.1)	35.9 (1.9)	*< 0.05*
5	4031 (293)	2858 (194)	*< 0.05*	81.5 (6.55)	57.5 (4.08)	*< 0.05*

Values in parentheses are standard errors of the mean (n = 3)

Nitrous oxide emissions

No significant N_2O emissions were detected from any of the control or treated slurry stores across all experiments. The dynamic open chamber technique as used in this study is less sensitive than closed chamber techniques, relying on headspace accumulation to enable detection of concentration increases, and it is possible that emission rates and differences between treatments may have been detected with such a closed chamber technique. Some authors have measured N_2O emissions from slurry storage (Van der Zaag et al., 2008), particularly where crusts or floating covers are put in place, but these tend to be very low emissions and do not contribute significantly to the overall greenhouse gas emission from the slurry store.

5.3 Models

5.3.1 Results of calibration

As explained in Material and Methods at the end of calibration procedure three tables were created:

1. Simulated and Measured fluxes
2. Optimised parameters
3. Statistics

The first Table that resulted from calibration process let us to compare simulated data with measured data.

For each dataset it was possible to draw 13 graphs, one for each model. They are shown in Appendix 2

Table 15 reports the output of the calibration procedure and it shows all the parameters optimised. Most of the parameters chosen referred to coefficients used in some of the model equations for calculating Henry constant (H) or the dissociation constant (k_d) or the mass transfer coefficient (k).

Table 7 Calibration parameters

	DATASET							
	1	2	3	4	5	6	7	8
Ck_1	0.66	0.66	0.80	0.66	0.66	0.73	0.73	0.63
Ck_2	0.83	0.85	1.25	0.50	0.50	0.55	0.55	0.73
Ck_3	0.23	0.23	0.32	0.42	0.42	0.32	0.32	0.33
Cf_1	-0.004	0.016	-0.007	0.036	0.036	0.024	0.024	-0.020
Cf_2	0.000	0.001	0.000	0.001	0.001	0.001	0.001	0.000
Ch_1	2003.4	3005.1	1860.3	1431.0	1431.0	1431.0	1431.0	3434.4
S2_kn1	0.1	0.2	0.9	0.1	0.1	0.0	-0.1	0.1
S2_kn2	1501.5	1774.4	1910.9	2593.4	2593.4	2456.9	2456.9	819.0
S2_k1	307.1	347.1	10617.7	106.8	93.5	40.1	35.6	146.9
BE_kl	2.25	1.55	1.90	0.25	0.20	0.90	-0.60	0.10
BE_kd	0.09	0.08	0.09	0.12	0.05	0.38	0.26	-3.34
Z_h1	76.52	25.27	50.30	1.80	1.68	3.71	20.72	18.44
Z_kg1	5.32	5.32	111.13	4.25	5.58	5.32	-647.08	21.53
Z_kg2	63.18	20.22	2.01	2.01	1.91	3.12	1.91	-0.50
DVP_kh	1.80	1.92	3.23	0.12	0.12	-30.78	-30.66	8.62
DVP_kg1	18.57	17.64	25.07	24.14	22.28	0.93	0.93	21.35
DVP_kg2	703.61	703.61	809.15	246.26	246.26	0.00	0.00	-35.18
DVS_f1	50.33	50.33	50.33	50.33	50.33	50.33	50.33	50.33
DVS_f2	2.90	2.90	2.90	-0.44	0.58	-5.37	-5.37	-555.49
DVS_f3	-2.09	-11.68	-12.66	2.37	2.39	1.27	1.51	-6.97
DVS_f4	0.26	0.25	0.12	0.01	0.01	0.05	0.05	0.20
DVS_f5	-3.61	19.47	45.91	4.09	3.85	10.58	10.34	42.79
H_f1	135.32	187.95	473.63	52.63	52.63	86.46	90.22	-597.68
H_f2	3.91	3.91	3.91	-0.98	0.59	0.00	-0.20	-398.62
H_f3	-1.72	-5.73	0.19	2.42	2.42	1.89	2.21	-6.77
H_f4	0.26	0.26	0.13	0.01	0.01	0.05	0.05	0.22
H_f5	7.50	22.51	72.02	5.25	4.88	10.88	11.25	-39.76

BL_Kl	2.25	1.55	1.90	0.25	0.25	4.75	1.15	0.10
BL_Kd	0.09	0.08	0.09	0.10	0.13	0.83	0.72	-3.23
T_kd	0.17	0.17	0.17	0.18	0.16	93.42	97.74	86.04
T_H	4.17	4.17	4.17	4.17	4.17	2.08	1.46	18.14
T_kgl1	0.82	0.82	0.82	0.82	0.82	0.45	0.37	0.53
T_kgl2	0.70	0.70	0.74	0.67	0.70	0.63	0.60	0.49
T_kgl3	0.50	0.50	0.50	0.65	0.50	0.25	1.15	0.73
T_kgl4	0.50	0.50	0.50	0.50	0.50	30.57	38.40	1.95
T_kgl5	0.64	0.67	0.57	0.87	0.90	0.67	0.67	0.87
CE_pKe	1.16	1.43	1.16	1.16	1.10	1.65	1.76	6.21
CE_ka	0.20	0.27	0.22	0.22	0.21	0.35	0.28	0.20
CE_k1	47.60	22.55	45.09	50.10	50.10	22.55	17.54	7.51
CE_k2	0.80	0.88	0.80	0.84	0.80	0.60	0.76	-0.04
CE_k3	1.40	1.40	0.98	2.10	2.10	1.96	1.96	1.96
A_ka1	0.55	0.37	0.18	3.52	3.52	3.89	4.07	0.18
A_ka2	0.07	0.09	0.13	-0.16	-0.17	0.06	0.06	0.07
A_ka3	-0.29	0.92	1.36	-0.63	-0.49	2.67	3.49	0.24
S_kn1	0.09	0.09	0.09	-0.17	0.07	-2.94	-2.89	0.09
S_kn2	2866.42	2866.42	3002.91	3002.91	3002.91	2456.93	2456.93	3002.91
S_kg1	0.82	0.82	0.86	0.53	0.78	9.20	9.24	1.03
S_kg2	0.70	0.70	0.70	0.74	0.74	0.74	0.74	0.74
S_kg3	0.48	0.48	0.53	-0.23	0.40	-0.13	-0.50	0.50
S_kg4	0.50	0.50	0.50	0.50	0.50	-10.58	-13.95	0.30
S_kg5	0.70	0.67	0.67	0.64	0.64	0.67	0.67	0.64
V_kol1	2.90E-11	1.40E-11	1.05E-10	1.00E-11	1.00E-11	8.00E-12	8.50E-12	1.00E-11
V_kol2	12.13	12.13	12.13	9.70	9.70	12.61	12.61	9.70
V_kol3	-0.56	-0.82	0.29	0.34	0.34	0.31	0.34	0.34
V_kol4	8.02	8.02	7.62	8.02	8.02	7.62	7.62	8.02
V_kol5	2.31	2.33	1.78	0.26	0.26	0.26	0.26	0.26

5.3.2 Model evaluation

Table 16 and 17 show the statistics indexes (NMSE, a, b, FB, BS, R) calculated before (Table 16) and after calibration (Table 17). In the Tables 16 and 17 the number of statics indexes optimised are indicated from a minimum of 0 to a maximum of 5. Each index was considered optimised when it exceeds the relative limit indicated in Table 5 (Section 4.3). Unlike those limits, a value of $R > 0.7$ and a value of $NMSE < 0.5$ were considered positive values. R is the less robust measure for model evaluation: it is sensitive to a few outlier data pairs, thus any reasonable dispersion model would be able to reproduce this pattern (Chang and Hanna, 2004). Consequently, also considering other works in literature, it was decides to lower the limit to 0.7. Observing the results NMSE only very few cases were inferior to 0.25, thus it was decide to increase this limit to 0.5.

Comparing table 16 and table 17, first of all, it can be noticed that calibration improved significantly the overall score of the models, meaning that there was an effective improvement on flux simulation after calibration. The methodology used in some cases successfully adapts NH_3 volatilization models for use in specific conditions. Furthermore it can be observed that for some pairs of models and datasets there were no improvement after calibration: this, for example, can suggest that calibration parameters were not chosen very well.

Other considerations that can be done observing the two Tables are:

- the best fitting models were found for dataset 3 – 6 – 7 (score = 5): this probably means that controlled experimental conditions permit better model calibrations. Furthermore the availability of measured fluxes calculated using chamber techniques surely permit a better comparison between simulated and measured fluxes.
- For DATASET 1 and 2 the best fitting models are the statistical models (De Visscher and Harper), where fluxes are function of slurry temperature, air velocity, TAN concentration, air velocity. DATASET 2 seems to be better but, as explained before, this is originated by the input data selected for each dataset and not by pH measurement position.
- For DATASET 3 the best fitting model was Sommer, which is based on two film theory but, at the same time, shows an empirical approach for calculating the mass transfer coefficient. Also models based on two film theory and boundary layer theory obtained good results. This means that mechanistic models tend to well simulate the potential NH_3 emission from different kind of samples.
- For DATASET 4 the best fitting models are De Visscher_Stat and Harper (statistical models), Cortus_lin (boundary layer theory), Sommer, Sommer_2, Visscher_Pro (two film theory). No model scored 5: probably this can be related to many variable factors (ambient conditions) which play a role during flux measurements, but models cannot consider. Another reason can be related to the presence in the same dataset of sample disturbed and undisturbed, two condition that again models does not take into account. Probably it would have been better split the data into two different dataset, one with disturbed sample and one with undisturbed ones, or exclude one of the two conditions from the dataset.
- DATASET 5 obtained a lower score compared with dataset 4: this time the difference can be related to pH measurements: pH taken at 10 cm seems to be preferable in order to obtain better simulation. A possible reason can be related to his stability. For undisturbed samples in fact, in the first 2 cm, a big variability is observed moving the probe from a point to another, unlike the pH measured deeper is much more stable and more easily to take. When samples are agitated it was found that pH is uniform in all the layers and this the reason why for the bottle system we have only one dataset (3).
- For DATASET 6 and 7, representing the UK field condition, Sommer, De Visscher_Stat, Harper, Teye were the best fitting models. Models based on boundary layer (Cortus_exp, Corus_lin and Teye) theory obtained good scores with dataset 6 and 7 but also with DATASE 4 and 5. This could mean that in field condition, where the state of the air layer is one the factor that more influenced the emission pattern, models that better described the atmospheric layer can give good simulations.
- Higher was the quality of the input data for model calibration higher was the possibility to obtained good results with mechanistic models compared with statistical models. DATASET 3 in particular is an example of this observation.
- Statistical models are the most elastic models: expect for DATASET 3 and 8 they always obtained score ≥ 4.
- The better results obtained with DATESET 6 and 7 than with dataset 4 may mean that models better simulate emissions from undisturbed slurries. Typically in fact models aim to simulate emission from storages which are usually undisturbed

- For solid manure (DATASET 8) no calibration had a successful result, meaning that for this type of material specific model have to be developed.

Table 8 Model evaluation before calibration: the score ranged from 1 to 5, to 0 is associated the red colour and to 5 is associated the green colour, values in between are characterised by intermediate colour gradations.

Before calibration		DATASET							
		1	2	3	4	5	6	7	8
MODEL	Corthus_exp	2	2	1	1	0	1	2	0
	Corthus_lin	1	1	1	1	0	2	2	1
	Arogo	0	0	1	0	1	1	1	0
	Sommer	1	0	1	1	0	1	1	0
	Sommer 2	0	0	1	1	0	2	2	0
	BEIJA ENV	0	1	1	0	0	1	1	0
	BEIJA LAB	0	1	1	0	0	1	1	0
	Vaddella	0	0	0	0	0	0	0	1
	Zhang	0	0	1	3	1	1	1	1
	Visscher Pro	3	3	1	1	1	1	1	0
	Visscher Stat	1	1	1	0	0	1	1	0
	Harper	1	1	1	1	0	1	1	0
	Teye	1	1	1	1	0	2	2	0

Table 9 Model evaluation after calibration: the score ranged from 1 to 5, to 0 is associated the red colour and to 5 is associated the green colour, values in between are characterised by intermediate colour gradations

After calibration		DATASET							
		1	2	3	4	5	6	7	8
MODEL	Cortus_exp	1	2	4	3	2	4	4	1
	Cortus_lin	2	2	1	4	4	4	4	1
	Arogo	1	1	4	2	1	4	4	2
	Sommer	1	1	4	4	2	5	5	2
	Sommer 2	2	3	5	4	2	4	4	2
	Beija_env	1	1	4	2	2	4	4	1
	Beija_lab	1	1	4	2	2	4	4	1
	Vaddella	0	0	0	0	0	1	2	1
	Zhang	2	1	4	3	2	4	4	2
	Visscher Pro	3	3	4	4	4	1	1	1
	VisscherStat	4	4	3	4	4	5	5	0
	Harper	4	4	3	4	4	5	5	0
	Teye	1	1	4	3	2	5	5	1

WHAT CAN BE DONE TO OBTAINED BETTER SIMULATION AND CALIBRATION?

Observing the results obtained the following further operations and controls can be done to improve the calibration and the model simulation :

- check the quality of input data: clean the anomalous data

- improve the calibration procedure in order to better define the optimal parameters (actually sub-optimal solution might be obtained)
- use of different statistics indexes: because there is not a single best performance measure or best evaluation methodology, different performance measures can be applied. Chang and Hanna (2004) for example stated that, because the major part of atmospheric pollutant is similar to a log-normal distribution, in these cases it is better adopt logarithmic indexes which can manage better very high values and very low values. Thus in alternative to NMSE, FB, FS and R others evaluation parameters can be considered
- use a validation set of data to check the results of calibrated models.

5.3.3 Considerations

In conclusion the results obtained showed that models can be very useful to predict NH_3 release from different storage conditions. For a good calibration the quality of input data is very important. Anyhow, it is important to underline that, in the context of emission inventories, it is not very important the single flux but the cumulative emissions. Future activities can concern also the comparison of cumulative emissions obtained with measured fluxes and simulated fluxes. I would also underline that for the models evaluated it is impossible to capture the effects of management options, because these are not input variables of the models. Unlike for the latter will be easier simulate the effect of an acidification treatment because pH is one of main input parameter. For these reasons from DATASET 6 and 7 slurries characterised by the presence of a clay granules cover were excluded: the presence of slurries with very similar chemical characteristics would have generated very similar fluxes but the corresponding measured fluxes would have been very different due to the presence or the absence of the clay granules cover influencing negatively the model evaluation, the aim of which is to is to predict the NH_3emission in different storage condition and not to consider the effect of a treatment. For these considerations probably, in this case it is recommendable to choose a model that well simulate the potential emission in different storage condition. Then if a treatment is applied or if a crust is developed, a corrective coefficient, previously estimated with comparative studies, can be applied to the Equation.

Otherwise the model calibration can be performed differently starting from the datasets structure. The latter will be organised in order to evaluate the effect of treatment and the storage condition together. Anyhow the first approach seems to be more logic and reliable.

6 Operative application of the research

The results obtained from the experimental activity carried out can be used to estimate the variations of the emissions during storage induced by treatments or mitigation techniques. It is thus possible to quantify the reduction of emissions with reference to the standard techniques that can be obtained if best practices are applied.

On the other side, the emissions from the standard technique can be based on models in order to consider the manure characteristics and the local conditions, as demonstrated by the results in the assessment of model to estimate ammonia emissions.

The practical application of these two findings consists therefore in a more accurate evaluation of the emissions from storage of slurry in a specific condition (animals, manure removal, treatment, location).
Knowing the initial characteristics of the untreated slurry we can predict its emissions in different climatic conditions. Than applying the coefficients, previously described, it is possible to calculate the emission if a treatment is applied, that otherwise it would not be included in the model.

To better explain the work hypothesis an example is given. NH_3 emission from a pig slurry was simulated using the model Sommer that showed good agreement with experimental data(Table 17, Chapter 5). In particular five simulations were made changing one by one the input variables of the model (slurry temperature, ambient temperature, pH, TAN concentration, air velocity). Table 1 shows the initial characteristics and the range of the variable parameter used in each simulation

Table 1 Input variables of the 5 simulations: the values of the parameters for the reference slurry were: TAN: 3.74; TS: 6.06; pH: 7.41; Tslurry: 15; Tamb: 15; Air velocity: 0.03

Simulation	TAN (gkg^{-1})	TS	pH	Tslurry (°C)	Tamb (°C)	Air velocity (ms^{-1})
1	3.74	6.06	7.41	5-30	15	0.03
2	3.74	6.06	7.41	15	5-30	0.03
3	3.74	6.06	6.5 - 9	15	15	0.03
4	0.7 - 4.5	6.06	7.41	15	15	0.03
5	3.74	6.06	7.41	15	15	0.01-1.5

The model simulate the "Control" slurry while the emissions from the treated slurry were obtained applying the coefficient described below

Considering normal storage conditions the reduction or the increment coefficients that on average were found for the treatment considered and for swine slurry were:

- -19 % for mechanical separation
- + 45 % for anaerobic digestion
- - 71 % for clay granules cover
- - 50 % for acidification with pH below 6

Fig.1 shows the NH_3 emission expected from the slurry when temperature, air velocity, pH and TAN concentration vary.

From the trend observed it can also be derived the possibility to mitigate ammonia emissions when the treatments like anaerobic digestion increase the TAN content and the slurry temperature.

However, a more comprehensive application of this results can be obtained with a specific software application that might be developed in the future.

Consequently the following considerations can be done:

- the model allowed to predict NH_3 emissions in different conditions, out of those ones considered during experimental activity
- the model is very sensitive to slurry temperature variation, TAN concentration and air velocity
- If a cumulative emission from a particular store has to be calculated the fluxes will be estimated considering the different climatic conditions and the changes in slurry compositions over the year. Then fluxes expressed in $mgm^{-2}h^{-1}$ have to be multiply for the surface and for the time of storage. Thus dividing the cumulative emission for the initial TAN concentration an emission factor is obtained.
- in this case the emission from treated slurries was obtained multiplying the emission for the coefficients previously showed: this method can be very suitable for treatment like cover, acidification that show low variability in the NH_3 abatement results. For mechanical separation and anaerobic digestion the results obtained using different slurries and different condition of storage were different, thus using a single coefficient for these treatments would have a huge uncertainty and give unreliable results. In this case models (Table 17) can represent a big opportunity: in fact they can predict NH_3 emissions both from liquid fraction and digestate considering their different chemical characteristics.

It is thus evident that models can be very useful instrument in order to evaluate emission factors. The application of a treatment can be easily considered by the model but the introduction of standard coefficient for each treatment should be careful assessed.

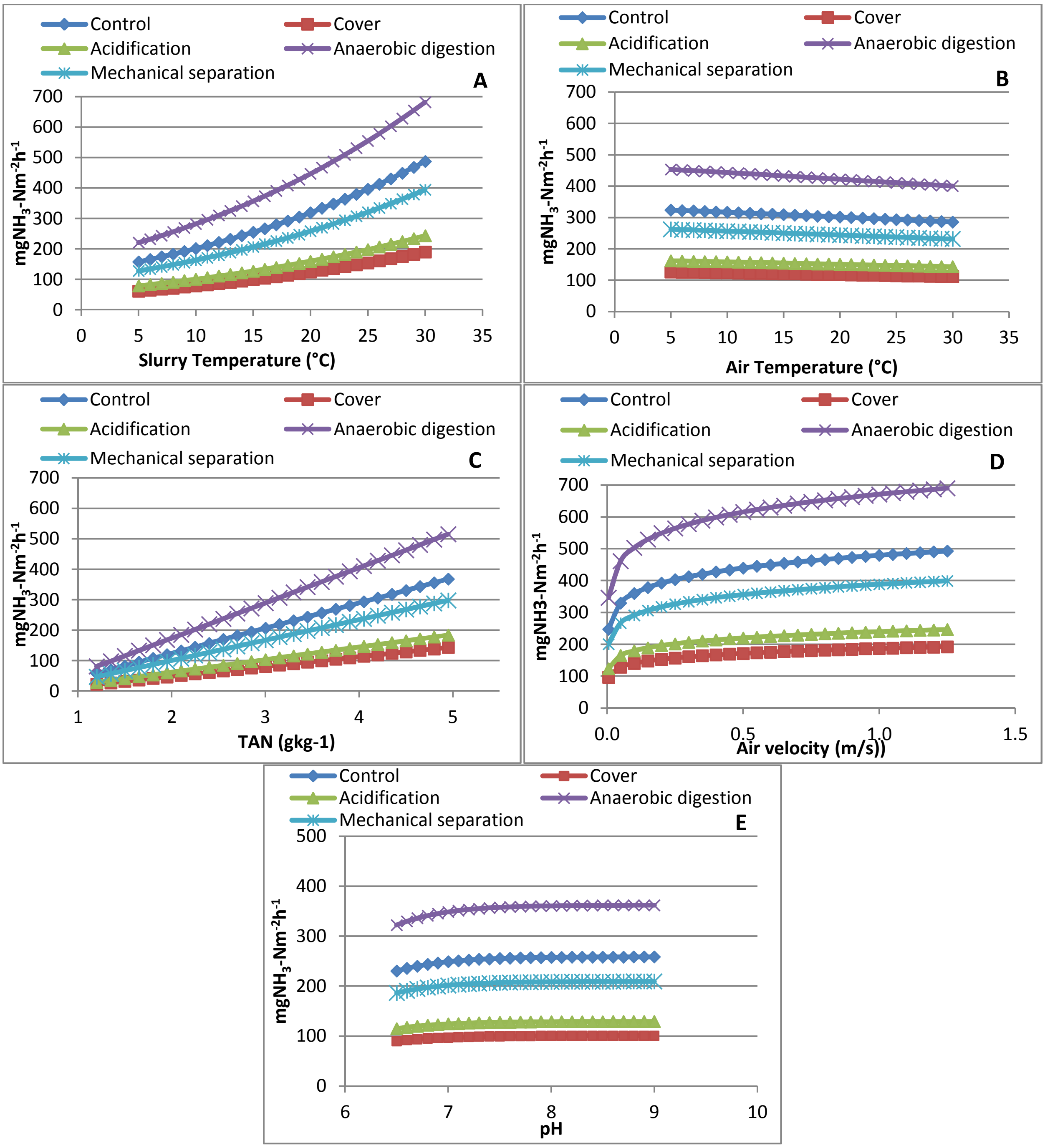


Figure 16 NH$_3$ emissions simulated with varying slurry temperature (a), ambient temperature (b), TAN concentrations (c), air velocity (d) and pH (e).

7 Conclusions

The experimental activities carried out have allowed to compare emissions from different types of manures stored in different condition. These results are particularly relevant to countries where the covering of slurry stores and/or acidification of manure is not a common practice. In particular the following conclusion can be drawn:

- Mechanical separation can cause a significant increment of ammonia e nitrous oxide emission during storage: the first one is related to the presence of the liquid fraction while the second is mainly caused by the solid fraction
- Anaerobic digestion can also increment significantly nitrogen losses, but at the same it represents a treatment that can effectively reduce methane emissions from digestate storage
- Handling operation have to be carefully considered: increments of nitrogen and carbon losses were observed from mixed slurries. Furthermore it was found that when slurries are mixed, the main factors influencing nitrogen emission are the TAN concentration and the TAN/TKN ratio. Under conditions of frequent mixing, the unseparated slurries were associated with higher NH_3 emission factors
- Floating clay granules proved to be a very effective NH_3 mitigation technique but had no significant effect on CH_4 emission from pig slurry
- Acidification of cattle slurry proved to be a very effective mitigation technique for both CH_4 and NH_3
- The derivation of country-specific emission factors for pig and cattle slurries in a revised inventory approach need to take into account duration and temperature of storage

In this context models can be very helpful instruments to predict ammonia emission factors in different storage conditions, and sometimes they can also evaluate the effect of a treatment when the latter influence the input variables of the model.

Future activities could include:

- Measurements from ‘dynamic slurry storage’ – i.e. where slurry is added to stores on a regular basis
- Longer term measurements representative of typical slurry storage periods
- Measurements from a range of pig and cattle slurries to provide robust values of emission factors
- Measurements from commercial-scale stores for validation
- A wider assessment of treatments across different slurry types
- Model validation
- Use of models to evaluate the effect of treatments

In conclusion the use and evaluation of models coupled with the study of slurry treatment effects is advisable for an improved inventory approach and to develop operational guidelines for improved manure management practices to reduce environmental impacts.

8 References

Alluvione F., Bertora, C., Zavattaro, L., Grignani, C. Nitrous oxide and carbon dioxide emissions following green manure and compost fertilization in corn. // Soil Science Society of America Journal. - 2010. - Vol. 74. - p. 384-395.

Amon B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry // Agriculture, Ecosystems and Environment. - 2006. - p. 153-162.

Amon B., Kryvoruchko, V., Fröhlich, M., Amon, T., Pöllinger, A., Mösenbacher, I., Hausleitner, A. Ammonia and greenhouse gas emissions from a straw flow system for fattening // Livestock Science. - 2007. - p. 199 - 207.

Aneja V. P., Bunton, B., Walker, J.T., Malik, B.P. Measurament and analysis of atmospheric ammonia emissions from emissions from anaerobic lagoons // Atmospheric Environment. - 2001. - p. 1949-1958.

Aneja V. P., Murray, G., Southerland, J. Atmospheric nitrogen compuonds: emissions, transport, transformation, deposition and assesment // Envirnomental Manager. - 1998b. - p. 22-25.

Aneja V. P., Schlesinger, W. H., Erisman, J. W. Effects of Agriculture upon the air quality and climate: research, policy, and regulations // Environmental Sciences Technology. - 2009. - p. 43, 4234-4240.

Aneja V. P., Maliki, B., P., Quansong, T., Daiwen, K. Measurement and modelling of ammonia emsissions at waste treatment lagoons-atmosphere interface // Water, Air, and Soil Pollution. - 2001. - p. 1949 - 1958.

Aneja V.P., Schlesinger, W., Erisman, J. W. Farming pollution // Nature Geoscience . - 2008. - p. 1, 409-411.

Aneja V.P.,Blunden,J., Caliborn, S.C.,Rogers, H.H. Dynamic Chamber System to Measure Gaseous Compounds Emissions and Atmospheric-Biospheric Interactions // Environmental Simulation Chambers: Application to Atmospheric Chemical Processes. - 2006. - p. 97-109.

APHA AWWA and WEF Standard Methods for the Examination of Water and Wastewater, 21st ed. - Washington, D.C. : American Public Health Association, 2005.

Aarnink, A.J.A., Elzing, A. Dynamic model for ammonia volatilization in housing with partially slatted floors, for fattening pigs // Livestock Production Science. -1998.- Vol. 53. -p. 153–169.

Arogo J., Zhang, R. H., Riskowski, G. L., Christianson, L.L., Day, D.L. Mass tranfer coefficient of ammonia on liquid swine manure and aqueous solutions // Journal of Agricultural Engeneering Resource. - 1999. - Vol. 73. - p. 77 - 86.

Bajwa K.S., Aneja, V.P., Arya, S.P. Measuremnt an estimation of ammonia emissions from lagoon-atmosphere interface using coupled mass trnfer and chemical reacions model, and equilibrium model // Athmospheric Environment. - 2006. - Vol. 40. - p. 275-286.

Balsari P., Gioelli, F., Airoldi, G. Ammonia emission from land applied farm yard // Proc. Greenhouse Gas Emissions from Agriculture, Mitigation Options and Strategies. - 2004. - p. 241-242.

Balsari P., Airoldi, G., Dinuccio , E. Gioelli, F. Ammonia emissions from farmyard manure heaps and slurry stores—Effect of environmental conditions and measuring methods // Biosystems Engineering.- 2007.- Vol. 97.- p. 456 - 463.

Berg W., Brunsch, R., Pazsiczki, L. Greenhouse gas emissions from covered slurry compared with uncovered during storage // Agriculture Ecosystem and Environment. - 2006. - Vol. 112. - p. 129–134.

Blanes-Vidal V., Guardia, M., Dai, X.R., Nadimi, E.S. Emissions of NH_3, CO_2 and H_2S during swine wastewater management: characterization of transient emissions afeter air-liquid interface disturbance // Athmospheric Environment. - 2012. - Vol. 54.

Blanes-Vidal V., Sommer, S.G., Nadimi, E.S. Modelling surface pH and emissions of hydrogen sulphide, ammonia, acetic acid and carbon dioxide from a pig waste lagoon // Biosystems Engineering . - 2009. - Vol. 104. - p. 510-521.

Burton C.H., Turner, C. Manure management - Treatment strategies for sustainable agriculture [Sezione di libro]. - Bedford : Silsoe Research Instiute, 2003.

Chadwick D. Emissions of ammonia, notrous oxide and methane from cattle manure heaps: effect of compaction and covering // Atmospheric Environment. - 2005. - Vol. 39 - p., 787-799.

Chadwick D., Sommer, S.G., Thorman, R., Fangueiro, D., Cardenas, L., Amon, B., Misselbrook, T. Manure management: implications for greenhouse gas emissions // Animal Feed Science Technology. - 2011. - p. 514-531.

Chowdhury A., Neergaard, A., Stoumann Jensen, L. Composting of solids separated from anaerobically digested animal manure: effect of different bulking agents and mixing ratios on emissions of greenhouse gases and ammonia // Biosystems Engineering. - 2014. - p. 63-77.

Clemens J., Trimborn, M., Weiland, P., Amon, B. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry // Agriculture Ecosystem Environment. - 2006. - Vol. 112. - p. 171-177.

Cortus E.L., Lemay, S.P., Barber, E.M., Hill, G.A. Modelling ammonia emission from swine slurry based on chemical and physical properies of the slurry // Canadian biosystems engineering. - 2009. - Vol. 51. - p. 6.9-6.22.

Cortus E.L., Lemay,S.P., Barer, E.M., Hill, G.A., Godbout,S. A dynamic model of ammonia emission from urine puddles // Biosystems Engineerin. - 2008. - Vol. 99. - p. 390-402.

Curtis S.E., Anderson, C.R., Simon, J., Jensen, A.H., Day, D.L., Kelley, K.W. Effects of aerial ammonia, hydrogen sulphide and swine-house dust on the rate of gain and respiratory-tract structure in swine // Journal of Animal Science. - 1975. - Vol. 41. - p. 735-739.

De Visscher A., Harper, L.A., Wasterman, P.W., Liang, Z., Arogo, J., Sharpe, R.R, Van Cleemput, o. Ammonia emissions from anaerobic swine lagoons: model development. // Journal of applied Meteorology. - 2001. - Vol. 41. - p. 426-433.

Denmead, O.T. Micrometeorological methods for measuring gaseous losses of nitrogen in the field // Developments in Plant and Soil Sciences. - 1983. - Vol. 9 - p. 133-157.

Dinuccio E., Berg, W., Balsari, P. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation // Atmospheric Environment. - 2008. - p. 42, 2448–2459.

EEA Annual European Union greenhouse gas inventory 1990–2012 and inventory report 2014 [Rapporto]. - Brussels : [s.n.], 2014.

Elwinger K., Svensson, L. Effect of Dietary Protein Content , Litter and Drinker Type on Ammonia Emission from Broiler Houses // Journal of Agricultural Engineering Research - 1996. - Vol. 64 - p. 197-208.

European Commission (EC) 1991. // Council Directive of 12 December 1991 concerning the protection of waters against the pollution caused by nitrates from agricultural sources. Directive 91/676/EEC, Brussels.

European Commission (EC) 2001. // Council Directive of 23 October 2001 on national emission ceilings for certain atmosphericfor pollutants.

European Commission (EC) 2010. // Council Directive of 24 November 2010 on industrial emissions (integrated pollution prevention and control. Directive 2010/75/EU, Brussels.

European Commission (EC) 2008. // Council Directive of 15 January 2008 concerning integrated pollution prevention and control. Directive 2008/1/EC, Brussels.

European Commission (EC) 2000. // Council Directive of 23 October 2000 establishing a framework for Community action in the field of water policy Directive 2000/60/EC, Brussels.

Fangueiro D., Coutinho, J., Chadwick, D., Moreira, N. Effect of cattle slurry separation on greenhouse gas and ammonia emissions during storage // Jouranal of Environmental Quality. - 2008. - Vol. 37. - p. 2322 – 2331.

Fangueiro D., Surgy, S., Coutinho, J., Vasconcelos, E. Impact of cattle slurry acidification on carbon and nitrogen dynamics storage and after soil incorporation // Journal of Plant Nutrition Soil Science. -2013. - Vol. 176. - p. 540 - 550.

FAO Livestock'Long Shadow // United Nations, Food and Agricolture Organization. - 2006.

Farrell, P., Culling, D., Leifer, I. Transcontinental methane measurements: Part 1. A mobile surface platform for source investigations // Atmospheric Environment.- 2013 - Vol. 74. -p.422 - 431.

Gao F., Yates, S.R., Yates, M.V., Gan, J.V., Ernst, F.F. Design, fabrication, and application of a dynamic chamber for measuring gas emissions from soil // Environmental Science and Technology. - 1997. -Vol. 31- p., 148-153.

Guarino A., Fabbri, C., Brambilla, M., Valli, L., Navarotto, P. Evaluation of simplified covering systems to reduce gaseous emissions from livestock manure storage // Transactions of the Asabe. - 2006. - Vol. 49. - p. 737-747.

Hales J.M., Drewes, D.R. Solubility of ammonia in water at low concentrations // Atmospheric Environment. - 1979. - Vol. 13. - p. 1133-1147.

Hansen M.N., Henriksen, K., Sommer, S.G. Observations of production and emission of greenhouse gases // Atmospheric Environment. - 2006. - Vol. 40 - p. 4172–4181.

Hashimoto A.G., Ludington, D.C. Ammonia desorption from concentrated chicken // Proc. International Symposium on Livestock-ASAE.. - 1971. - p. 117-121.

Hinz T., Linke, S. A comprehensive experimental study of aerial pollutants in and emissions from livestock buildings. Part 1: Methods. // Journal of Agricultural Engineering Research. - 1998. - p. 111 - 118 .

Hornig G., Turk, M.,Wanka, U. Slurry Covers to reduce Ammonia Emission and Odour Nuisance // J. Agric. Engng Res.. - 1999. - p. 73, 151-157.

Hutchings N. J., Sommer, S. G., Andersen, J. M., Asman, W.H.A. A detailed ammonia emission inventory for Denmark // Atmospheric Environment. - 2001. - Vol. 35. - p. 1959-1968.

IPCC Climate change. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. The physical science basis. In S. Salomon, et al. (Eds) [Rapporto]. - Cambridge, UK : Cambridge University Press., 2007.

IPCC Guidelines for National Greenhouse Gas Inventories, vols.1-3 - London : Intergovernmental Panel on Climate Change, 1996.

Liang Z.S., Westerman, P.W., Arogo, J. Modelling ammonia emission from swine anaerobic lagoons. // Transictions of ASAE 45, 787 - 798., 2002. - p. 787-798.

Loyon L., Guiziou, F., Beline, F., Peu, P. Gaseous emissions (NH_3, N_2O, CH_4 and CO_2) from the aerobic treatment of piggery slurry - comparison with a conventional storage system . - 2007. - Vol. 97. - p. 472-480.

Louro, A., Sawamoto, T., Chadwick, D., Pezzolla, D., Bol, R., Baez, D., Cardenas, L. Quantifying annual N_2O emission fluxes from grazed grassland under a range of inorganic fertiliser nitrogen inputs // Agriculture, Ecosystems & Environment.- 2013. - Vol. 181.- p.1-11.

Mackay D., Yeun, A.T.K. Mass Transfer Coefficient Correlations for volatilization of organic solutes from water // Environmental Science Technology. - 1983. - Vol. 17. - p. 211-217.

Massè D.I., Masse, L., Croteau, F. The effect of temperature fluctuations on psychrophilic anaerobic sequencing batch reactors treating swine manure // Bioresource Technology. - 2003. - Vol. 89. - p. 57-62.

Misselbrook T., Brookman, S.K.E., Smith,K.A., Cumby,T. Crusting of Stored Dairy Slurry to Abate Ammonia Emissions: Pilot-Scale Studies // Atmospheric Pollutants and Trace Gases. - 2005. - p. 411-419.

Moller H.B., Ahring, B.K. and Sommer, S.G. Methane productivity of manure , straw and solid fractions manure. // Biomass Bioenergy. - 2004. - p. 26, 485-495.

Moller H.B., Sommer,S.G., Ahring, B.K. Biological degradation and greenhouse gas emissions during pre-storage of liquid animal manure // Journal of Environmental Quality. - 2004. - Vol. 33. - p. 27-36.

Montes F., Meinen, R., Dell, C., , Rotz, A., Hristov, A.N., Oh, J., Waghorn, G., Gerber, P.J., Henderson, B., Makkar, H.P.S., Dijkstra,J. Mitigation of methane and nitrous oxide emissions from animal operations: II. A review of manure management mitigation options // Journal of animal society. - 2013. - Vol. 91. - p. 5070-5094.

Moore K. D., Young, E., Gurell, C., Wojcik, M. D., Martin, R. S., Binghamn, G.E., Pfeiffer, R. L., Prueger, J.H., Hatfield, J.L. Ammonia measurements and emissions from a california dairy using point and remote sensors. // Transaction of ASABE. - 2013. - Vol. 57 - p. 181-198.

Moset V., Cambra-Lopez, M., Estelles, F., Torres, A.G., Cerisuelo, A. Evolution of chemical composition and gas emissions from aged pig slurry during outdoor storage with and without prior solid separation // Biosystem Engieering. - 2012. - Vol. 3. - p. 2-10.

Ni J. Mechanistic models of ammonia release from liqud manure: a review // Journal of Agricultural Engineering Resource. - 1999. - Vol. 72. - p. 1-17.

Ni J.Q., Heber, A.J. Sampling and measurement of ammonia at animal facilities [Sezione di libro] // Sampling and Measurement of Ammonia Concentration. - Sacramento, California, USA : ASAE, 2001.

Ni J.Q., Heber, A.J., Sutton, A.L., Kelly D.T. Mechanism of gas releases from swine wastes // Transactions of the ASABE. - 2009. - Vol. 52. - p. 2013-2025.

Denmead O.T. Micrometeorological methods for measuring gaseous losses of nitrogen in the field // Developments in Plant and Soil Sciences. - 1983. - Vol. 9 - p. 133-157.

Ottosen L.D.M.,Poulsen, H.V., Aagren Nielsen,D., Finster, K., Peter Nielsen, L., Peter Revsbech, N. Obsarvations on microbial activity in acidified pig slurry // Biosystems Engineering. - 2009. - Vol. 102 - p. 291-297.

Patni N.K, Jui, P.Y. Volatile fatty acids in stored dairy-cattle slurry // Agricultural Wastes. - 1985. - Vol. 13. - p. 159-178.

Patni N.K., Jui, P. Y. Nitrogen concentration variability in dairy-cattle slurry stored in farm tanks // Transactions of ASAE. - 1991. - Vol. 34. - p. 609 - 615.

Paul J.W., Beauchamp, E.G. Relationship between volatile fatty acids, total ammonia, and pH in manure slurries // Biological Wastes. - 1989. - Vol. 29. - p. 313-318.

Petersen O.S., Andersen, A.J., Eriksen, J. Effects off cattle slurry acidification on ammonia and methane evolution during storage. // Atmospheric pollutants and traces gases. - 2012. - p. 88-94.

Petersen O.S., Andersen, A.J., Eriksen, J. Effects off cattle slurry acidification on ammonia and methane evolution during storage. // Atmospheric pollutants and traces gases. - 2012. - p. 88-94.

Petersen S. O., Amon, B., Gattinger, A. Methane oxidation in slurry storage surface crusts. // Journal of Environmental Quality. - 2005. - Vol. 32. - p. 455-461.

Petersen S. O., Sommer, S.G.. Ammonia and nitrous oxide interactions - the role of manure organic matter management. // Animal Feed Science Technology. - 2011. - p. 503-513.

Petersen S.O., Blanchard, M., Chadwick, D., Del Prado, A., Edouard, N., Mosquera, J., Sommer, S.G. Manure management for greenhouse gas miitigation // Animal. - 2013. - p. 7, 266-282.

Petersen S.O., Dorno, N., Lindholst, S., Feilberg, A., Eriksen, J. Emissions of CH_4, N_2O, NH_3 and odorants from pig slurry during winter and summer storage // Nutrient Cycling in Agroecosystems. - 2013. - Vol. 95. - p. 103-113.

Petersen S.O., Nielsen, T.H., Frostegard, A., Olesen,T. Oxygen uptake, carbon metabolism, and denitrification associated with manure hor-spots // Soil Biological Chemestry. - 1996. -Vol 28 - p. 341-349.

Petersen S.O., Skow, M., Droscher, P., Ademsen, A.P.S. Pilot scale facility to determine gaseous emissions from livestock slurry during storage // Journal of Environmental Quality. - 2009. - Vol. 38. - p. 1560-1568.

Piccinini, S., 2013. Biogas e biometano: una filiera bionergetica sostenibile. Ravenna, 14/03/2013. http://www.crpa.it/media/documents/crpa_www/Convegni/20130314_BiogasBiometano_RA/Piccinini_RA_14-3-2013.pdf.

Reidy B., Dammgen U., Dohler, H., Eurich-Menden, B., Van Evert, F.K., Hutchings, N.J., Luesink, H.H., Menzi, H., Misselbrook, T.H., Montey, G.-J., Webb, J. Comparison of models used for national agricultural ammonia emission inventories in Europe: Liquid manure systems // Agricultural Air Quality. - 2008. - p. 3452-3464.

Rodhe L.K.K., Abubaker, J., Ascue, J., Pell, M., Nordberg, A. Greenhouse gas emissions from pig slurry during storage and after field application in northern European conditions // Biosystem Engeeniring. - 2012. - Vol. 113. - p. 379-394.

Sanchez-Monedero M.A., Serramia, N., Garcia-Ortiz Civantos, C., Fernandez-Hernandez, A., Roig, A. Greenhouse gas emissions during composting of two-phase olive mill wastes with different agroindustrial by-products // Chemosphere. - 2010. - Vol. 81. - p. 18-25.

Schievano A., Scaglia, B., D'Imporzano, G., Malagutti, L., Gozzi, A., Adani, F. Prediction of biogas potentials using quick laboratory analyses: upgrading previous models for application to heterogeneous organic matrices // Bioresource Technology. - 2009. - Vol. 100. - p. 5777-5782.

Sharpe R.R., Schomberg, H.H., Harper, L.A., Endale, D.M., Jenkins, M.B., Franzluebbers, A.J. Ammonia volatilization from surface-applied poultry litter under conservation tillage management practices // Journal of Environmental Quality. - 2004. - Vol. 33. - p. 1183-1188.

Sherlock R.R., Sommer, S.G., Khan, R.Z., Wood, C.W., Guertal, E.A., Freney, J.R., Christopher, O.D., Cameron, K.C. Ammonia, methane, and nitrous oxide emission from pig slurry applied to a pasture in New Zeland // Journal of Environmental Quality. - 2002. - Vol. 31. - p. 1491-1501.

Smith E., Gordon,R., Bourque, C., Campbell, A. Comparison of three simple field methods for ammonia // Canadian Journal of Soil Science - 2007. - p. 469-476.

Sommer S. G., Morten, L., Christensen, L., Schmidt, T., Stoumann Jensen, L. Animal Manure Recycling. Wiley, 2013.

Sommer S.G. Ammonia volatilization from farm tanks containing anaerobically digested animal slurry // Atmospheric Environment. - 1997. - Vol. 31. - p. 863-868.

Sommer S.G., Olesen J.E., Petersen S.O., Weisbjerg M.R., Vallis L., Rodhe L., Béline F. Region-specific assessment of greenhouse gas mitigation with differnet manure managemnt strategies on four agroecological zones // Global Change Biology. - 2009. -Vol. 15 - p., 2825-2837.

Sommer S.G., Christensen, B.T., Nielsen, N.E., Schjorring, J.K. Ammonia volatilization during storage of cattle and pig slurry: effect of surface cover // Journal of Agricultural Science. - 1993. - Vol. 121. - p. 63-71.

Sommer S.G., Zhang, G.Q, Bennink, A., Chadwick, D., Misselbrook, T., Harrison, R., Hutchings, N.J., Menzi, H., Monteny, G.J., Ni, J.Q., Onema, O., Webb., J. Alghorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores // Advances in Agronomy. - 2006. - Vol. 89. - p. 261–335.

Teye F.K., Hautala, M. Adaptation of an ammonia volatilization model for a naturally ventiled dairy building // Atmospheric Environment. - 2008. - Vol. 42. - p. 4345-4354.

UNFCCC, 2012, http://unfccc.int/kyoto_protocol/doha_amendment/items/7362.php

UNECE, 2012, http://www.unece.org/env/lrtap/multi_h1.html

Vaddella V.K., Ndegwa, P.M., Ullman, J.L., Jiang,A. Mass transfer coefficients of ammonia for liquid dairy manure // Atmospheric Environment. - 2013. - Vol. 66. - p. 107-113.

VanderZaag A.C., Gordon, R.J., Jamieson, R.C., Burton, D.L., Stratton, G.W. Gas emissions from straw covered liquid dairy manure during summer storage and autumn agitation // Transactions of the ASABE. - 2009. - Vol. 52. - p. 599-608.

VanderZaag A.C., Gordon, R.J., Glass, V.M., Jamieson, R.C. Floating covers to reduce gas emissions from liquid manure storage: a review // Applied Engineering in Agriculture. - 2008. - Vol. 24. - p. 657-671.

VanderZaag A.C., Wagner-Riddle, C., Park, K.H., Gordon, R.J. Methane emissions from stored liquid dairy manure in a cold climate // Animal Feed Science and Technology. - 2011. - Vol. 166-167. - p. 581-589.

VanderZaag A.C., Gordon, R.J., Jamieson, R.C., Burton, D.L., Stratton, G.W. Effects of winter storage conditions and subsequent agitation on gaseous emissions from liquid dairy manure // Canadian Journal of soil science. - 2010. - Vol. 90. - p. 229-239.

Velthof G. L., Mosquera, J. The impact of slurry application technique on nitrous oxide emission from agricultural soils // Agriculture, Ecosystems & Environment. - 2011. -Vol.140. - p.298 - 308.

Webb J., Sommer, S.G., Kupper, T., Groenestein, K., Hutchings, N.J., Eurich-Menden, B., Rodhe, B., Misselbrook, T., Amon, B. Emissions of ammonia, nitrous oxide and methane during the management of solid manures // Sustainable Agriculture Review. - 2012.- Vol. 8 - p. 67-107.

Whelan M.J., Everitt, T., Villa, R. A mass tranfer model of ammonia volatilisation from anaerobic digestate // Waste Management. - 2010. - Vol. 30. - p. 1808-1812.

Wood J.D., Gordon, R.J., Wagner-Riddle, C., Dunfield, K.E., Madani, A. Relationships between dairy slurry total solids, gas emissions, and surface crusts // Journal of Environmental Quality. - 2012. - Vol. 41. - p. 694-704.

Wulf S., Vandre, R., Clemens, J. Non-$C0_2$ Greenhouse Gases: Scientific understanding, control options and policy aspects. Eds. VanHam, J; Baede, APM; Guicherit, R., 2002 - p. 487-492 -.

Yamulki S., Jarvis, S.C. Automated chamber technique for gaseous flux measurements: Evaluation of photoacoustic infrared spectrometer – trace gas analyser // Journal of Geophysical Reseource. - 1999. - Vol. 104. - p. 5463-5469.

Zhang R. H., Day, D. L., Christianson, L. L., Jepson, W. P. A computer model for predicting ammonia release rates from swine manure pits // Journal of Agricultural Engineering Research. - 1994. - Vol. 58 - p. 223-229.

Zhang R., Rumsey, T., Fadel, J., Arogo, J.,Wang, Z. Development of an Improved Process Based Ammonia Emission Model: Final Science Document. - 2005.

Zhao, B., Chen, S., 2003. Ammonia volatilization from dairy manure under anaerobic and aerated conditions at different temperatures. ASAE Paper Number 034148. American Society of Agricultural Engineers(ASAE), St. Joseph, MI.

Appendix 1: description of the models evaluated

In this appendix each model is described: all the formula and equations used to obtain the flux values are explained.

__Model 1 and 2: Cortus et al. 2009__

Description

The overall objective of this experiment was to develop a model to simulate the NH_3 emission rate from slurry pits within swine barns that is suitable over a range of slurry chemical and physical properties, namely pH, temperature and concentration. The specific objectives were: (1) to build on pre-existing models and develop a model to simulate the NH_3 emission from slurry; (2) to collect slurry composition and emission rate measurements from slurry samples varying in composition in a bench-scale slurry pit set-up; and (3) to calibrate and validate the model using the bench-scale measurements.

The *Boundary Layer Theory* has been applied

$F= k * (C_G – C_{air})$

F = flux expressed in $mgm^{-2}h^{-1}$ (1)

K = mass transfer coefficient

C_G = NH_3 concentration in the gas film

C_{air} = NH_3 concentration in the free air stream

In the paper two models are compered. The two ones differ for k and F calculations.

In the first, called Lin-pH a linear equation for determining F was used, while in the second one, called Exp – pH, exponential equation was adopted.

The slurry collected from eight pigs was placed in emission boxes, which were stored in an instrumentation room. For each slurry sample in both trials, the NH_3 was allowed to volatilize from the slurry samples for 8 – 6 days until the NH_3 concentration levels for all boxes were below 1000 ppm. The slurry was emptied into a bucket and remixed with the paint stirrer before being placed back in the box. At day 0 and 5 a subsample of 1 l was drawn to be analysed from TAN, pH and EC

Two data sets were obtained, the first was utilised to develop the new model, the second one for the validation process.

In table 1 the experiments parameters are summarised.

Table 1 Parameters of experimental procedure

Air velocity	0.0 - 0.5 ms^{-1}
Temperature range	19 – 20 C
TAN range	4200 – 15400 mg-/l
pH range	8.3 – 9.1

Temperature has a large impact on the emission rate calculations for both the Lin-pH and Exp-pH models. In the Lin-pH model, an increase in temperature results in a higher mass transfer coefficient and thus a higher emission rate. In the Exp-pH model, an increase in temperature decreases the mass transfer coefficient, but the emission rate still increases because of the strong positive relationship between f and T. Changing the variable air velocity had the smallest impact in both models compared with other variables and, again, the effect was smaller with the Lin-pH Model because of the differences in mass transfer coefficient determination for the Lin-pH model and the Exp-pH model. The Lin-pH Model shows a reduced sensitivity to TAN compared to the Exp-pH Model, and this is attributed to the negative relationship between f and TAN, as shown in Eqn. 7. The relative effect of pH is significantly larger on the emission rate calculations with the Exp-pH model. For every 0.1 unit increase in pH from 8.8, the Lin-pH model estimates a 48% increase in emission whereas the Exp-pH model estimates a 1% increase in emission.

Model application

Input data

1) Lin-pH model:

pH of slurry
TAN = gkg^{-1}
T_s = slurry temperature (°C)
T_a = air temperature (°C)
U = air velocity (ms^{-1})
Rh = relative humidity (%)
L = the characteristic length

2) Exp – pH model

pH of slurry
TAN = gkg^{-1}
T_s = slurry temperature (°C)
T_a = air temperature (°C)
U = air velocity (ms^{-1})

Calculation of mass transfer coefficient

1) Lin-pH model:

The mass transfer coefficient is based on the properties of the gas flowing over a flat surface of length L for laminar ($Re < 5*10^5$; Eqn. 2) or transitional/ turbulent flow (Re > 5*105; Eqn. 3).

$$k = \frac{0.664*Re^{0.5}*Sc^{0.333}*D_{A,B}}{L} \qquad Sc \geq 0.6 \qquad (2)$$

$$k = \frac{0.0296*Re^{0.8}*Sc^{0.333}*D_{A,B}}{L} \qquad 0.6 < Sc < 3000 \qquad (3)$$

To calculate Re, Sc eqn. 12 and 13 were used.

The air density was calculated as in Arogo et al. (1999), while the kinematic air viscosity and the air diffusivity were obtained as shown by eqn. 4 e 5.

$$\upsilon = 4 * 10^{-10} * T_{film}^{1.859} \qquad (4)$$

$$D_{air,T_2} = D_{A,B\,T_1} * (\frac{T_2}{T_1}) \qquad (5)$$

D_{airT1} = diffusivity in air at 298 K = $0.28 * 10^{-4}\ m^2s^{-1}$

The temperature values are expressed in K.

In the studied conditions the resulted flux was laminar and the Sc value is approximately equal to 0.6, thus Eqn.2 was always used.

2) Exp-pH model

K was estimated as in Aarnik and Elzing, 1998

$k = 50.1 * v^{0.8} * T_{film}^{-1.4}$ (6)

Calculation of ammonia concentration in the liquid solution

1) Lin-pH model:

The fraction F of TAN as NH_3 was calculated using multiple regression, performed with combinations of TAN and other measured variables. The resulting equation was the following:

$f = -0.0444 * TAN + 0.00105 * pH$ (7)

Cortus stated that this equation is applicable for swine slurry with an average TAN concentration between 4200 – 15400 mg/l, and pH between 8.3 – 9.1.

However it was decided to apply this formula even if the pH and the TAN measured in the experiments were out of the indicated range to test the model in different condition.

2) Exp-pH model

$$f = \frac{10^{pH_E}}{10^{pH_E} + \frac{1}{K_a}}$$

$$pH_E = pH + 1.1$$

$K_a = 0.2 \times 10^{-\left(0.0897 + \frac{2729}{T_{flm}}\right)}$ (Aarnink and Elzing 1998) (8)

Eqn. 8 represents the exponential-type relationship

Calculation of ammonia concentration in the air

In both models C_G was calculated using the Henry's law. H was obtained with eqn. 9.

$H = \frac{C_L}{C_G} = 1431 \times 1.053^{(293 - T_{film})}$ (9)

Calculation of the flux

Eqn.1 indicates how to calculate the flux.

A value of 0.129 (mgl^{-1}) was used for C_{air}. It was obtained by averaging the measured air concentration, recorded during the field experiments with the acid traps. To express the flux in terms of mgm^2h^{-1} Eqn. 1 must be multiplied for 1000000*3600.

Model 3: Arogo et al. 1999

Description

The objectives of this study were to determine the overall mass transfer coefficient of NH_3 transferring from liquid swine manure into the air under different environmental conditions and to develop a correlation between the mass transfer coefficient of NH_3 and the pertinent manure properties and environmental conditions.

Eqn. 10 is based on the two film theory.

$\frac{dM}{dt} = KA_0(C_L - C_{air})$ (10)

M = mass of volatile compound in kg

K = overall mass transfer coefficient of the volatile compound in ms^{-1}

A_0 = interfacial surface area in m^2

C_L= concentration of the volatile compound in the liquid in (gl^{-1})
C_{air} = concentration of the volatile compound in the air (gl^{-1})
t = time in seconds

Arogo to include the influence of system geometry and other air, liquid manure properties in the mass transfer coefficient correlations, decided to use the dimensionless number approach. The advantage of using dimensionless numbers and groups is that, once they are defined, they can be used for any scale of the system. The common dimensionless numbers that have been used in mass transfer correlations include the Sherwood Sh (Eqn.11), Schmidt Sc (Eqn.12), and Reynolds Re number (Eqn.13).

$$Sh = \frac{K_{OL}L}{D_{A-air}} \tag{11}$$

$$Sc = \frac{\mu_{air}}{\rho_{air}D_{A-air}} \tag{12}$$

$$Re_x = \frac{\rho_{air}\mu_{air}L}{\mu} \tag{13}$$

K_{OL} = overall mass transfer coefficient for NH_3, ms^{-1}
L = characteristic length of the convective emission chamber, m
$D_{A\text{-}air}$ = diffusivity of NH_3 in air, m^2s^{-1}
μ_{air} = air viscosity, $kgm^{-1}s^{-1}$
ρ_{air} = air density, kgm^{-3}
U_{air} = air velocity above the liquid, ms^{-1}

Correlations for the overall mass transfer coefficient of NH_3 with liquid properties and environmental conditions were developed for NH_3 volatilizing from aqueous solutions as well as from liquid manure in a convective emission chamber where the air velocity, temperature, turbulence, and relative humidity were precisely controlled (Table 2).

Liquid samples (1500 ml) for every test were preparing by diluting 30% ammonium hydroxide (NH_4OH) solution either with tap water for the aqueous solution or partially digetsted liquid swine manure, to make solution with an initial TAN concentration of approximately 2000 mg-N/l.

The manure used in this study was collected from the finishing building. The digested manure had on average a total solid content < 1% and 2000 mg/l TAN.

Table 2 Parameters of experimental procedure

Air velocity	0.1 to 0.5 ms^{-1}
Temperature range	15 – 35 C
Initial TAN concentration	4000 mg-N/l
Initial pH	12

Model application

Input data

pH of slurry
TAN = g/l
Ts = slurry temperature (°C)

Ta = air temperature (°C)
U = air velocity (ms^{-1}
Rh = relative humidity (%)

Calculation of mass transfer coefficient

For estimating the dimensionless numbers, air viscosity (Eqn. 14), air density (Eqn.15) and NH_3 air diffusion (16) need to be determined.

$$\mu_{air} = 0.3768 * 10^{-6} * (273.15 + T_{air})^{0.683} \qquad (14)$$

$$\rho_{air} = \left(\frac{353}{273.15+ T_{air}}\right)\left(\frac{(760-0.3783)*(R_h)e^{0.0596T_{air}+1.6662}}{760}\right) \qquad (15)$$

$$D_{A-air} = \frac{10^{-7}(273.15+T_{air})^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_{air}}\right)^{1/2}}{P[\left(\sum_A v_i\right)^{\frac{1}{3}}+\left(\sum_{air} v_i\right)^{\frac{1}{3}}]^2} \qquad (16)$$

where M_A is the molecular weight of NH_3 in gmol^{-1}, *Mair*, the molecular weight of air in gmol^{-1}, *P* is the atmospheric pressure in atm, $\sum_A vi$ is the sum of all atomic diffusion volumes of the elements in NH_3, and $\sum_{air} vi$ is the diffusion volume of air.

M_A = *17* gmol^{-1}
Mair = 28.98 gmol^{-1}
$\sum_A vi$ = *25.725* gmol^{-1}
$\sum_{air} vi$ = *20.1* gmol^{-1}
P = 1 atm

Using the dimensionless analyses procedure, a mathematical relationship is defined by Eqn.17

$$Sh = C_k*(Re)^a*(Sc)^b*(T_{air}/T_s)^e \qquad (17)$$

C_k = constant

The results for the constants and exponents in Eqn. 17 are reported in Table 3.

Table 3 Values of constant C_k and exponents a, b, and c for calculating the mass transfer coefficient of NH_3 in Eqn.8

Parameter	Aqueous solution	Liquid manure
Ck	3.12	3.70
a	0.12	0.1
b	0.53	0.53
c	-0.77	-0.97

K_{OL} ca be estimated indirectly by Eqn.18.

In the case of liquid manure:

$$K_{OL} = \left[3.70 \times (Re)^{0.10} \times Sc^{0.53} \times \left(\frac{T_{air}}{Ts}\right)^{-0.97} \times D_{A-air}\right]/L \qquad (18)$$

L= characteristic length of the convective emission chamber. In our case L= diameter of bottle/tank

Calculation of NH_3 concentration in the liquid solution

The concentration of molecular NH_3 can be calculated as:

$$C_L = F * TAN \qquad (19)$$

$[NH_3]_L$= free NH_3concentration in solution g/l
$[NH_3]_L$ depends on dissociation constant (k_d) and pH

$$K_d = 10^{-\left(0.0897+\frac{2729}{T_S+273.15}\right)} \quad (20)$$

$$F = \frac{K_d}{K_d+10^{-pH}} \quad (21)$$

Calculation of NH_3 concentration in the air

The NH_3 air concentration can be calculated using Henry's law

$C_{air}= HC_L$ (22)

H= Henry's constant

In Arogo et al. is not reported the equation for determining H. Thus it was decided to use a non-dimensional Henry constant because this form is more convenient in the calculation than the others. (Ni, 1998).

$H = 1384 * 1.053^{(293-T)}$ (23)

T is expressed in K.

Calculation of the flux

The equation for calculating the flux ($mgm^{-2}h^{-1}$)

$F = K_{OL} *(C_{L}-C_{air}) *1000000*3600$ (24)

Sensitivity analyses

A sensitivity analyses was done to determine the relative changes in the overall mass transfer coefficient of NH_3 from liquid to air with respect to changes in air velocity, liquid temperature, and air temperature.

The change in mass transfer coefficient per unit change of air velocity was higher than the changes caused by unit changes in air and liquid temperatures. At the lower air velocity range,0.1-0.2 ms^{-1}, the mass transfer coefficient is more sensitive to velocity changes compared to the higher velocity ranges, 0.2-0.3 ms^{-1}. Similarly, for both air and liquid temperatures, the mass transfer coefficient is more sensitive to temperature changes in the lower, 15 – 20 °C, compared to the higher, 30-35 °C.

Model 4 and 5 Sommer et al. 2006 - 2013

Two Sommer's models were applied. The references are:

1) *The simple gradient approach : Algorithms determining NH_3 emission from building housing cattle and pigs and from manure store*
2) *Two layer transport and release model: animal manure recycling*

Description

1) For systems where we have insufficient knowledge about the transport processes or not enough input data are available one may use a simple gradient technique. The rate of NH_3 emission from liquid surface with TAN is given by eqn.25 and K is determined empirically

   $F_{NH3} = K (C_G-C_a)$ (25)

   NH_3 gas ($\mu g\ N\ m^{-3}$)

   U= mean wind speed (ms^{-1})

   This model was actually elaborated by Sherlock et al. (2002)
2) The calculations assume that the barrier (residences) to emission is diffusion through the stagnant liquid and air film layers and the release from the liquid to the air.

Model application

Mass transfer coefficient

K is determined with eqn. 26 and is affected by the height at which the wind speed has been measured.

1) $K= 89*u*10^{-4}$ (26)

NH_3 gas (kg N m^{-3})

U= mean wind speed (ms^{-1})

2) $K = 1/(1/k_w+ H/k_a)$ (27)

K_L = transfer velocity in water (cms^{-1})

K_G= transfer velocity in air (cms^{-1})

$K_G= D_G/z_{w,a}$

$K_L = D_L/z_{w,a}$

D_L = diffusion in the liquid phase (cm^2s^{-1})

D_G = diffusion in the gas phase (cm^2s^{-1})

$Z_{a,w}$ = air boundary layer thickness (cm)

$Z_{w,a}$ = liquid boundary layer thickness (cm)

H was calculated 98 and 69.

D_G and D_L was determined with eqn.6 and eqn.46. respectively. The thickness of air boundary layer was estimated indirectly by eqn.85. The liquid boundary layer thickness was assumed to be 10 times lower than the air one (Sommer,2013).

NH_3 concentration in the liquid

In both models the equilibrium constant K_d was calculated with eqn. 28 and 29

$\log K_N = -0.09018 -2729.92/T$ (K) (Sherlock et al., 2002) (28)

$$[NH_3]_{solution} = \frac{[TAN]}{1+([H_3O^+]/K_N)} \quad (29)$$

$[H_3O^+]= 10\text{^}^{-pH}$ (30)

[TAN] = kgm^{-3}

NH_3 concentration in the gas

1) Henry's constant was calculated with eqn. 31-32:

- It's expressed in $moll^{-1}atm^{-1}$. To compare it with a non- dimensional form ideal gas law must be applied

  $\ln K_H = = -160.559+8621.06/T+25.6767*\ln(T)-0.035388*T$ (Sommer et al., 2013) (31)

  $H=K_H = K_H \times 1 \times 0.0821 \times 298$ (32)

Once H was calculated C_G is given by the following expression:

$[NH_3]_{gas} = [NH_3]_{solution}/K_H$ (33)

2) H was calculated with equations 31 and 32

Flux

1) See eqn. 26 and 34. To convert the flux in $mgm^{-2}h^{-1}$a factor of 3600 x 1000000 must be applied
2) $F = k \times (C_L - C_G)$ (34)

Model 6 and 7: Beija et al. 2006

Description

Make a comparison of measured emission fluxes from swine waste treatment lagoon system and modelled NH_3 fluxes using the Coupled and the Equilibrium models developed by Aneja et al. 2001.
This thesis will deals only with the Equilibrium model.
The model is based on the two-film theory of molecular transfer of NH_3 across the lagoon-air interface. But Coupled model takes into account pseudo-first order reaction of NH_3 with water and acid species.
Without the chemical reactions, NH_3 flux (Aneja et al., 2001a) to the atmosphere (F) is given by the Eqn.**35.**

$F = -K(C_a-HC_L)$ (35)

K=overall mass transfer coefficient (ms^{-1})

$K= (H/k_L+1/k_a)^{\wedge-1}$ (36)

H = Henry's constant

C_a = is the concentration of NH_3 at the top of the gas phase film (gl^{-1})

C_l = is the concentration of NH_3 the bottom of liquid film (gl^{-1})

k_L = mass transfer coefficient for an inert gas in liquid phase

k_A = mass transfer coefficient for an inert gas in air phase

Mass transfer coefficients were used from Meckey and Yeon (1983), who calculated mass transfer coefficient as function of wind speed (at 10m height) in term of friction velocity[1] and Schmidt number for each phase.
k_L and k_A depend on the prevailing turbulence level as determined by water currents or wind, on temperature, and on properties of solute such as diffusivity or molecular size.
NH_3 flux measurements were made at a "farrow to finish" commercial hog operation in North Caroline. The NH_3 flux measurements were made on the lagoon surface using a dynamic chamber system (Aneja et al., 2000). The main parameters of the experimental procedure are summarized in Table 4.

Table 4 Parameters of experimental procedure

Air velocity	0.5 - 7 ms^{-1}
Temperature range	0 - 37.7 C
TAN range	50- 700 mgl^{-1}
pH range	6 – 8.2

---

[1] **Shear velocity**, also called **friction velocity**, is a form by which a shear stress may be re-written in units of velocity. It is useful as a method in fluid mechanics to compare true velocities, such as the velocity of a flow in a stream, to a velocity that relates shear between layers of flow.

In Aneja et al. (2001) it says that lagoon temperature is the most sensitive factor affecting the NH_3 flux. In some cases, wind speed and lagoon pH are also significant variables in predicting NH_3 emissions. The predictions of this model, without the chemical reactions, are the best in unstable conditions.
Model simulations show that as long as the lagoon surface temperature remains constant, an increase of air temperature from 5 – 4°C indicates a corresponding decrease of NH_3 flux of less than 0.1%. The variation of ambient NH_3 concentrations of 1 to 100 ppmv provides a flux change within the same scale.

Model application

Input data

pH of slurry
TAN = g/l
T_s = slurry temperature (°C)
T_a = air temperature (°C)
U = air velocity (ms^{-1})
Rh = relative humidity (%)
In this model it should be entered the velocity at 10 meters height. In our model application the superficial velocity was entered.

Calculation of mass transfer coefficient

Eqn. 36 shows how to calculate the overall mass transfer.
Meckey and Yeon (1989) suggest for laboratory and environmental calculations the following equations be used:

$$Ka = 1.0 * 10^{-3} + 46.2 * 10^{-3} U^{*} Sc_G^{-0.67} \quad (37)$$

$$Kl = 1.0 * 10^{-6} + 34.1 * 10^{-4} \mathrm{U}^{*} \mathrm{Sc_L}^{-0.5} \ (U^{*} > 0.3) \quad (38)$$

$$Kl = 1.0 * 10^{-6} + 144 * 10^{-4} U^{*2.2} Sc_L^{-0.5} \ (U^{*} < 0.3 \quad (39)$$

U* = friction velocity
Sc_G = Schmidt number for the gas phase
Sc_L = Schmidt number for liquid phase

$$Sc_G = \mu_{air} / (\rho_{air} * D_{A\text{-}air}) \quad (40)$$

$D_{A\text{-}air}$ = diffusivity of NH_3 in air, m^2s^{-1}
μ_{air} = air viscosity, $kgm^{-1}s^{-1}$
ρ_{air} = air density, kgm^{-3}
For the calculation of air diffusivity, air viscosity, and air density, equations 6, 7, 8 were used.
Concerning the Sc_L the following equations were used to estimate $D_{A\text{-}L}$ and μ_L:

$$D_{NH3} = 6.14526 * 10^{-15} \frac{T}{\exp\left(\frac{1622}{T} - 12.40581\right)} \quad \text{(De Visscher et al., 2001)} \quad (41)$$

T is expressed in Kelvin.
μ_L was indirectly estimated by the following equation:

$$D_L = (13.26 \times 10^{-5}) / \eta_L^{1.14} * Vi^{0.589} \quad \text{(Sommer et al., 2013)} \quad (42)$$

η_L = the solution viscosity (in centipoises (cP); 10^{-2} g cm^{-1} s^{-1}) and Vi is the molar volume of the compound (cm^3mol^{-1}). The molar volume of NH_3 is 14.9 cm^3mol^{-1}. For this parameter Sommer et al. 2013 reported a value of 25.725 cm^3mol^{-1}. In this case, to be consistent the value reported by De Visscher (2001) was used.
Concerning the friction velocity the following equations were used:

- environment condition:

$$U^{*} = [10^{-4} (6.1 + 0.63 * U)]^{0.5} * U \quad (43)$$

- laboratory condition

$U^{*}= 2.0 \times 10^{-2} \times U^{\infty 1.5}$ (44)

U_{∞} = free stream velocity (ms^{-1})

In our model application U_{∞} was equal to the velocity measured inside the tank.

Henry's law coefficient was calculated as given by Hales and Drewes (1979):

$\log H = -1.69 + \frac{1477.7}{273.15+T}$ (Dimensionless) (45)

T is the absolute temperature (K).

Calculation of NH_3 concentration in the liquid solution

C_L was calculated with Eqn. 19-20-21.

Calculation of NH_3 concentration in the air boundary layer

C_{air} was obtained using Henry's law:

$C_{air}= HC_L$ (46)

Calculation of the flux

$F = -K(C_a-HC_L)$ ($kgm^{-2}s^{-1}$) (47)

Ca is the NH_3concentration in the atmosphere. A value of 0.129 (mg/l) was used. It was obtained by averaging the measured air concentration, recorded during the field experiments with the acid traps. To express the flux in terms of $mgm^{2}s^{-1}$ eqn. 47 must be multiplied by 1000000*3600.

Model 8: Vaddella et al., 2013

Description

The overall objective of this research was to develop a statistical model using experimentally derived NH_3 mass transfer coefficients for dairy wastewater to improve the reliability of NH_3 emission process-based models applications in liquid dairy manure systems. Measured data were compare with simulated data.

The experimental data were obtained using a convective emission chamber (4.2m x 0.45m x 0.15m). The experimental conditions are summarized in Table 5.

Table 5 Experimental parameters

Air velocity	0.5- 4 ms^{-1}
Temperature range	5 – 35 C
TAN range	500 mg-/l
Air velocity	0.99– 10.16 ms^{-1}
pH range	12
TS %	0.5 – 2.5%

A sensitivity analyse was performed by increasing respective variables by 10% within the range of experiment conditions. Analyses showed k exhibited sensitivity to the factors considered in descending order: T_S, T_{AIR}, V_{AIR} and TS concentration.

Model application

Mass transfer coefficient

$$K_{OL} = 4.85 * 10^{-11} \frac{(T_L)^{9.7}(V_{air})^{0.34}}{(Tair)^{8.02}(TS)^{0.26}} \qquad (\mathrm{ms}^{-1}) \qquad (48)$$

T is expressed in C

NH_3concentration in the liquid

It’s not clear how Teye et al. calculated the fraction of TAN in form of volatile NH_3. It was decide to express it as in Arogo et al. (1999).

NH_3 concentration in air boundary layer

In this paper this CG is considered negligible.

Flux

$$Qa = K_{OL}A([NH_3]_L - [NH_3]_a) \qquad (49)$$

Qa = NH_3 flux (g s^{-1}),
K_{OL} =overall convective mass transfer coefficient for NH_3 (m s^{-1})
A = area of emitting surface (m^2)
$[NH_3]_L$ = NH_3 concentration at the lagoon liquid surface (gm^{-3}),
$[NH_3]_a$ = NH_3ncentration in air (gm^{-3})
Two key input parameters required in Equation (49) are the K_{OL} for NH_3 . In general, $[NH_3]a$ is very small and can be considered negligible.

<u>Model 9: Zhang et al., 2005</u>

Description

Liquid Manure Storage Emission Sub-Model calculates the emission rate from manure storage structures in response to manure properties (pH, temperature, NH_3 concentration, and organic N concentration), structural and storage parameters (surface area, retention time) and environmental conditions (temperature and air velocity). This mechanistic model simulates the chemical and physical processes that occur in storage, such as and NH_3 volatilization from the manure surface.

The two film theory was applied

Model application

Mass transfer coefficient

To determine the overall mass transfer k_L, k_G and H are needed.

$$K_L = \frac{k_L H_N k_G}{k_L + H_N k_G} \qquad (50)$$

K_L= mass transfer coefficient for the liquid phase (ms^{-1})

K_G = mass transfer coefficient for the gas phase (ms^{-1})

H = Henry constant

$$H = \frac{2.395\times10^{5}}{T+273.15} \times e^{(\frac{-4151}{Ts+273.15})} \quad (51)$$

To predict the surface temperature is possible to use a relation with the ambient air temperature.

$$Ts = 2.9 + 0.86T_{air} \quad (52)$$

$$Kl = 2.229 * 10^{-6}e^{0.236U_8} \quad (53)$$

$$k_G = 5.317 * 10^{-5} + 2.012 * 10^{-3} * U_8 \quad (54)$$

<u>NH_3 concentration in the liquid</u>

$$\mathrm{F} = \frac{\mathrm{K_d}}{\mathrm{K_d}+10^{-\mathrm{pH}}} \quad (55)$$

$$\mathrm{K_d} = 10^{-\left(0.0897+\frac{2729}{\mathrm{T_s}+273.15}\right)} \quad (56)$$

<u>Flux</u>

$$E_{NH3-N} = K_L * (FC_{TAN} - C_{TANair}) \quad (57)$$

A = surface area of storage (m^2)
F = fraction of TAN present as free ammoniacal N.
K_L = mass transfer coefficient (ms^{-1})
E = rate TAN volatilized from storage surface (kgs^{-1})
C_{TAN} = concentration of TAN in the storage liquid (kgm^{-3})
$C_{TAN\ air}$ = concentration of TAN in the ambient air (kgm^{-3})

<u>*Model 10, 11 and 13: De Visscher et al. 2002*</u>

Description

Develop a model to use commonly available measurements, including effluent concentration, water temperature, wind speed, and effluent pH, a statistical model was developed as well.
Volatilization of NH_3 is modelled as <u>two-film model</u>.

The process model was applied to measurements made by Harp and Sharpe (1998).
The statistical model of Harper and Sharpe (1998) based on the measured daily averages, is given by the following equation:

$$F_{NH3} = -75.1776 + 3.91u + 0.4656T_W + 0.0127[NH_4^+] + 7.5023(pH) \quad (58)$$

F= flux ($kgha^{-1}d^{-1}$)
U= wind speed
T = effluent temperature (°C)
[NH_4^+]= TAN concentration (g/l)

The statistical model of Harper and Sharpe (1998) was also applied to the 4-h data. The best fitting was expressed by eqn.59:

$$F_{NH3} = -50.3267 + 2.9u + 0.3913T_w + 0.0132[NH_4^+] + 4.8076(pH) \quad (59)$$

Table 6 summarised the main parameters used.

Table 6 Parameters of experimental procedure

Air velocity	0.100 – 10.16 ms^{-1}
Temperature range	6.1- 29.5 C
TAN range	183 – 741 mgl^{-1}
pH range	7.4 - 8

Any sensitivity analysis was done. Anyhow it was observed the statistical models generally underestimates high fluxes and overestimates low fluxes. De Visscher found that at low pH and temperature, large negative fluxes are produced by the statistical model, which is unrealistic. It was concluded that the process model is more reliable than the statistical model, despite the fact that the former led to a lower r^2 than did the latter.

Model application

Input data

1) Process model

pH of slurry
TAN = gl^{-1}
T_s = slurry temperature (°C)
T_a = air temperature (°C)
U = air velocity ms^{-1}
Rh = relative humidity (%)
C_{air} = concentration in the free air stream

2-3)Statistical model

pH of slurry
TAN = g/l
T_s = slurry temperature (°C)
U = air velocity (ms^{-1})

Calculation of mass transfer coefficient

1) Process model

$$\mathrm{K} = \frac{\mathrm{k_L k_G K_{H,apparent}}}{\mathrm{k_G K_{H,apparent} + k_L}} \tag{60}$$

k_L= mass transfer coefficient in the liquid boundary layer
k_G = the mass transfer coefficient in the gas boundary layer
K_H=H= Henry's constant.
In conditions where there is no proton transfer (which would occur at high pH levels), $K_H$apparent=k_H
De Visscher derived the equations for k_G and k_L by linear regression of the data. For k_L and k_G the units are centimetres per hour (cmh^{-1})

$$k_G = 18.568 + 703.61u_8 \tag{61}$$

u_8= wind speed at 8-m height

$$k_L = 0.6034\exp(0.2361u_8) \tag{62}$$

Wind speed measured at any height in the field may be adjusted to an 8-m height by assuming a logarithmic wind profile.

$$u_8 = u_z \frac{\ln(\frac{8}{z_0})}{\ln(\frac{z}{z_0})}$$

U_z= wind speed

Z = anemometer height

Z_0 = Roughness height = $8*10^{-5}$ m, which is typical for a water surface (De Visscher et al. 2002).

k_L and k_G are converted to appropriate values at the appropriate temperature with eqn.63 and 64

$$k_{G_{NH3}} = k_{G_{H2O}} \left(\frac{D_{air_{NH3}}}{D_{air_{H2O}}}\right)^{0.67} \qquad (63)$$

$$k_{L_{NH3}} = k_{L_{O2}} \left(\frac{D_{water_{NH3}}}{D_{water_{O2}}}\right)^{0.57} \qquad (64)$$

with D_{airNH3} and D_{airH2O} being the diffusion coefficients of NH_3 and H_2O in the air phase, and $D_{waterNH3}$ and $D_{waterO2}$ being the diffusion coefficients of NH_3 and O_2 in the liquid phase. The units of k_L and k_G had to be converted to meter per second dividing for $3.6*10^5$. NH_3 and H_2O diffusivity in air were calculated as in Arogo 1999.

The diffusion volumes in lagoons are

V_{air} = 20.1 cm^3mol^{-1}

V_{NH3} = 14.9 cm^3mol^{-1}

V_{H2O} = 12.7 cm^3mol^{-1}

The diffusion coefficients in water were calculated as eqn.45 and 46 show.

$$D_{O2} = 7.28236 * 10^{-15} \frac{T}{\exp(\frac{1622}{T} - 12.40581)} \qquad (45)$$

(46)

$$D_{NH3} = 6.14526 * 10^{-15} \frac{T}{\exp(\frac{1622}{T} - 12.40581)} \qquad (46)$$

In De Visscher (2002) NH_4^+ diffusivity is considered equal to NH_3 diffusivity.

Calculation of NH_3 concentration in the liquid boundary layer

The fraction of total TAN that is not dissociated in water is

$$F_{uncorrected} = \frac{1}{1+(\frac{10^{-pH}}{ka})} \qquad (67)$$

K_a = acid dissociation constant 10^{-pka}

P_{ka} =acid dissociation constant

The fraction of TAN that is free in lagoon liquids, accounting for adsorption of NH_4^+on the suspended organic material is

$$F_{corrected} = \frac{1}{1+10^{-pH}\frac{(1+K_{ads})}{Ka}} \qquad (68)$$

K_{ads} = equilibrium constant of adsorption of NH_4^+ on the suspended organic material.

A K_{ads} equal to 3 was adopted.

Calculation of NH_3 concentration in the air boundary layer

C_G was calculating using Henry's law constant where Henry's constant was obtained with following formula

$$H = \frac{2.395\times10^5}{T+273.15}\times e^{(\frac{-4151}{Ts+273.15})} \quad (69)$$

T is expressed in K

Calculation of the flux

1) Process model

$$F = K_L(\frac{F_{corrected}}{F_{uncorrected}}[TAN]_{bulk}\text{-}\frac{[NH_3]_{gas,bulk}}{K_{H,apparent}}) \quad (70)$$

As the TAN concentration is expressed in kgm^{-3}s^{-1} (equivalent to gl^{-1}). These units are converted to mgm^{-3}s^{-1} by multiplying by 1000000*3600, and to kilograms of nitrogen per hectare per day by multiplying by 8.64*10^{8}.

2) Statistical model

See eqn. 58-59

Model 13: Teye et al., 2008

Description

The objective of this paper is to describe the adaptation of NH$_3$ volatilization model for use in a naturally ventilated dairy building, and to compare the results of the model to experimentally measured emissions. In particular the model of Zhao et al. (2003) and the analogy of Cortus et al. (2006) are employed for estimating NH$_3$ emissions in naturally ventilated dairy building.

The air boundary layer thickness was calculated directly by the water evaporation process from a flat plate. The *two films theory* has been applied.

Model application

Input data

pH
TAN
Ts = slurry temperature
Tair = air temperature
L = characteristic length = 0.6 m

Mass transfer coefficient

K = D/z (71)
D= air diffusivity (m^2/s)
Z= thickness of air boundary layer (m) (72)

As the mass transfer coefficient is affected by the air characteristics and air velocity above the manure surface k can rewritten in two different ways depending if the air conditions are laminar (eqn. 73) or turbulent (eqn.74):

$$k_g = Sh\frac{D_g}{L}\frac{L}{\delta_g} = Sh = 0.664Re^{1/2}Sc^{1/3} \quad (73)$$

$$kg = Sh\frac{D_gL}{L\delta_g} = Sh = 0.037Re^{4/5}Sc^{1/3} \quad (74)$$

Sh = Sherwood number
Sc = Schmidt number

Re= Reynolds

$$Re = \frac{\nu \mathrm{L}}{\nu} \tag{75}$$

ν = kinematic viscosity

L = characteristic length= tank radius (=0.6)

$$\nu = 4 * 10^{-10}\mathrm{T}^{1.8599} \tag{76}$$

The diffusion coefficient was expressed with following formula:

$$D_g(T) = D_g(298K)(\frac{T}{298})^{1.5} \tag{77}$$

$D_G(298K) = 0.28*10^{-5}\ m^2s^{-1}$ (78)

For turbulent air conditions, the mass transfer coefficient can be calculated from the relation between Re, ν, and DG at 298 K

$$kg = 3T^{0.13}v^{0.8}L^{-0.2}D^{0.678} \tag{79}$$

and for laminar conditions

$$k_g = 0.821T^{0.7}v^{0.5}L^{-0.5}D^{0.678} \tag{80}$$

<u>NH_3 concentration in the liquid</u>

K_d value was calculating using eqn. 81- 82. C_L was derived multiplying F x TAN.

$$K_d = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} = 0.2 \times 10^{-(0.0897+2729/T)} = 0.16 \times 10^{-2729/T} \tag{81}$$

$$F = \frac{K_d \times 10^{\mathrm{pH}}}{K_d \times 10^{\mathrm{pH}} + 1} \tag{82}$$

<u>NH_3 concentration in the air boundary layer</u>

The Henry's constant and the subsequent C_G were calculating using eqn. 85 – 84

$$H = 4.169 \times 10^{-6} \times (273.15 + Ts) \times e^{\frac{4151}{(273.15+Ts)}} \approx 4.169 \times 10^{-6} \times (273.15 + Ts) \times 10^{\frac{1800}{(Ts+273.15)}} \tag{83}$$

$$C_{g,0} = \frac{Cm{,}0}{H} = \frac{C_{TAN}F}{H} \tag{84}$$

Flux

$$j = D_g\frac{C_{g,0} - C_g}{\delta_g} = k_g(C_{g,0} - C_g) \approx k_g C_{g,o} \tag{85}$$

F= flux ($kg(m^{-2}s^{-2})$)

The boundary layer thickness above the manure can be derived by eqn. 85.

Thanks to this relation I've estimated the boundary thickness that I've applied in Sommer's model. The liquid boundary layer thickness was then estimated assuming that the liquid one is 10 times smaller than the air one (Sommer et al., 2013, pag.144)

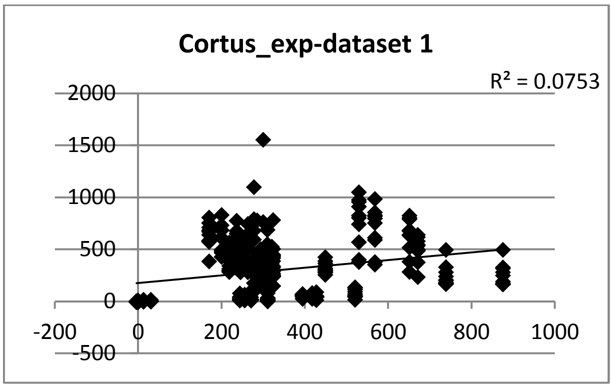
Usually the boundary air boundary layer is between 1 and 10 mm.

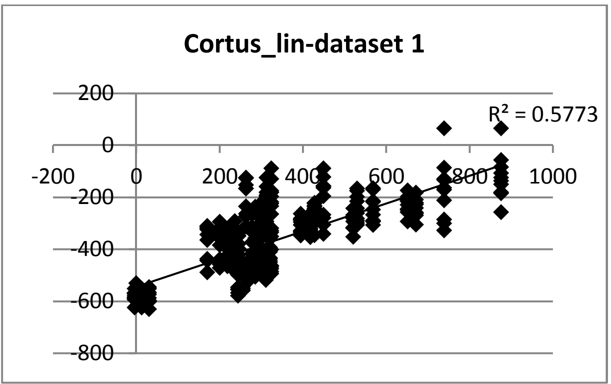
Appendix 2: simulation results

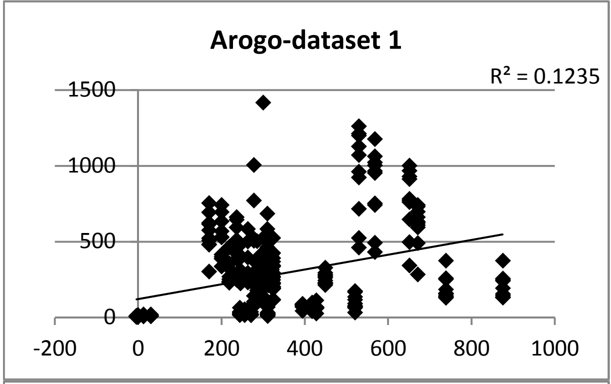
This appendix collects all the graphs (divided by dataset) which compared the simulated ammonia fluxes with the measured fluxes.

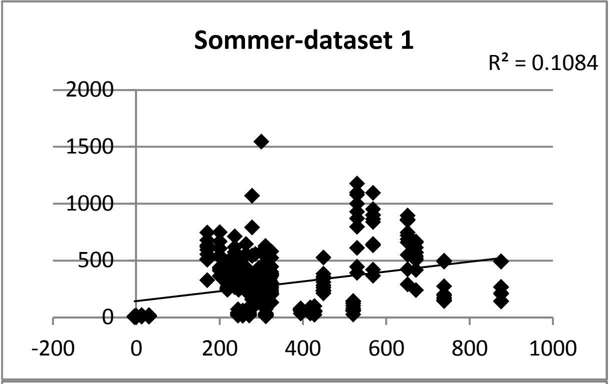
DATASET 1

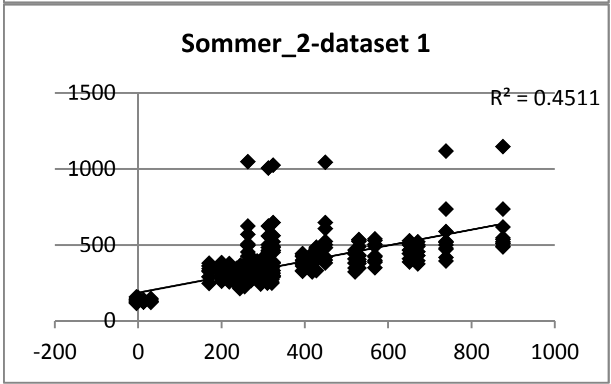
For this set the models with higher R^2 value were Cortus_lin ($R^2 = 0.58$), De Visscher_stat ($R^2 = 0.61$) and Harper ($R^2 = 0.61$). All of these models are statistical models.

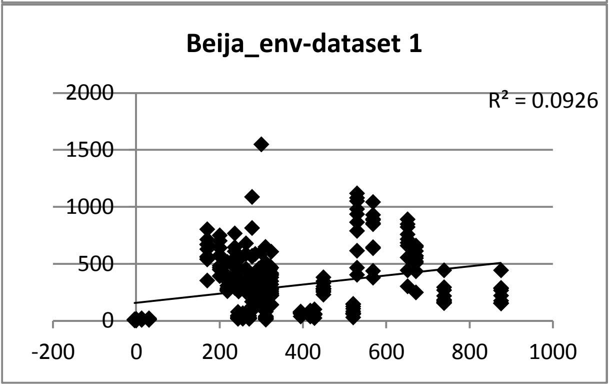


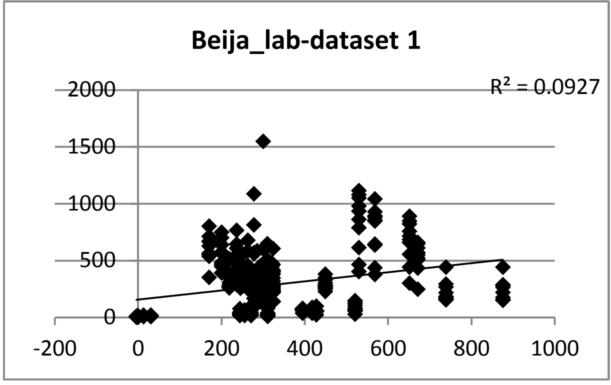


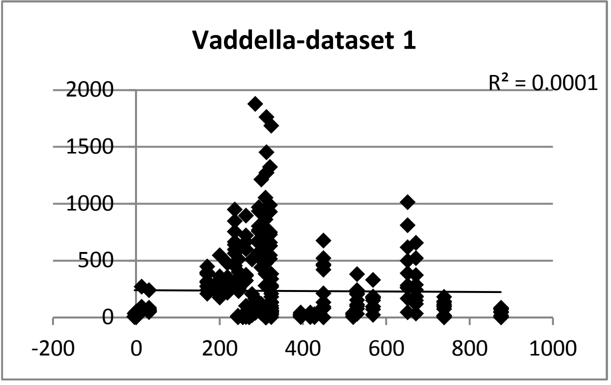












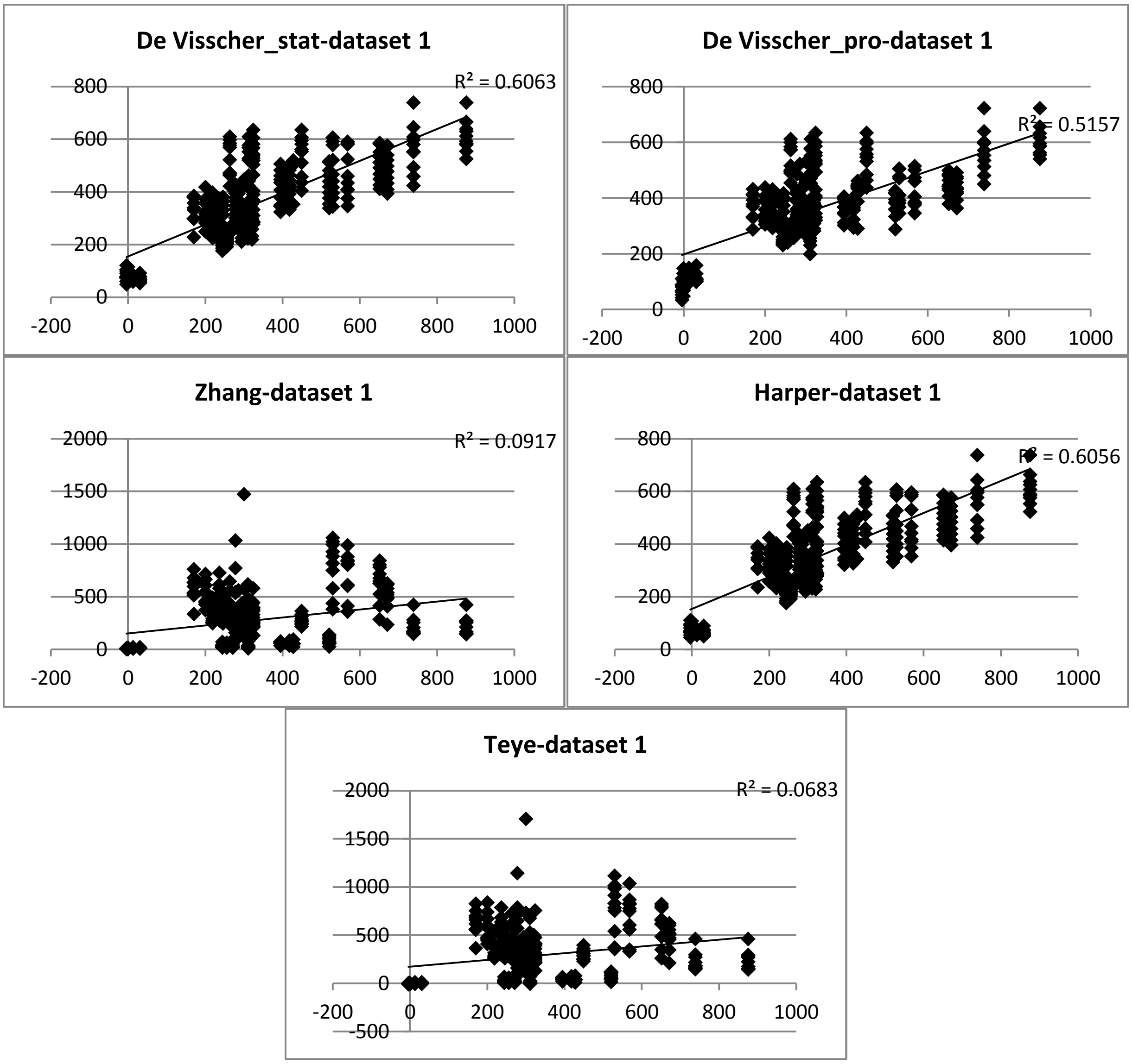
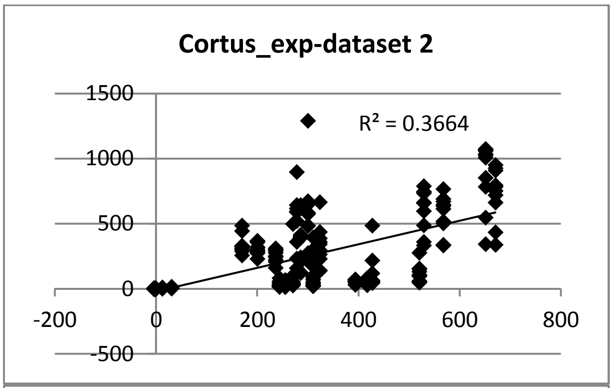
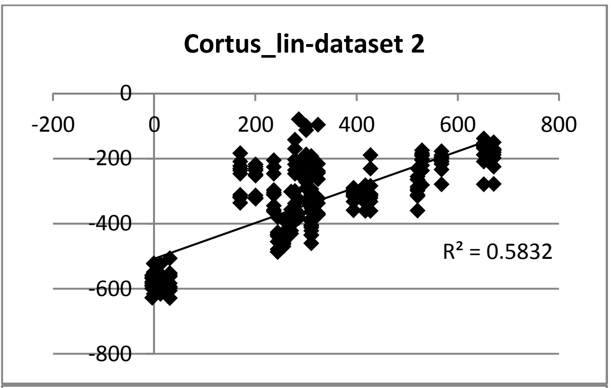


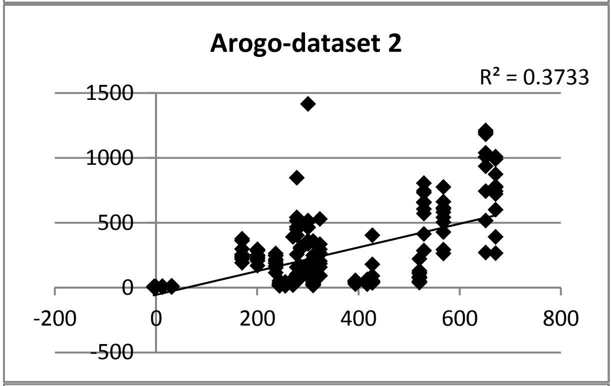
Figure 1 Linear regression for DATASET 1 between NH_3 fluxes measured (independent) and simulated (dependent)

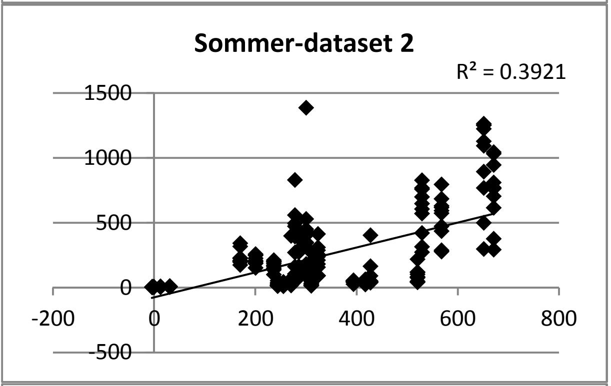
DATASET 2

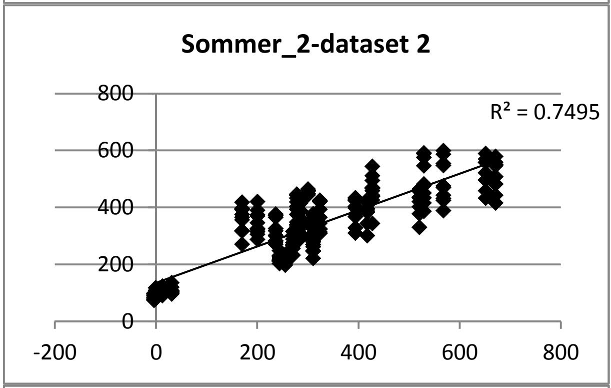
Observing the graphs it can be pointed out that R^2 value improved from the previous dataset. In this case also Sommer_ 2 improved showing a value of R^2 equal to 0.75. One of the reason can be related to the experiments included in the dataset: Exp. 1 and 2 were not used. In Exp. 1 some anomalous ambient temperatures were observed: some values exceeded 30 °C. The problem is that this increment of temperature did not correspond to a slurry temperature increment and consequently no flux increment was also measured. In Sommer_2-dataset 1 it is evident that these high temperatures have generated isolated points characterised by higher fluxes compared with the average. This observation permits to underline the importance of the input data quality. During Exp. 1 probably there was a problem related to the HOBO instrument for temperature acquisition data, thus the dataset has to be clean from these wrong temperatures. Due to this error it's difficult to evaluate the effect of pH measurement position.

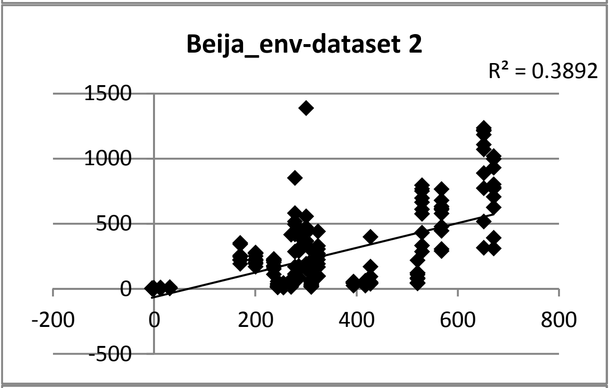

Cortus_exp-dataset 2
R² = 0.3664
1500
1000
500
0
-500
-200
0
200
400
600
800

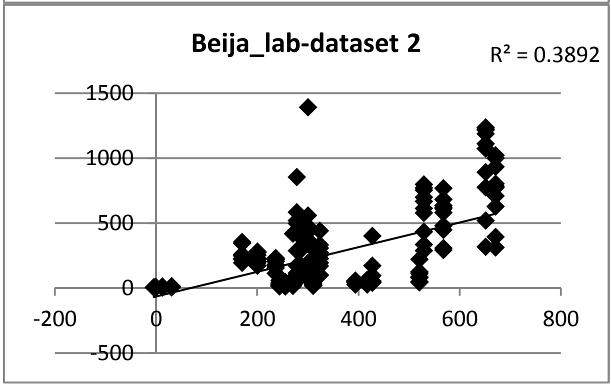

Cortus_lin-dataset 2
R² = 0.5832
0
-200
-400
-600
-800
-200
0
200
400
600
800

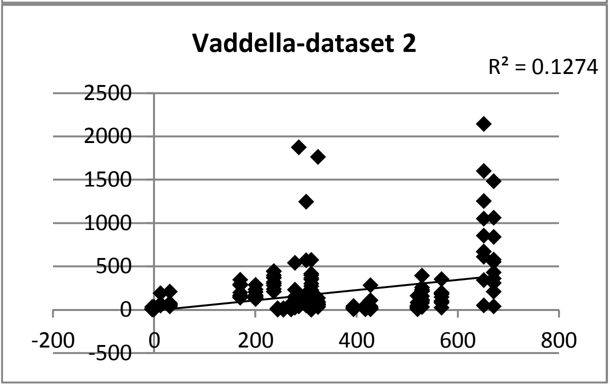

Arogo-dataset 2
R² = 0.3733
1500
1000
500
0
-500
-200
0
200
400
600
800


Sommer-dataset 2
R² = 0.3921
1500
1000
500
0
-500
-200
0
200
400
600
800


Sommer_2-dataset 2
R² = 0.7495
800
600
400
200
0
-200
0
200
400
600
800


Beija_env-dataset 2
R² = 0.3892
1500
1000
500
0
-500
-200
0
200
400
600
800


Beija_lab-dataset 2
R² = 0.3892
1500
1000
500
0
-500
-200
0
200
400
600
800


Vaddella-dataset 2
R² = 0.1274
2500
2000
1500
1000
500
0
-500
-200
0
200
400
600
800

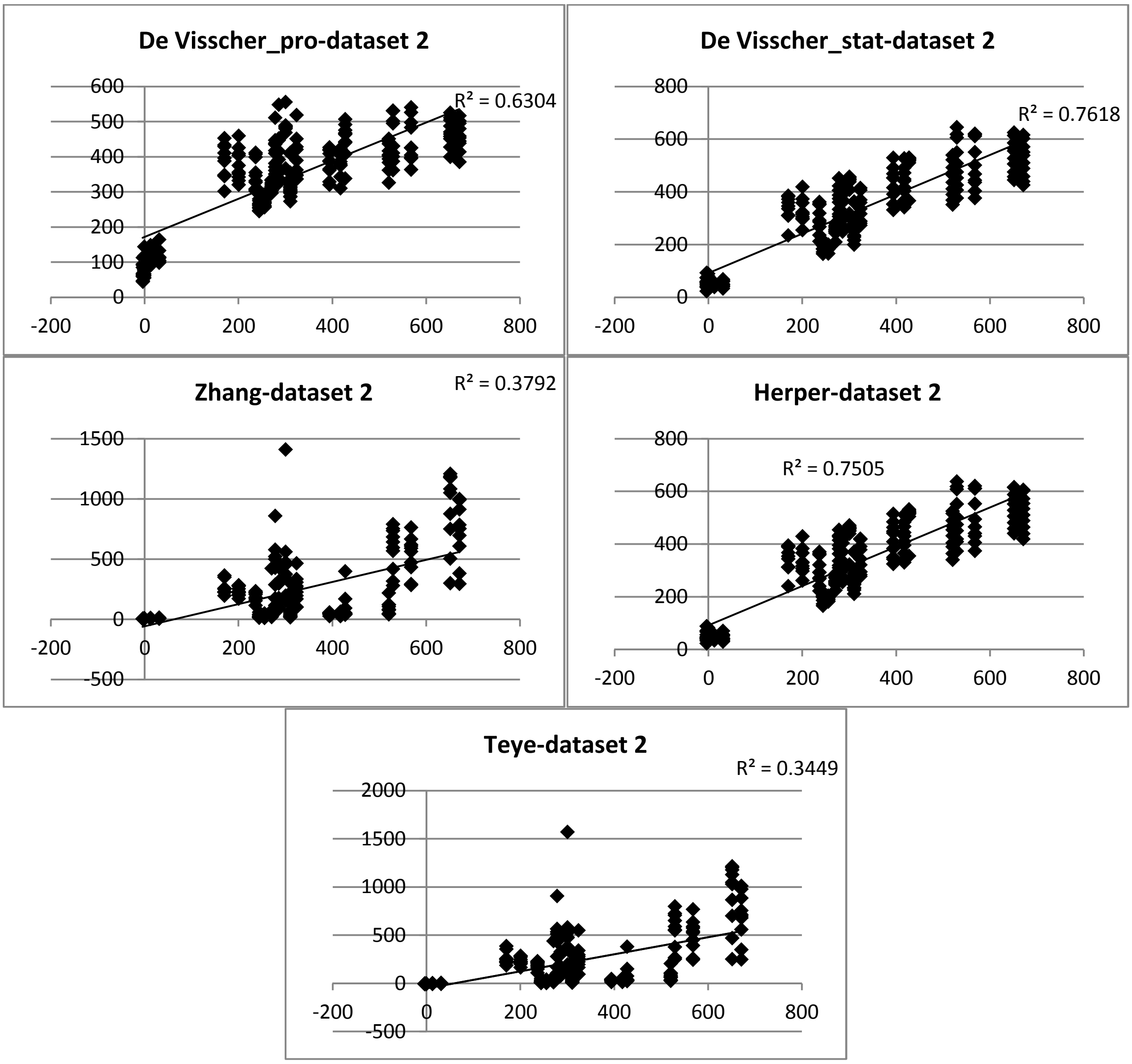
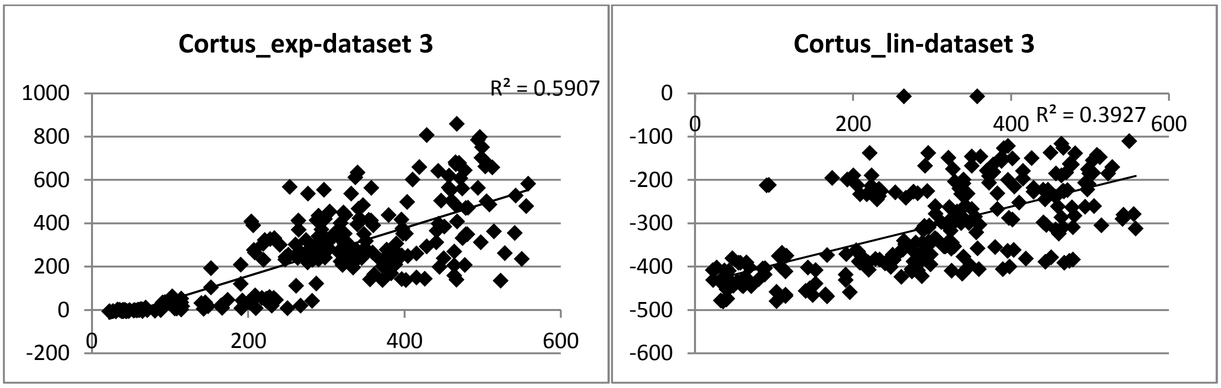
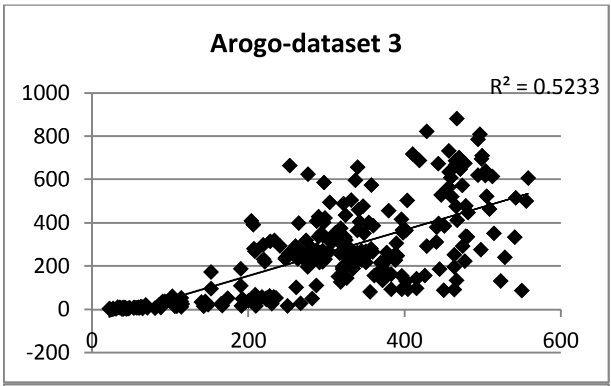


Figure 2 Linear regression for DATASET 1 between NH3 fluxes measured (independent) and simulated (dependent)

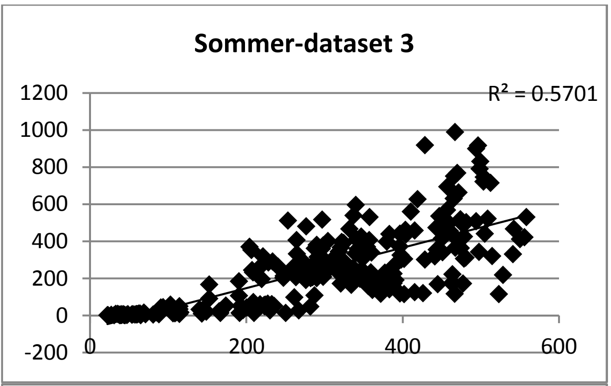
DATASET 3

Except Cortus_lin, Arogo e Vaddella, all the other models reported R^2 values greater than 0.55. For some models R^2 improved passing from a linear regression to a logarithmic regression (in this case R^2 values are reported in the graphs with bold style). In this case De Visscher_Pro, De Visscher_Stat and Harper are characterised by R^2 values of 0.61, 0.71, 0.79 respectively.

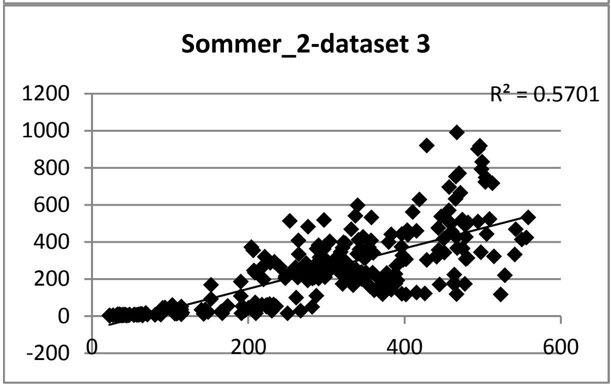




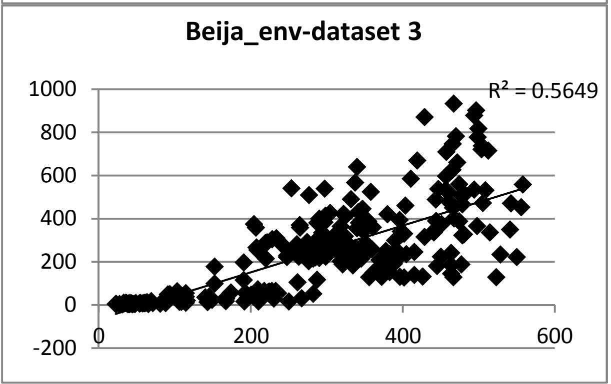
Arogo-dataset 3



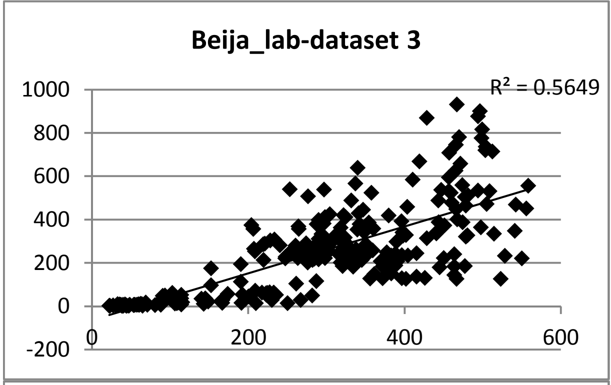
Sommer-dataset 3



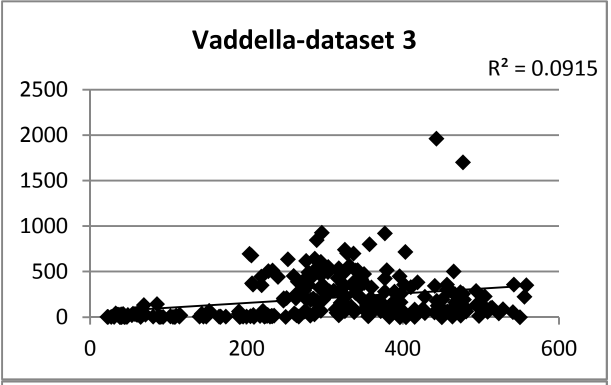
Sommer_2-dataset 3



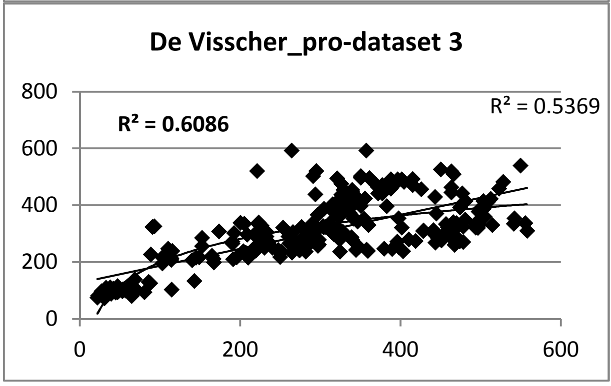
Beija_env-dataset 3



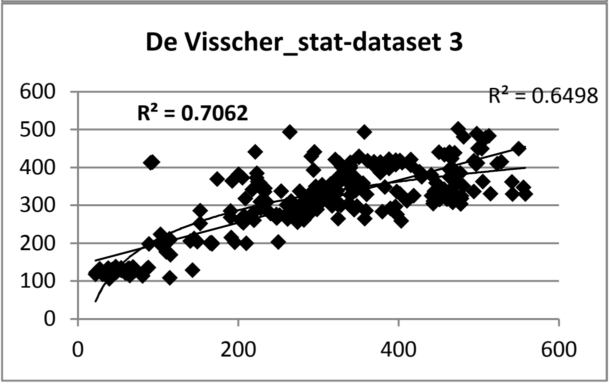
Beija_lab-dataset 3



Vaddella-dataset 3



De Visscher_pro-dataset 3



De Visscher_stat-dataset 3

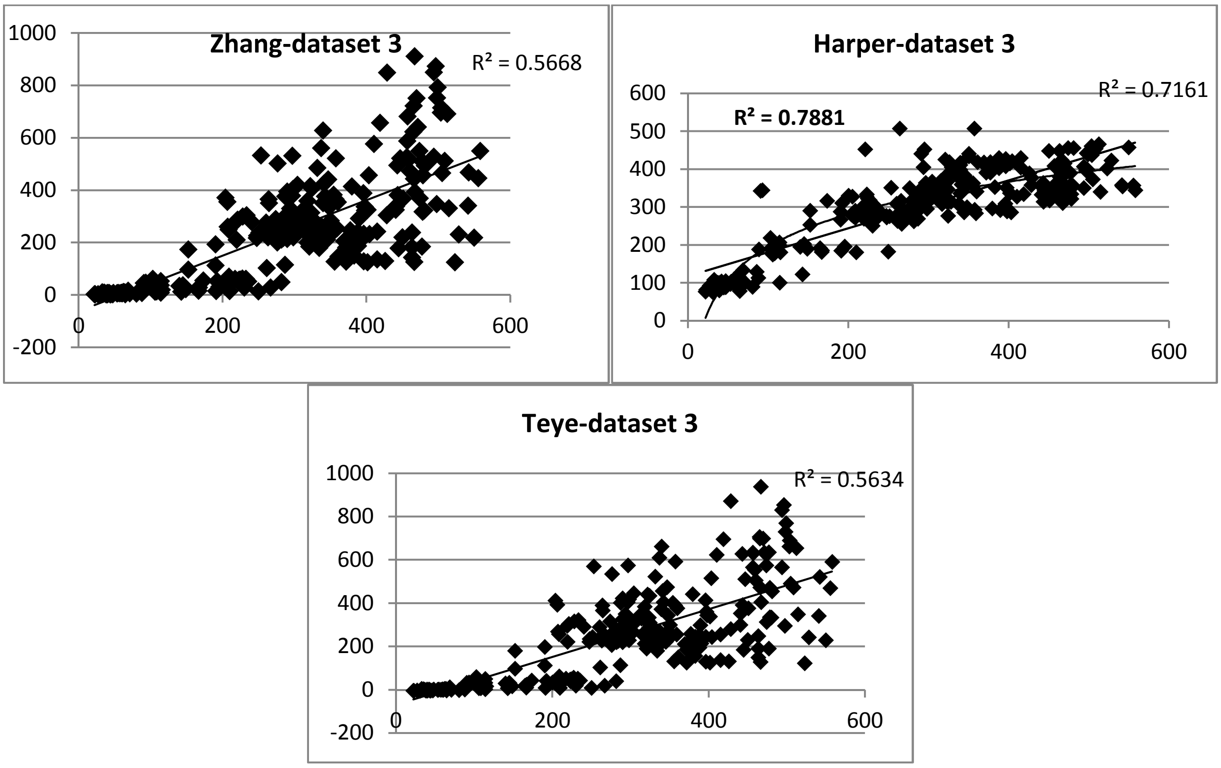
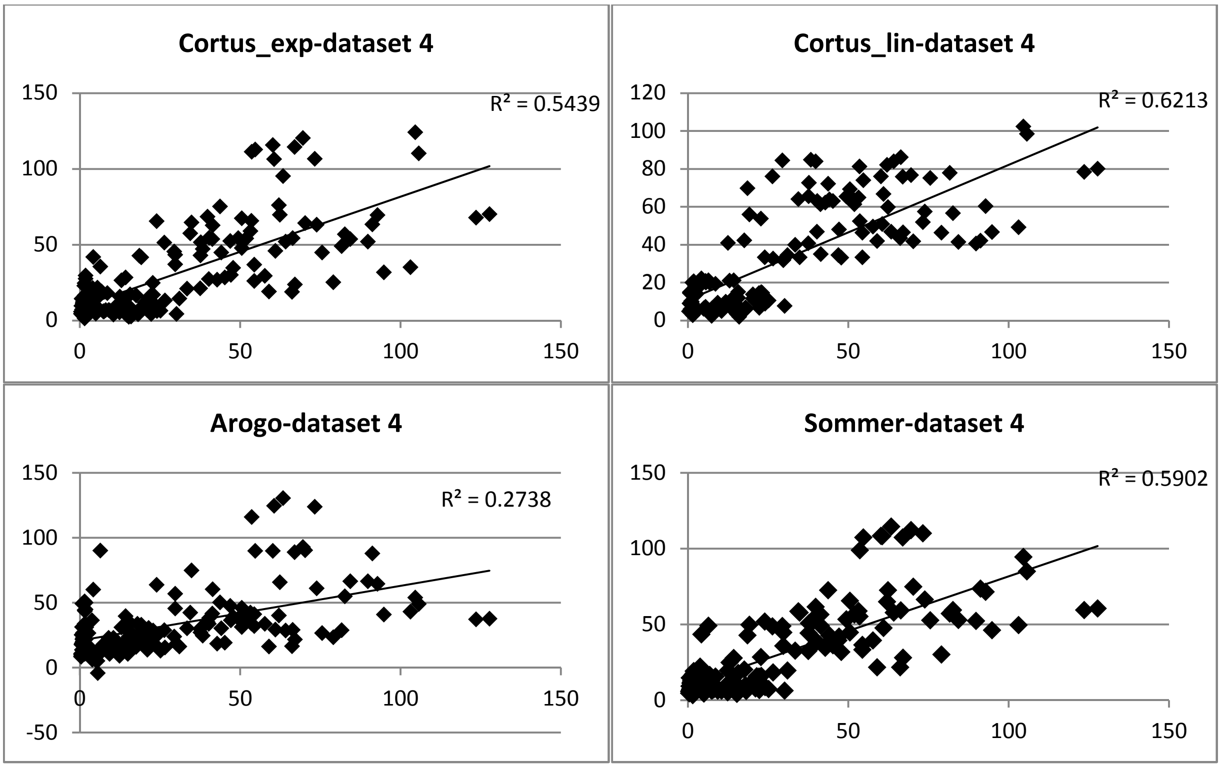
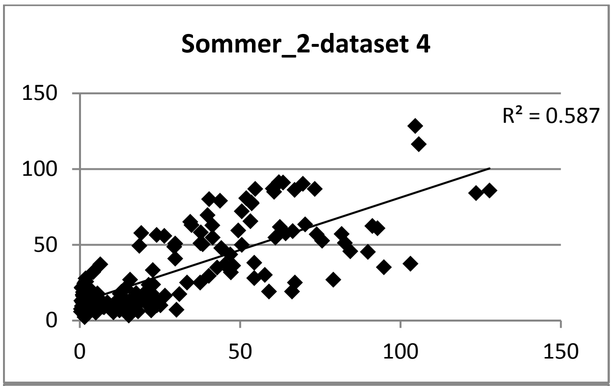


Figure 3 Linear regression for DATASET 1 between NH_3 fluxes measured (independent) and simulated (dependent)

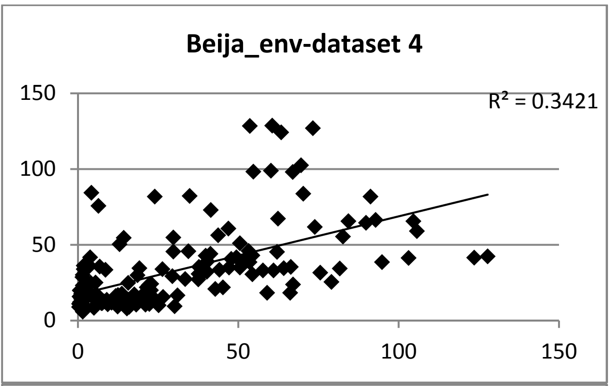
DATASET 4

In field conditions value of $R^2 > 0.55$ are observed for Cortus_lin, Sommer, Sommer2, De Visscer_Pro, De Visscher_Stat, Harper. It is possible to notice that many points are near the origin of axes. The very low fluxes measured and simulated during the cold season of Exp.1 of this dataset are the explanation.

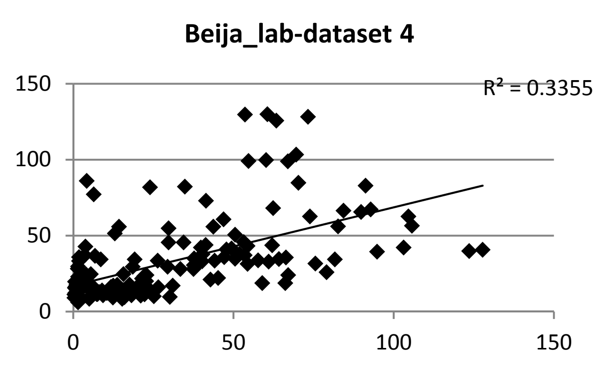




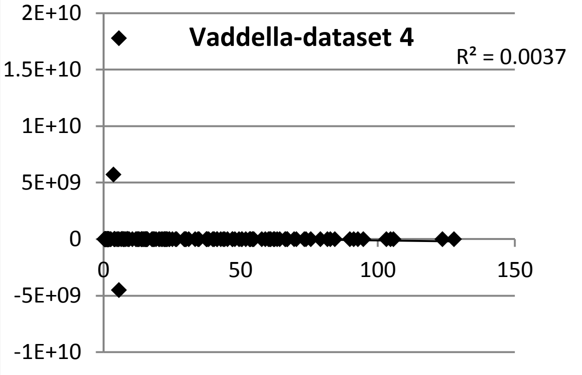
Sommer_2-dataset 4



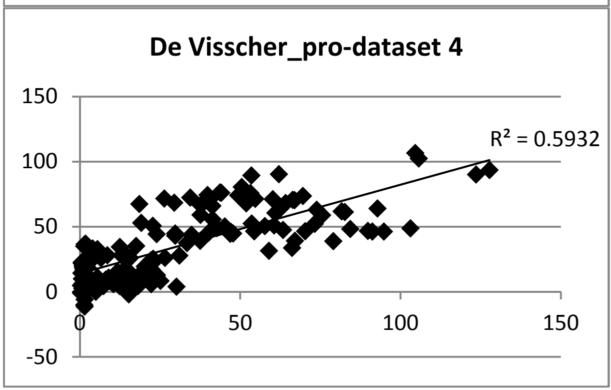
Beija_env-dataset 4



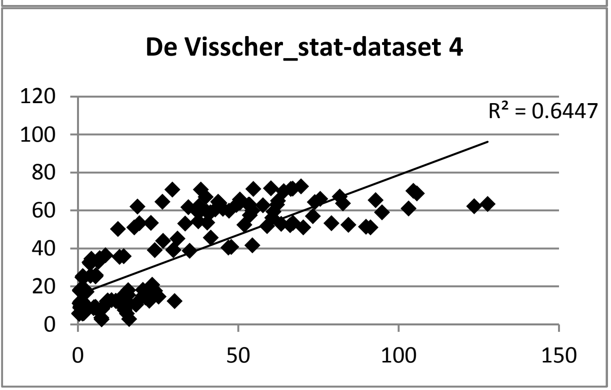
Beija_lab-dataset 4



Vaddella-dataset 4



De Visscher_pro-dataset 4



De Visscher_stat-dataset 4

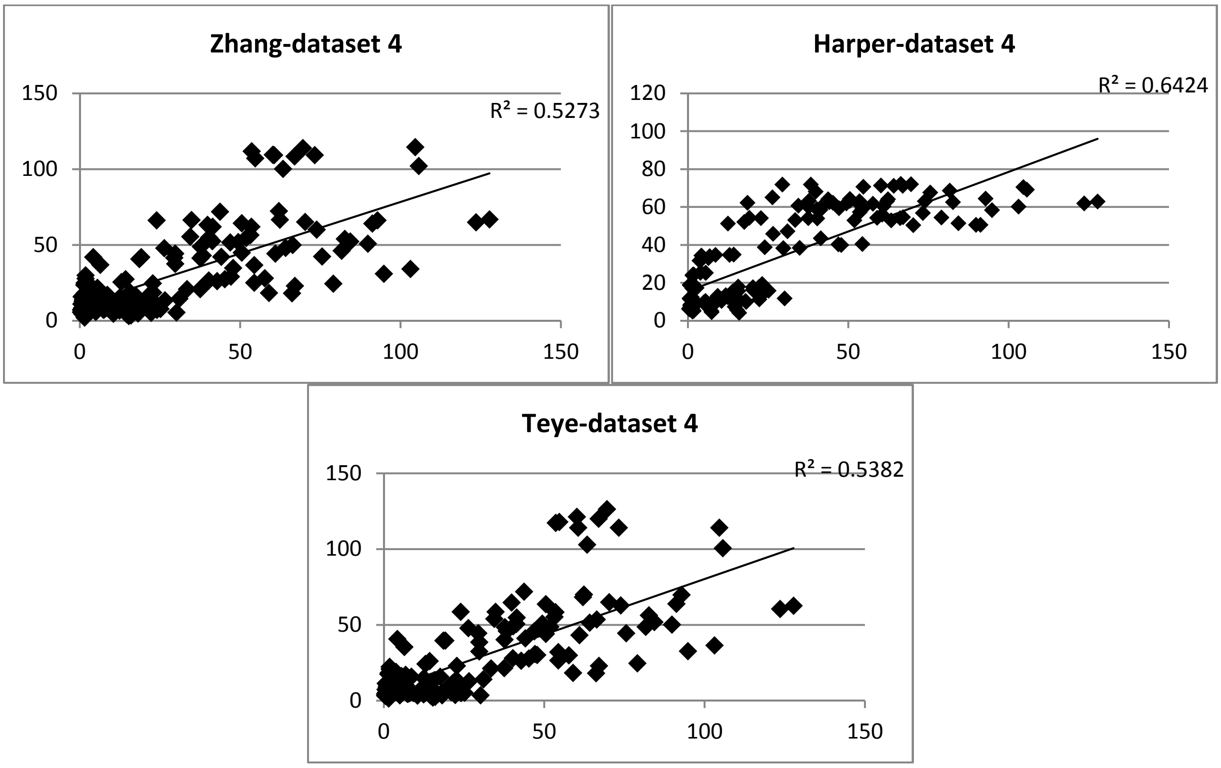
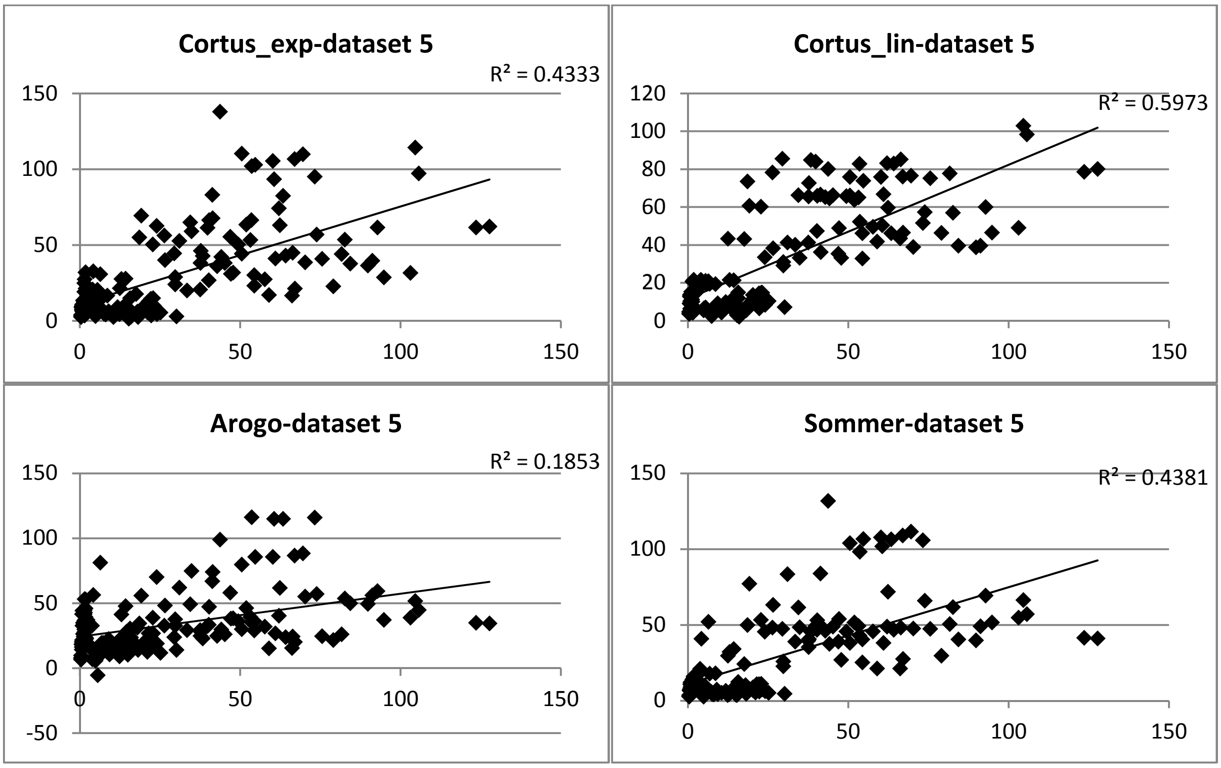
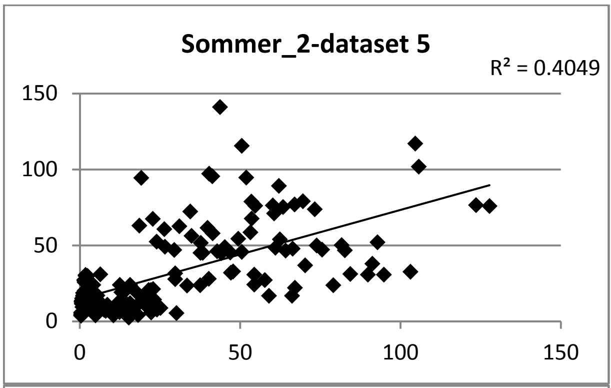


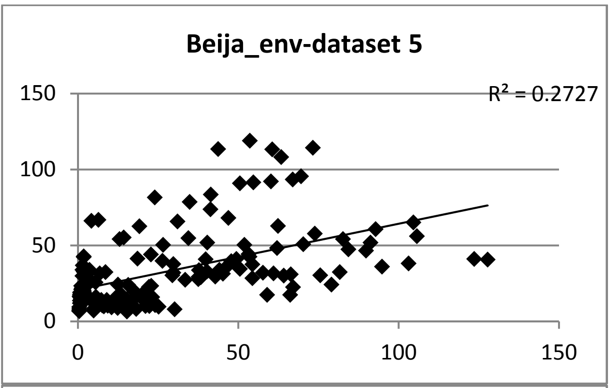
Figure 4 Linear regression for DATASET 1 between NH_3 fluxes measured (independent) and simulated (dependent)

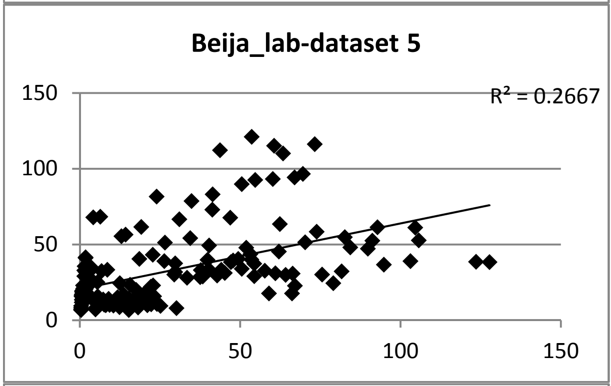
DATASET 5

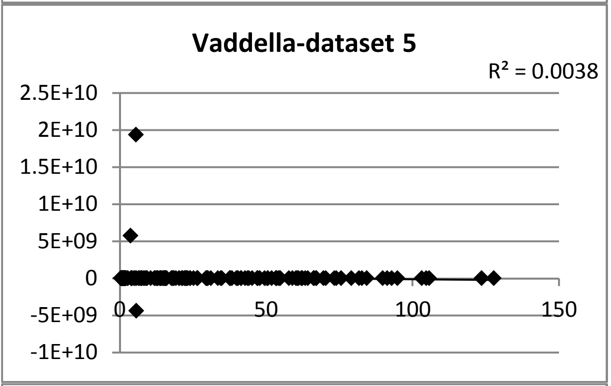
Values of R^2 worsen from the previous ones. Probably this result can be related to pH measurement position: with pH measurements done at 10 cm depth better R^2 were obtained.

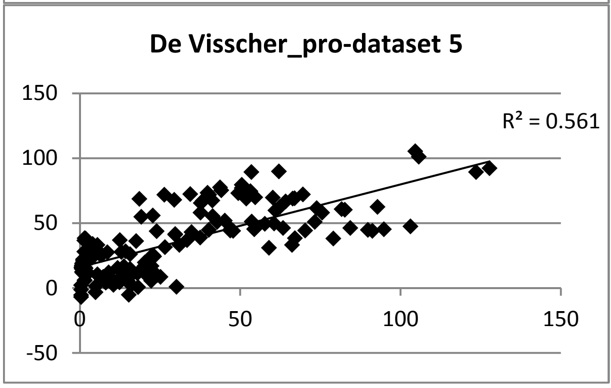


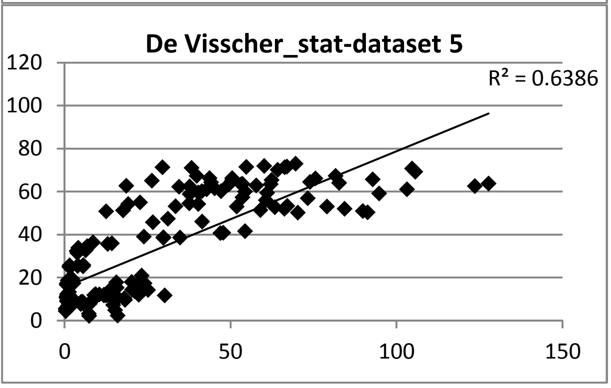

Sommer_2-dataset 5


Beija_env-dataset 5


Beija_lab-dataset 5


Vaddella-dataset 5


De Visscher_pro-dataset 5


De Visscher_stat-dataset 5

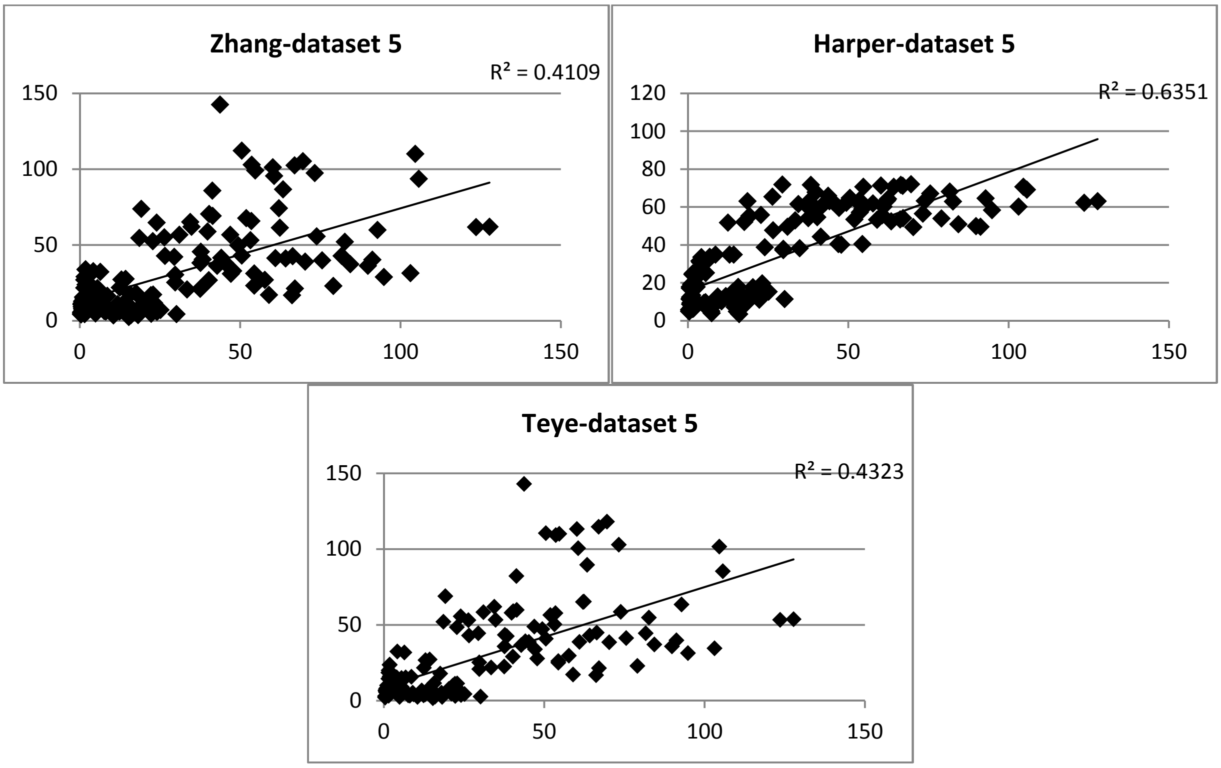
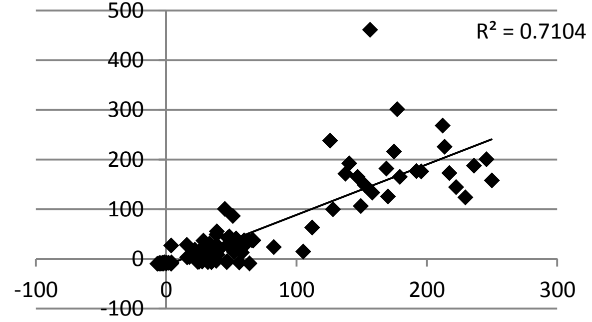


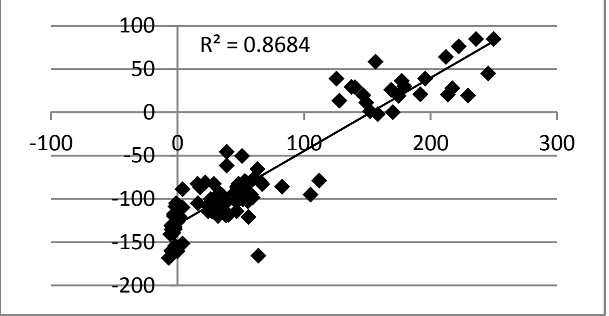
Figure 5 Linear regression for DATASET 1 between NH_3 fluxes measured (independent) and simulated (dependent)

DATASET 6

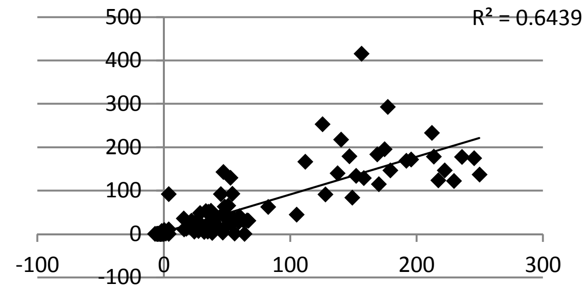
For this dataset the highest R^2 values were observed (R^2 = 0.89). Cortus_lin, Sommer, De Visscher_Pro, De Visscher_Stat and Teye are characterised by R^2 > 0.8. This result is in part due to the presence of very low fluxes related to the acidified slurries. For this reason a group of points accumulated near the origin of axes is observed. This phenomena is typically involved in generating good R^2 values and is particularly evident in case of De Visscher_Stat and Harper: in these models two groups of data are generated meaning that, probably, models are not very sensitive to pH changes. Some anomalous high values of flux can be seen in some graphs (e.g. Sommer 2). Errors in measuring some of the input variables of the model may be the explanation. De Visscher_Pro that in the previous datasets show good results, in this case is one of the worst model. This observation can mean that this model is not suitable to be use in such condition, with slurries characterised by low content of TAN and low pH.



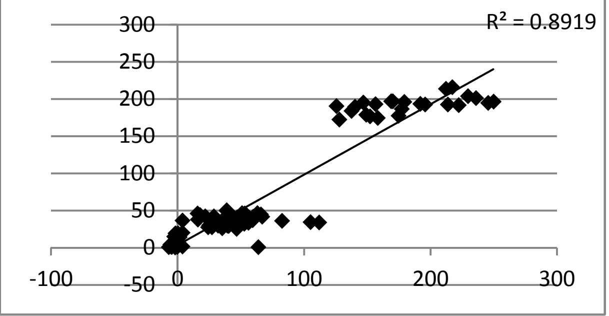
Cortus_exp-dataset 6



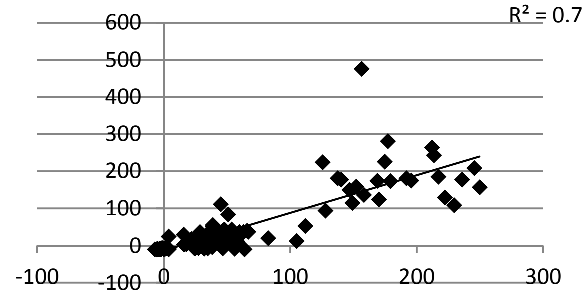
Cortus_lin-dataset 6



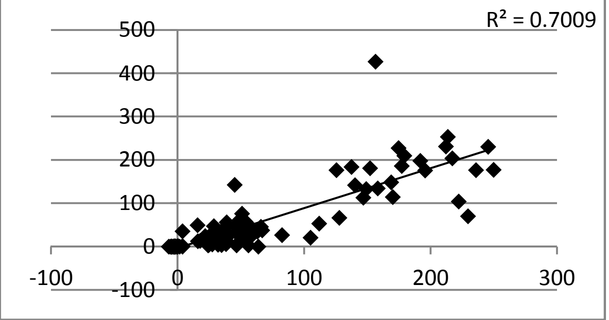
Arogo-dataset 6



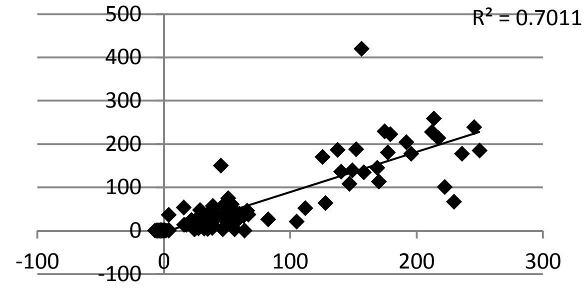
Sommer-dataset 6



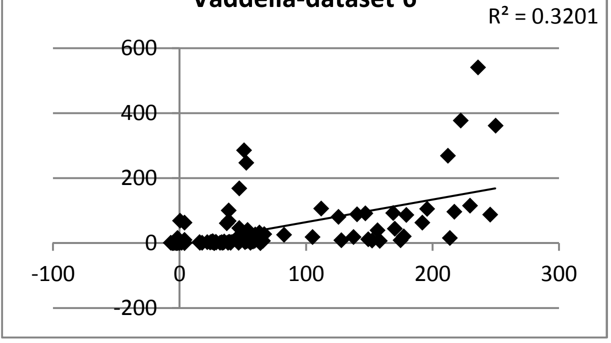
Sommer_2-dataset 6



Beija_env-dataset 6



Beija_lab-dataset 6



Vaddella-dataset 6

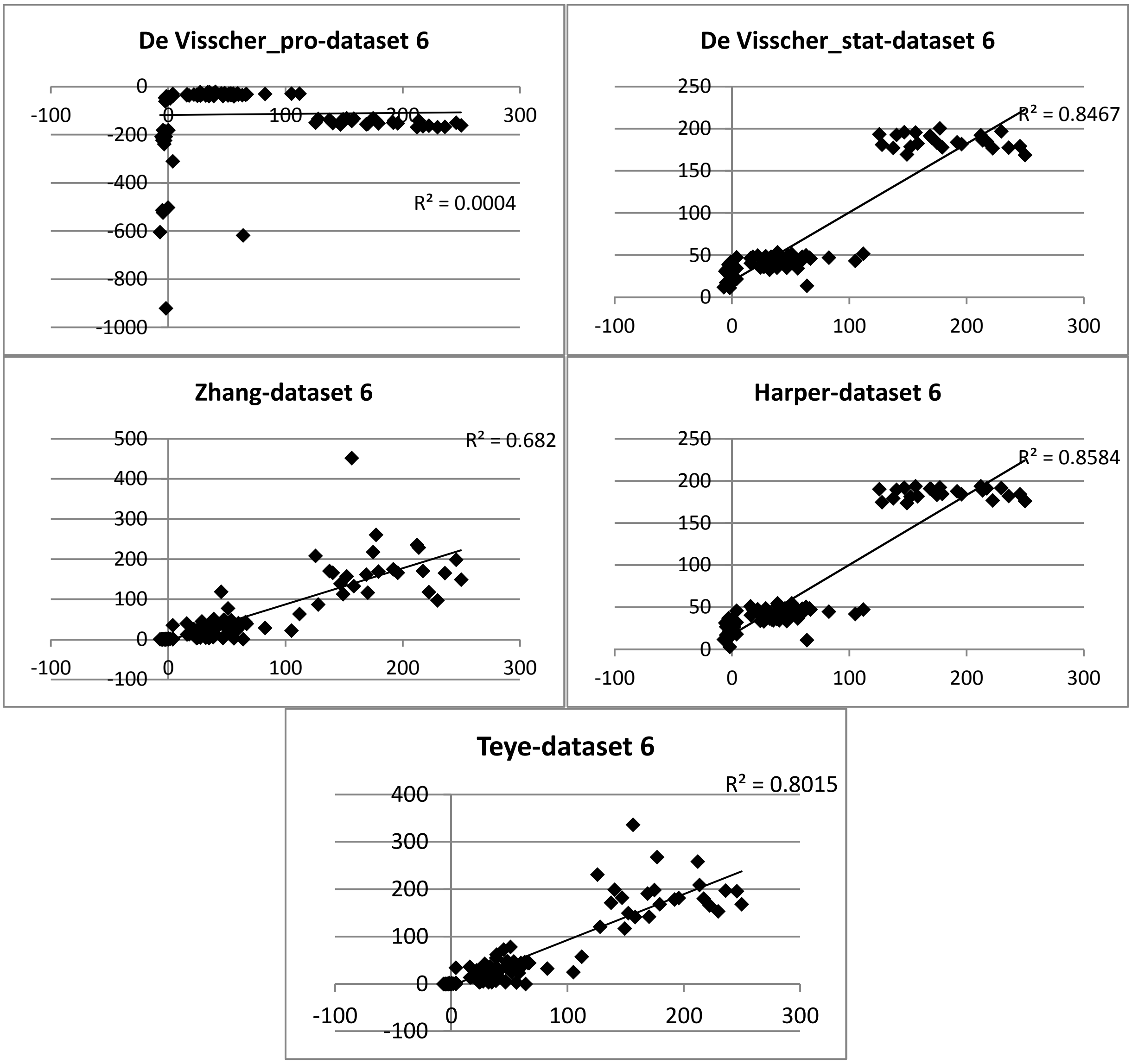
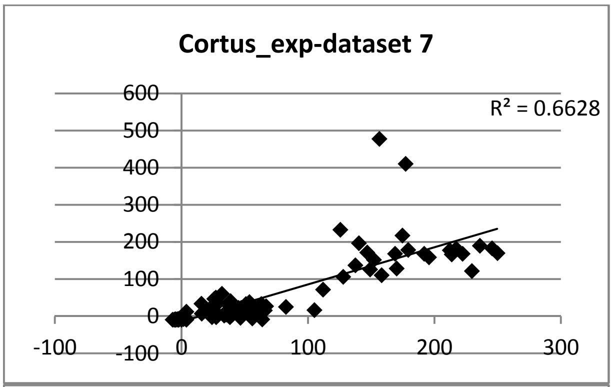
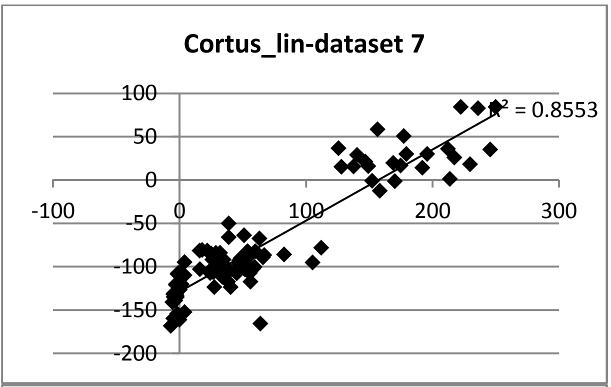


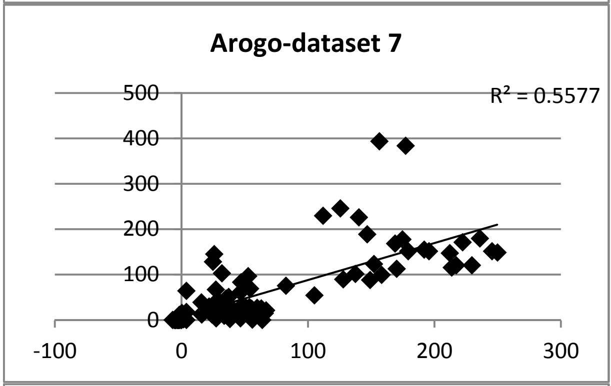
Figure 6 Linear regression for DATASET 1 between NH_3 fluxes measured (independent) and simulated (dependent)

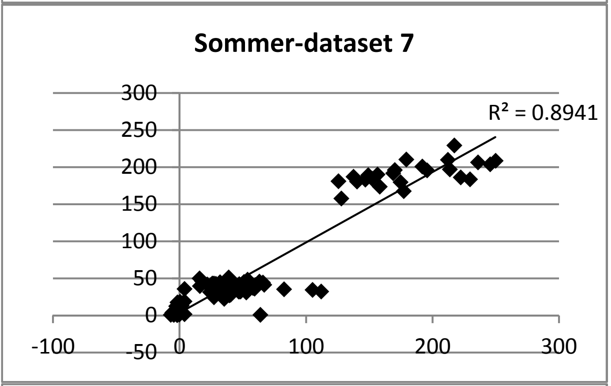
DATASET 7

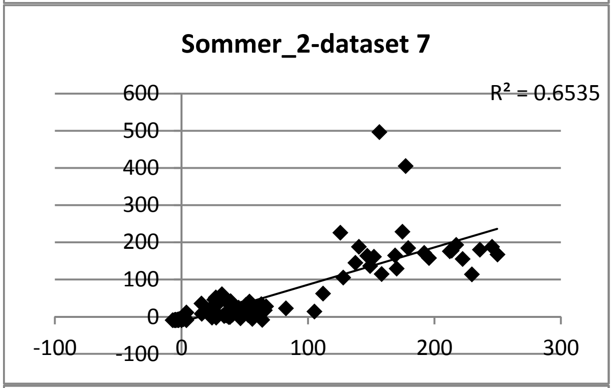
In general the R^2 values are very similar to those of the previous dataset, sometime slightly lower (e.g. Teye) and sometimes slightly higher (e.g. Cortus_lin) . This means that, probably, models on average are not very influenced by the pH measurements position. Anyhow this affirmation has to be done observing also the other statistics indexes.

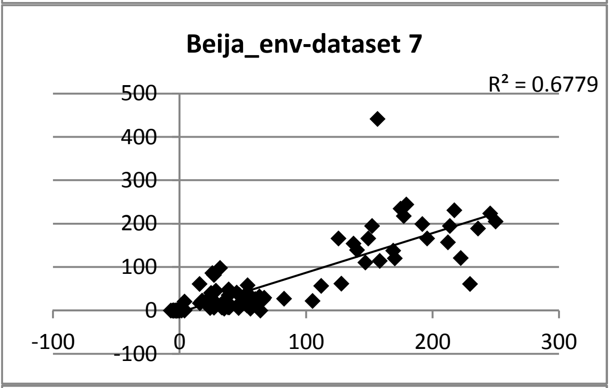

Cortus_exp-dataset 7
R² = 0.6628
600
500
400
300
200
100
0
-100
-100
0
100
200
300

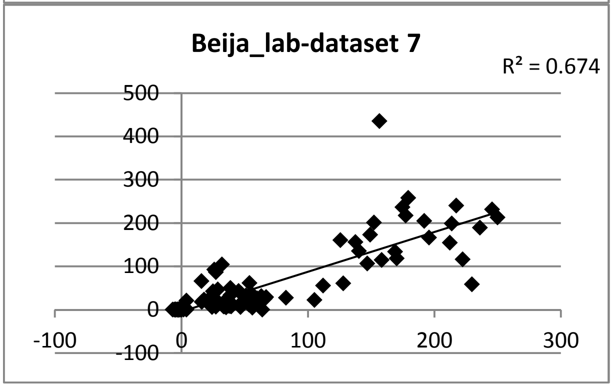

Cortus_lin-dataset 7
R² = 0.8553
100
50
0
-50
-100
-150
-200
-100
0
100
200
300

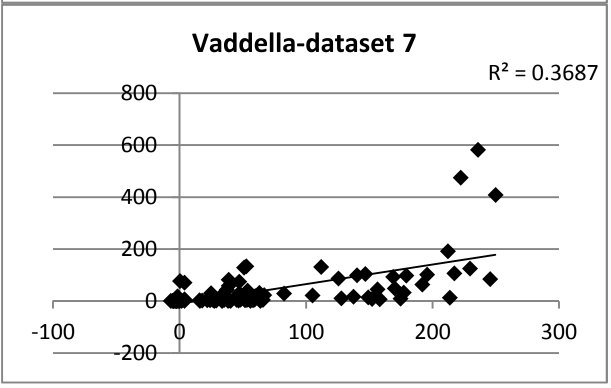

Arogo-dataset 7
R² = 0.5577
500
400
300
200
100
0
-100
0
100
200
300


Sommer-dataset 7
R² = 0.8941
300
250
200
150
100
50
0
-50
-100
0
100
200
300


Sommer_2-dataset 7
R² = 0.6535
600
500
400
300
200
100
0
-100
-100
0
100
200
300


Beija_env-dataset 7
R² = 0.6779
500
400
300
200
100
0
-100
-100
0
100
200
300


Beija_lab-dataset 7
R² = 0.674
500
400
300
200
100
0
-100
-100
0
100
200
300


Vaddella-dataset 7
R² = 0.3687
800
600
400
200
0
-200
-100
0
100
200
300

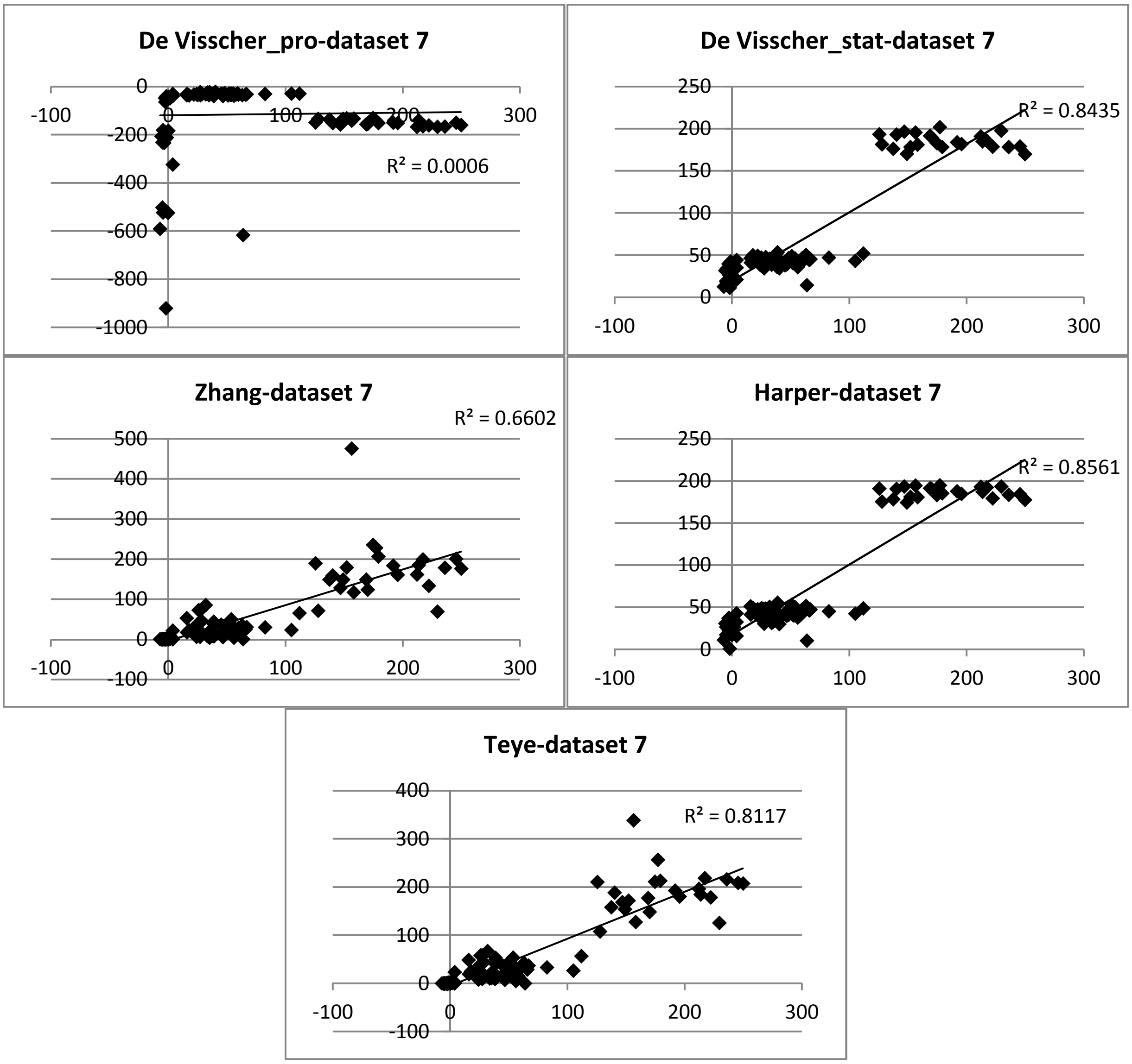


Figure 7 Linear regression for DATASET 1 between NH_3 fluxes measured (independent) and simulated (dependent)