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Publication realized by DiProVe
University of Milan - Italy

ISBN 978-88-903746-0-9

9 788890 374609 >

www.tipografi.it

Anaerobic Digestion:

Opportunities for Agriculture and Environment

edited by

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Opportunities for Agriculture and Environment

Contents

Introduction

The European Commission has recently highlighted the fact that biogas production through anaerobic digestion could play a primary role in energy diversification and for a sustainable environment, representing also an important economic opportunity for agriculture. Besides biogas, another product of anaerobic digestion is the digestate. It represents a biologically stabilised product with a high fertilising value that can be used in farming with positive effects on agriculture and the environment. The increase in nutritional value of biomass after anaerobic digestion suggests the use of digestate as a fertiliser, either as a total or partial substitute for mineral fertilisers, which have high cost and high fossil energy requirements. In addition, the digestate is a good soil amendment material as it is rich in "humus-precursor" molecules. On the other hand, anaerobic digestion reduces methane and odour emissions from untreated biomass and ensures total or partial pathogen removal, thereby contributing to the safe disposal of organic wastes. Anaerobic digestion of biomass is now accepted as having the potential to provide a major portion of the projected renewable energy and fertiliser production in the near future. To what extent this can be realised depends on scientific, technological, economic, and political factors.

The present book aims to contribute to the increase and spread of scientific knowledge in the field of anaerobic digestion and digestate use.

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WHAT IS THE DIGESTATE?

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SUMMARY

As anaerobic digestion (AD) is quickly being harnessed in Italy and in other European countries, there is a need for a more in-depth description of the main by-product of the process, the digestate. Little information on digestate characteristics and composition is available and unclear legislation causes problems in biogas plant management. In this work, the organic matter (OM) of this matrix was described through chemical, biological, spectroscopic, and statistical approaches. It was shown that AD results in a strong reduction of the easily degradable fraction of the OM and an accumulation of recalcitrant molecules (possible humus precursors). This contributes to a relatively high biological stability of the residual OM content in the digestate and may lead to good amendment properties. Besides, the observed relative accumulation and the high mineralisation of nitrogen and phosphorus may point to the digestate as a readily available liquid fertiliser for agronomic use. Moreover, xenobiotics and pathogens respected limits for both biosolids and compost in Italian and European legislation.

1. INTRODUCTION

Anaerobic digestion (AD) is a biological process that transforms the initial substrate (ingestate) into the desired product (biogas) and into a solid-liquid by-product (digestate) (Cecchi et al., 1988).

Products such as compost and biosolids from sewage treatment plants are already well-known and, in Europe, legislation clearly regulates their

agronomic use or disposal. Therefore, while clear information on these products is readily available, data on digestates from AD processes are scarce. In Italy, for example, legislation involving use of digestate is completely deficient compared with those dealing with compost and biosolids. This is due to the lack of information about digestate composition, its agronomic properties and the potential environmental impacts or benefits connected to agronomic reuse or disposal.
The literature reports only a little information about digestate; we know that many organic molecules, such as carbohydrates, proteins, lipids, cellulose and others, are totally or partially biodegraded to some gaseous products (methane, carbon dioxide) and also transformed into molecules forming microbial cells (Muller et al., 1998, Connaughton et al, 2006). Nevertheless, nothing is known about the chemical and biological characteristics of the digestate and of the changes that occur during AD.
The aims of this study were to analyse these modifications in depth and to describe the composition and characteristics of the digestates using chemical, biological, spectroscopic and statistical analyses.

2. MATERIALS AND METHODS

Twelve ingestates and the consequent digestates were sampled from a full-scale biogas plant co-digesting swine manure, various energy crops, organic residues and the organic fraction of municipal solid waste (OFMSW).
Chemical analyses were performed to determine organic matter (OM) content and degradation yields in terms of mass balance of total solids (TS), volatile solids (VS), biochemical oxygen demand (BOD_5,) and chemical oxygen demand (COD) between ingestates and digestates. The OM quality was then determined through wet analyses, i.e., cell solubles (CS), acid detergent lignin (ADL), cellulose, and hemicellulose. Biological stability and degradability were determined by two biological tests: oxygen demand in 20 h (OD_{20}) and anaerobic bio-gasification potential test (ABP). The most important nutrient concentrations (total, mineral and organic nitrogen, total phosphorus) were also measured in both ingestates and digestates to determine their fate during the AD process. Representative samples were used to carry out all analytical tests. The TS and VS were determined according to standard procedures (APHA,

1998). Total Kjeldahl nitrogen (TKN) and ammonia were determined on fresh material, following the analytical method used for wastewater sludge (IRSA CNR, 1994; ISO, 1994). Analyses were performed to determine neutral detergent fiber (NDF), acid detergent fiber (ADF) and ADL, according to Van Soest method (Van Soest et al., 1991). Values of CS, ADL, cellulose (ADF-ADL), and hemicellulose (NDF-ADF) were calculated according to Van Soest et al. (1991). All analyses were done in duplicate. ABP and OD20 were determined following the methods of Schievano et al. (2008). Spectroscopic characteristics of the samples were studied by solid-state CP MAS ^{13}C-NMR analysis (this is a powerful technique for examining the chemical composition of complex OM, since it can be used on bulk samples). In particular, the CP MAS ^{13}C-NMR spectra on sample ingestates and digestates were acquired at 10 kHz on a Bruker AMX 600 spectrometer (Bruker BioSpin GmbH, Rheinstetten) using a 4-mm CP-MAS probe. The pulse repetition rate was set at 0.5 s; contact time was 1 ms and the number of scans was 3200. The chemical shift scale of CP MAS ^{13}C-NMR spectra was referred to tetramethylsilane (d = 0 ppm).
To compare results, the same analyses were carried out on samples of compost (90-d aerobic stabilisation), bio-solid, and fresh and pre-digested pig slurry. All results describing OM quality were analysed using principal component analysis (PCA) (Tabachnick and Fidell, 2001). PCA is a multivariate statistical technique used to investigate the relationships among quantitative variables. Its use allows a number of variables to be reduced in a multivariate data set, while retaining as much variation in the data set as possible. This reduction was achieved by taking p variables X_1, X_2, …, Xp and finding their combinations to produce principal components (PCs) PC_1, PC_2,…, PCp, which are uncorrelated.

3. ORGANIC MATTER DEGRADATION AND MODIFICATION DURING THE AD PROCESS

3.1. Chemical and biological approach

Considering both quantitative and qualitative aspects, the obtained results confirmed that AD greatly modifies the OM of an ingestate. Strong reductions (65±10%) in OM content, in terms of VS balance, were noticed (Figure 1a). In parallel, the COD and BOD_5 concentrations

in the digestate were almost half of the initial concentrations (Figure 1b and 1c).
The OM quality and degradability were also affected, as respirometric activity (OD_{20}) was halved in the digestates (Figure 1d) and the residual potential biogas (ABP) was almost one-third of the initial one (Figure 1e). Besides, a direct correlation between these two parameters, both representing biological stability of OM (D'Imporzano and Adani, 2007, Schievano et al., 2008), was found (Figure 2). This finding confirmed the observation that biological stability increases during AD, suggesting that degradation processes determine a concentration of the more recalcitrant molecules, while the more easily degradable matter is transformed into biogas. Further confirmation was obtained from the results of the wet analyses (Figure 3). The more degradable fractions, represented by the CS, significantly decreased in the digestates, while recalcitrant molecules, measured with the ADL, strongly accumulated. Other kinds of molecules such as cellulose and hemicellulose resulted in almost constant percentages of TS. This means that, as TS content decreased during AD, cellulose and hemicellulose degradation occurred, even at a lower extent, when compared with CS.

3.2. Spectroscopic approach

The results obtained from the chemical and biological approach were confirmed in the spectroscopic analysis. The spectra obtained by NMR showed four regions representing four different types of organic molecules (Figure 4), respectively from left to right, the carboxyl-C, the aromatic-C, the O-alkyl-C, and the aliphatic-C. Comparing the spectra of one of the considered ingestates and its relative digestate, the more degradable molecules,(the region of the O-alkyl-C [polysaccharides]), resulted in a net decrease in the digestate, while the more recalcitrant OM fraction (first, second, and fourth regions), evidently resulted in a relative increase. This confirmed the relative accumulation of molecules containing carboxyl-C, aromatic-C, and aliphatic-C, which include more recalcitrant fractions such as lignin, cutin, humic acids, steroids, and complex proteins. Similar results were found by comparing the spectra of fresh and digested pig slurries, even though the effect was less visible. This was due to a lower concentration of easily degradable molecules in the OM, with respect to the ingestate.

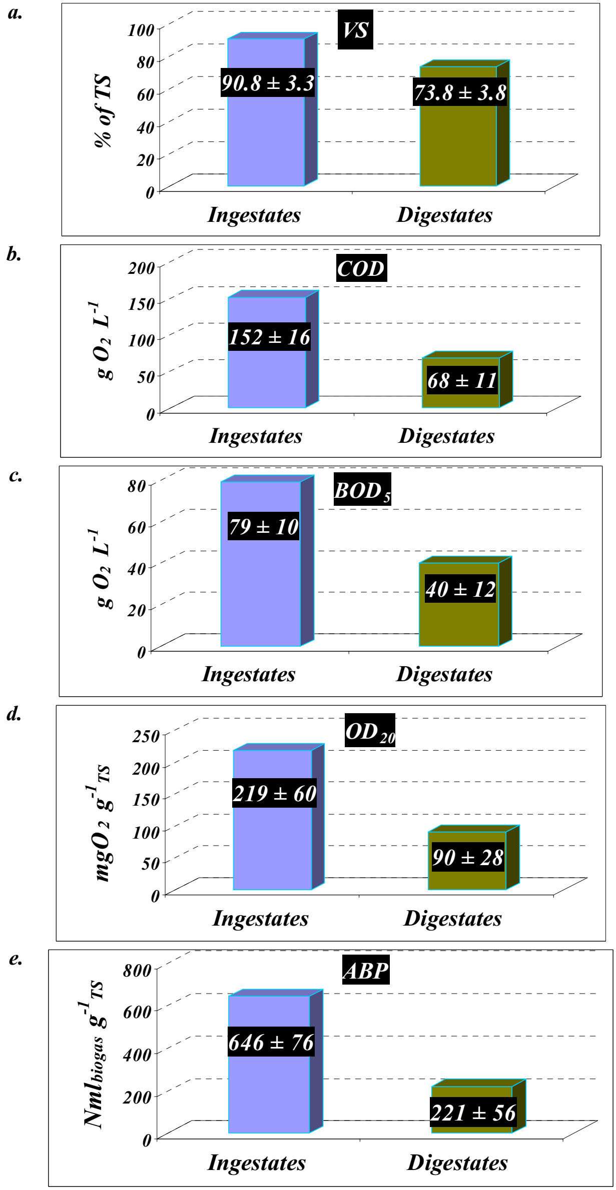

Figure 1. *Organic matter degradation during AD process: chemical and biological approach, a. Volatile solids, b. Chemical oxygen demand, c. Biochemical oxygen demand, d. Oxygen demand in 20 h, e. Anaerobic biogasification potential.*

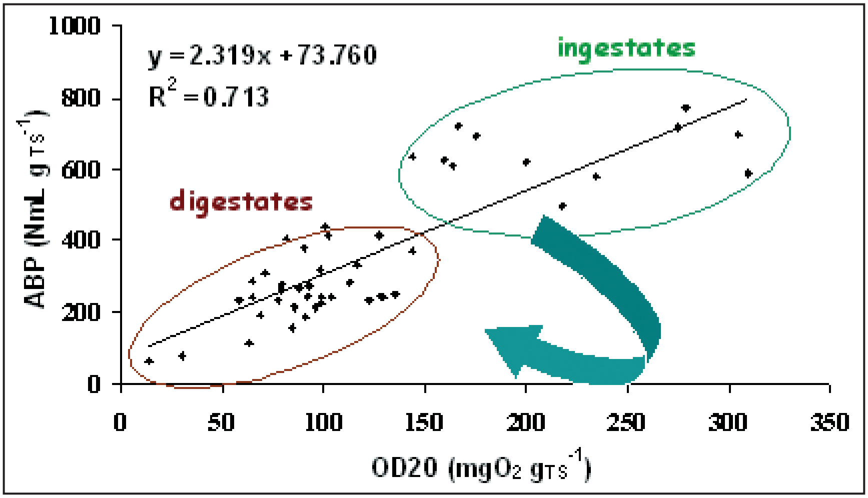

Figure 2. *Changes in OM quality and degradability during the AD process: correlation between ABP and OD_{20}.*

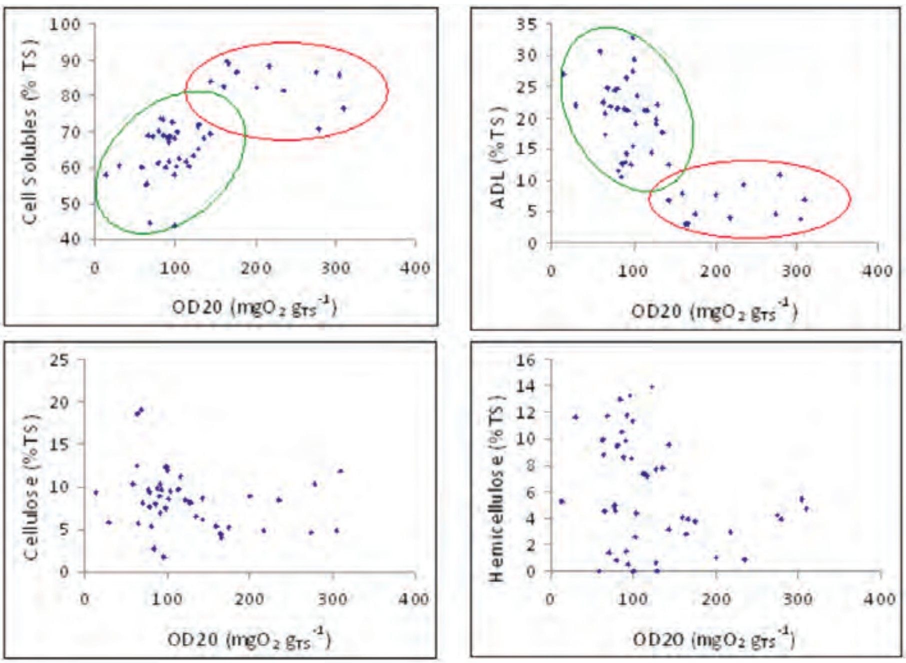

Figure 3. *Changes in OM quality during AD process: wet analyses. Ingestates (red circle); digestates (green circle).*

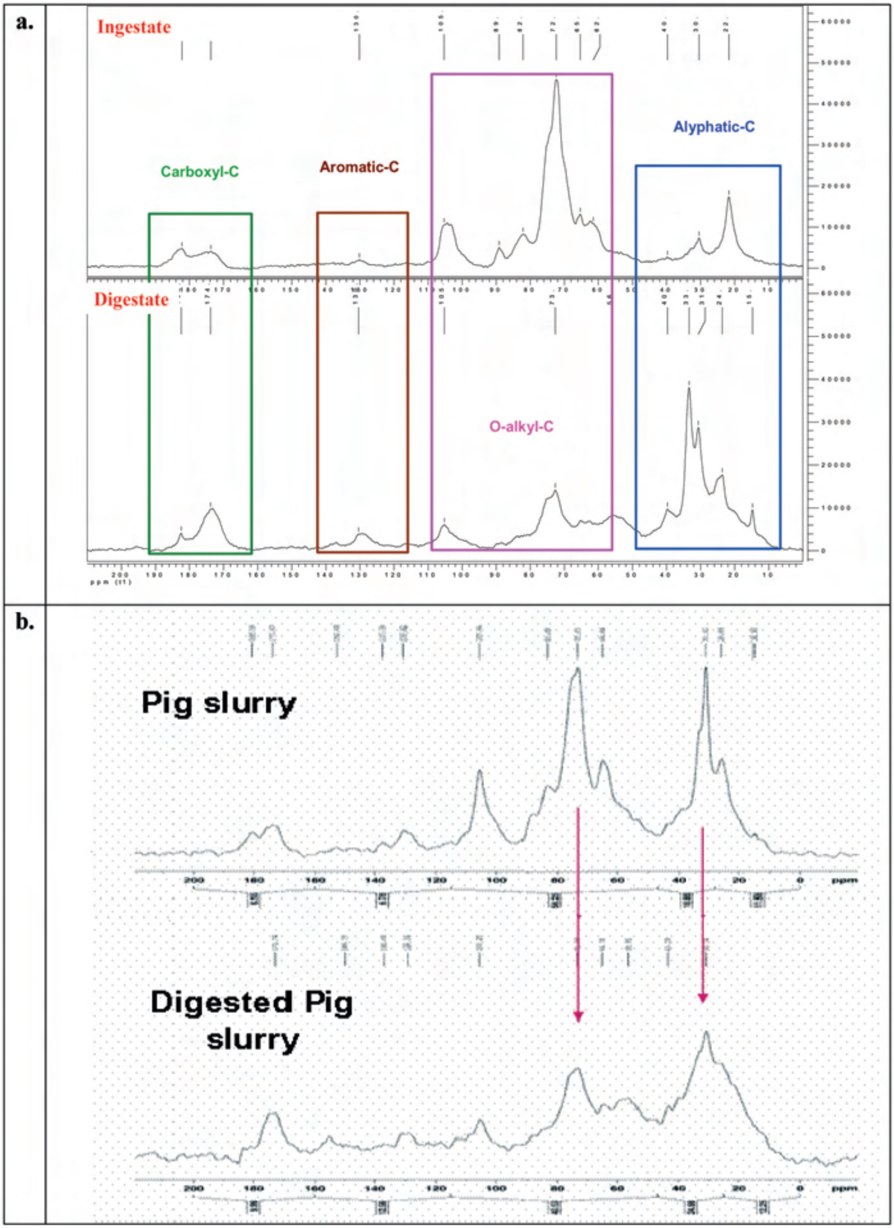

Figure 4. *CMAS* ^{13}*C-NMR spectra. a. Comparison between ingestate and digestate. b. Comparison between pig shurry before and after AD.*

3.3. Statistical approach: PCA

The PCA method resulted in a more accurate and complete description of the quality of the OM in the digestate, in comparison with other organic matrices. The quantitative variables considered were biological parameters (ABP, OD_{20}), chemical composition (VS content), and the NMR responses on carbon links, i.e., aliphatic-C, aromatic-C, carboxyl-C, and O-alkyl-C. The biplot obtained from PCA results (Figure 5) showed that the first component, which explained 63.8% of the total variance, was positively and highly correlated (r>0.6) with ABP, OD_{20}, VS, and O-alkyl C and negatively correlated with aliphatic-C, aromatic-C, and carboxyl-C. The second component, which explained 31.9% of total variance, was positively and highly correlated (r>0.6) with aliphatic-C and negatively correlated with O-alkyl-C and aromatic-C fractions.

Therefore, the first component represents a biological stability gradient (the biological stability value increases from negative to positive PC_1 value). Besides, PC_2 can be associated with the type of carbon links. The ingestate was in the fourth quadrant, i.e. low biological stability and high presence of O-alkyl-C (easily biodegradable fraction). The fresh swine manure was located in the first quadrant because of limited presence of O-alkyl-C. The pre-digested swine manure, the digestate, and the bio-solid were all located in the second quadrant, indicating medium-high biological stability and prevalence of aliphatic-C fraction. The compost was in the third quadrant due to a medium-high level of biological stability and a high concentration of recalcitrant fraction (aromatic-C fraction). That probably depends on the lignocellulosic material normally contained in compost.

Therefore, the digestates had high biological stability, showing values very similar to compost. Italian law allows the agronomic use of stabilised compost and bio-solids. It can be concluded that the digestate can be considered a good organic amendment, thanks to the concentrate recalcitrant and humus-precursor molecules, which enhance soil quality and agronomic properties.

3.4. Nutrients

The literature says that macronutrient total content tends to be not influenced or is only slightly decreased during AD processes (Massè et al., 2007, Uludag-Demirera et al., 2008). This was confirmed by the accumulation observed in this study of both total N and total phosphorus (Fig. 6). In fact, while degradable OM was transformed into biogas, the relative content of nutrients in the TS increased proportionally to biological stability (Fig. 6).

A high accumulation of ammonia was observed, whereas organic N percentage on the TS was constant. This indicates a net mineralisation of N during AD. Sørensen and Møller (2008) demonstrated that AD of animal slurries, as it increases the mineral N to organic N ratio, enhances the efficiency of N assimilation by the crop because ammonia is a soluble form of N, which is readily available to the plants in a soil-crop system. Besides, N losses in the form of leached nitrates and volatilised ammonia are reduced. Therefore, AD increases the efficiency of N utilisation, by transforming organic N into mineral N. The obtained efficiency is comparable with that of mineral fertilisers (Sørensen and Møller, 2008).

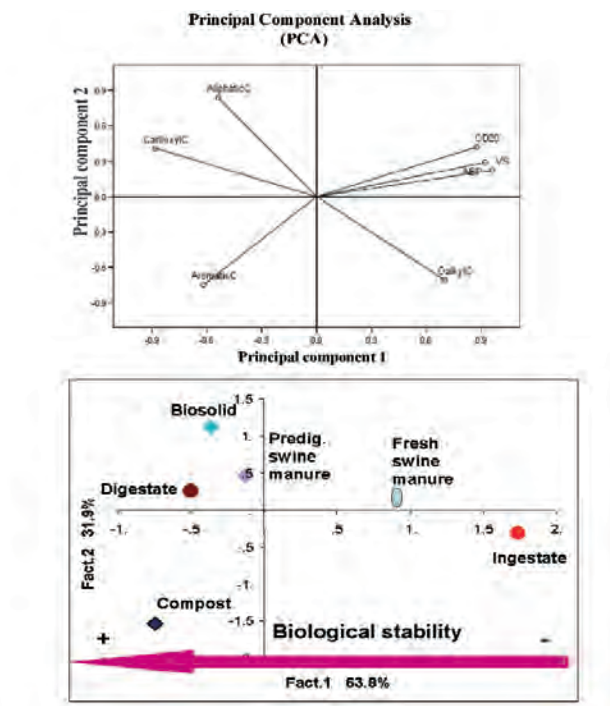

Figure 5. *Principal component analysis: a comparison of OM quality and composition of an ingestate, a digestate and other organic matrices.*

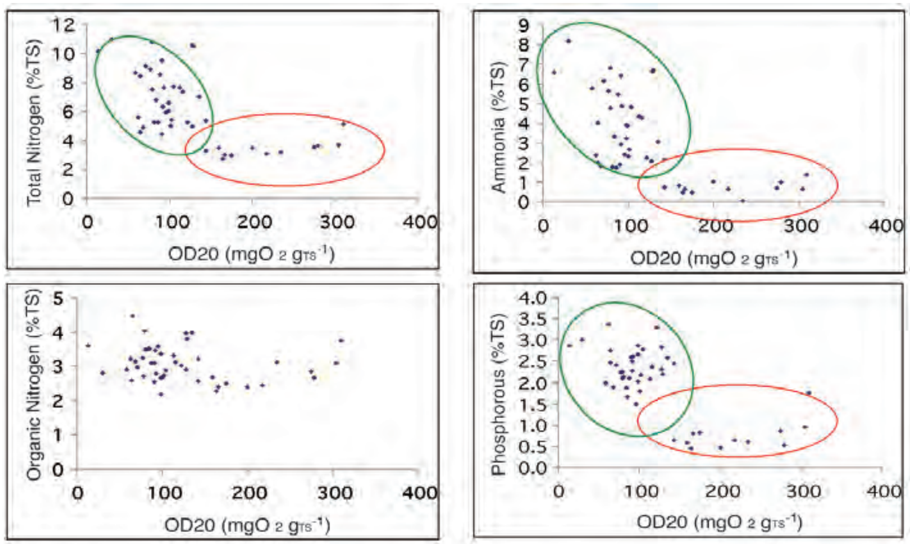

Figure 6. *Changes in N and phosphorous content during the AD process. Ingestates (red circle); digestates (green circle).*

4. XENOBIOTICS AND HYGIENIC PARAMETERS

The most important xenobiotics, the same variable considered in defining the quality of composts and bio-solids, were measured and found to be within standard limits of concentration for both compost and bio-solid (Table 1). The same result was obtained for the main hygienic parameters (Table 1).

It must be noted that the analysed digestates were sampled from a full-scale biogas plant processing OFMSW, which is a matrix that may present risks of containing pollutants or pathogens.

Table 1. *Xenobiotic concentrations and hygienic parameters in the digestate (ni = not indicated).*

Metal	Value	Biosolid Limit	Compost Limit
Cd (mg kg_{TS}^{-1})	0.21	20	1.5
Hg (mg kg_{TS}^{-1})	1.19	10	1.5
Ni (mg kg_{TS}^{-1})	12.48	300	100
Pb (mg kg_{TS}^{-1})	18.16	750	140
Cu (mg kg_{TS}^{-1})	49.58	1000	230
Zn (mg kg_{TS}^{-1})	74.83	2500	500
Cr (mg kg_{TS}^{-1})	1.16	750	-
As (mg kg_{TS}^{-1})	0.05	10	-
Cr VI (mg kg_{TS}^{-1})	0.08	10	0.5
Hygienic Parameter	**Value**	**Biosolid Limit**	**Compost Limit**
Fecal Coliform (MPN g^{-1}_{TS})	100	10	n.i.
Vital Helminthes eggs	Absent	Absent	n.i.
Salmonella	Absent	<100	Absent
Escherica coli	Absent	n.i.	<1000

5. CONCLUSIONS

An identification of the digestate was provided, focusing on various aspects such as OM amount, composition, quality and stability, nutrient content, and concentrations of xenobiotics and pathogens.
The results showed large reductions in OM amount during the AD process and a relatively high biological stability of the residual OM. Compared with other kinds of digested matrices, only compost showed a higher stability. Moreover, a concentration of recalcitrant fractions such as aromatic and aliphatic molecules, which are possible humus precursors, was evidenced. Thus, the digestate may be considered to have good amendment properties. The content of the considered nutrients (total N and P) tended not to be influenced during the AD process. At the same time, N was shown to be mineralised at a high extent and to concentrate as ammonia. As ammonia is a readily available source of N for plants, the digestate may be act as a good fertiliser.

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CONTRIBUTION OF BIOGAS PLANTS TO NUTRIENT MANAGEMENT PLANNING

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SUMMARY

In Denmark, anaerobic digestion of slurry is recognised as contributing to a better utilisation of slurry as a plant fertiliser. Many field trials have documented this. It is also evident that digestion reduces the smell odour problems after spreading the slurry.

1. INTRODUCTION

In Denmark, biogas production rests on three legs: energy production, agriculture, and environment (Fig. 1). If you saw off one leg, the whole structure will tip over. A biogas plant is at the centre of the intersection. If the plant is correctly located and if all three legs carry equal weight, large synergistic effects can be achieved for the benefit of agriculture, the environment, the energy sector, and thereby the surrounding community.

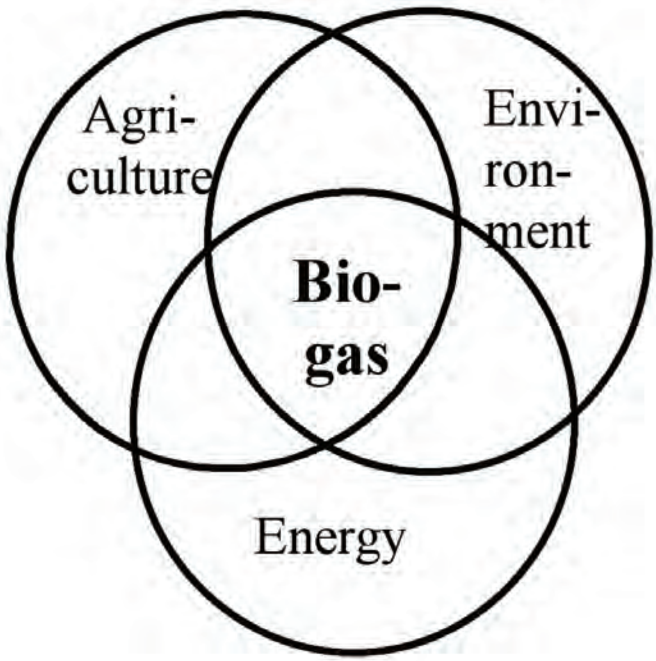

Figure 1. *Biogas is an intersection of energy production, agriculture, and the environment.*

2. BIOGAS PROVIDES MANY ADVANTAGES

In the last 12 to 15 years, Denmark has made determined efforts to promote biogas production based on co-digestion of animal manure and organic waste. The normal procedure in Denmark is to co-digest about 75% animal manure with about 25% organic industrial and domestic waste. By far, most organic waste originates from the industrial sector (Anonymous, 1999).

In the course of this period, a wide range of advantages, not necessarily concerning energy production, has been demonstrated (Table 1). Some experts may even claim that energy production is of secondary importance. The following paragraphs describe the most important advantages from both agricultural and environmental perspectives.

Table 1 *Advantages of biogas production for the energy sector, agriculture, and the environment. (Issues discussed in this paper are in* ***boldface****).*

Energy sector	Agricolture	The environment
• energy production • CO_2 neutral	• **improved utilisation of nitrogen from animal manure** • **balanced phosphorus/** • **potassium ratio in slurry** • **homogeneous and light-fluid slurry** • reduced transportation of slurry • possible to get large amounts of slurry with a full declaration of contents • slurry free from weed seeds and disease germs	• reduced nitrogen leaching • **reduced odour problems** • reduced greenhouse gas emissions • controlled recycling of waste

3. WHAT IS DIGESTED SLURRY?

Digested slurry must be transported, stored, and spread in the same way as slurry that has not been used for biogas production. However, there are some important differences: several types of slurry and waste are mixed and the organic matter (OM) of slurry is partly degraded.

Table 2 *Content of dry matter and nutrients in sllurry used in field trials at the Danish Agricultural Advisory Service in 1999-2001. The digested slurry used is likely to be a digested mixture of about 50% pig slurry, 25% cattle slurry, and 25% organic industrial waste. Source: Pedersen, 2001.*

	Dry matter, %	N-total, kg per tonne	NH_4-N, kg per tonne	P, kg per tonne	K, kg per tonne	pH factor	NH_4-N-share, %
Digested slurry (20)	4,8	4,4	3,5	1,0	2,3	7,6	81
Pig slurry (28)	5,0	4,8	2,9	1,1	2,3	7,1	74
Cattle slurry (15)	7,5	3,9	2,4	0,9	3,5	6,9	61

To consider the nutrient value of nitrogen, it is important to note that

- the dry matter is relatively low in digested slurry due to degradation in the biogas reactor. This makes the slurry more liquid.
- the ammonium (NH_4-N) content is higher in digested slurry than in untreated slurry due to degradation of organic-bound nitrogen in the reactor.
- the pH factor rises due to degradation of organic acids in the slurry. This increases the risk of ammonia volatilisation.

4. DIGESTION INCREASES THE FERTILISING EFFECT OF SLURRY

The physical and chemical processes taking place in the biogas plant change the fertilising effect of slurry in the field. It is important to make an allowance for this when fertilisation plans are prepared and also when handling and spreading the slurry. In planning, the high ammonium content has to be considered as crops are primarily capable of utilising ammonium nitrogen. In other words, it is often possible to replace nitrogen from commercial fertiliser by digested slurry and thus save money (Ørtenblad *et al.,* 1995).

The thin, low-viscosity digested slurry seeps relatively quickly into the soil. This reduces the normally very high risk of ammonia volatilisation. Trials have shown that ammonia evaporation from surface-applied digested slurry actually is lower than that from surface-applied pig slurry (Hansen, *et al.* 2004).

Field trials with digested slurry in winter wheat have demonstrated higher nitrogen utilisation with pig slurry; it was much higher than with cattle slurry (Fig. 1). This means, for example, that if a farmer fertilises a field of winter wheat with 170 kg of total nitrogen in digested slurry (instead of the 170 kg of nitrogen in cattle slurry), he can save about 54 kg of nitrogen of mineral fertiliser and still get the same yield.

By reducing the supply of nitrogen in mineral fertiliser, a reduction in nitrate leaching can be expected. The specific reduction is dependent on the autumn and winter cover of the fields, soil type, etc. In general, a reduction in nitrate leaching of 0.33 kg nitrate-N per kg reduction in nitrogen in mineral fertiliser was used in the evaluation of the Second Danish Environmental Protection Plan (Jørgensen, 2004).

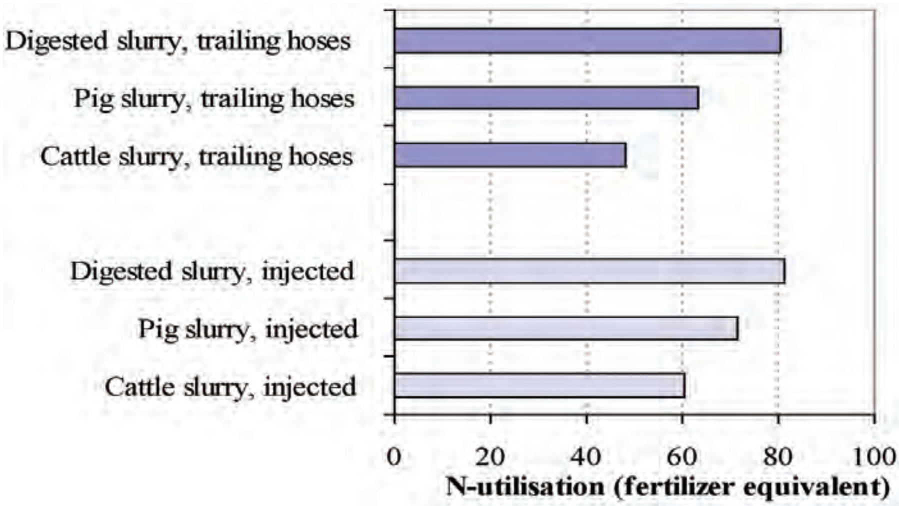

Figure 1. *Utilisation of nitrogen in digested slurry compared with pig and cattle slurry in field trials at the Danish Agricultural Advisory Service. Average of 11 trials with digested slurry, 15 trials with pig slurry and 15 trials with cattle slurry. Sources: Pedersen, 2001; Pedersen, 2003.*

5. PHOSPHORUS AND POTASSIUM

The utilisation of phosphorus and potassium in animal manure is normally a matter of avoiding the oversupply of these elements to the crops. The best solution is only to supply until the requirement of, for instance, phosphorus is covered. If the requirement of potassium is not covered at the same time, extra potassium in mineral fertiliser must be supplied.

The phosphorus-potassium ratio of digested slurry is often about 1:3. This ratio is excellent for crop rotation schemes, including, for instance, grain and rape?these crops often require about 20 kg phosphorus and about 60 kg potassium. Crop rotation schemes dominated by roughage crops require extra potassium from commercial fertiliser as the demand for potassium is much higher in, for instance, grass, beet, and maize, than in cereal and rape. If a relatively large share of the slurry to the biogas plant originates from cattle, the phosphorus-potassium ratio of the digested slurry will be considerably higher, and the slurry will be more suitable for roughage crops.

If there is a high concentration of phosphorus in the digested slurry, it is possible to use simple separation techniques at the biogas plant to reduce phosphorus concentration.

6. DIGESTION REDUCES THE SMELL FROM THE SLURRY

In a biogas reactor, almost all easily degradable organic compounds are degraded and converted into biogas (methane). Among these compounds are a lot of volatile organic compounds with very bad smell e.g., a great number of fatty acids. When these compounds are degraded, the smell will be reduced compared with untreated slurry after this is spread on the fields. In Figure 2, the content of four fatty acids in untreated and digested pig slurry is shown. A significant reduction is demonstrated. In Figure 3, the slurry has been spread on a field, and air samples have been collected and analysed by a smell panel. A significantly lower emission of smell after the spread of digested slurry compared with that of untreated pig slurry was detected. Apparently, a higher emission of smell was observed after 260 min than after just 20 min. The reason is probably the considerably higher temperature after 260 min as it was in the middle of the day.

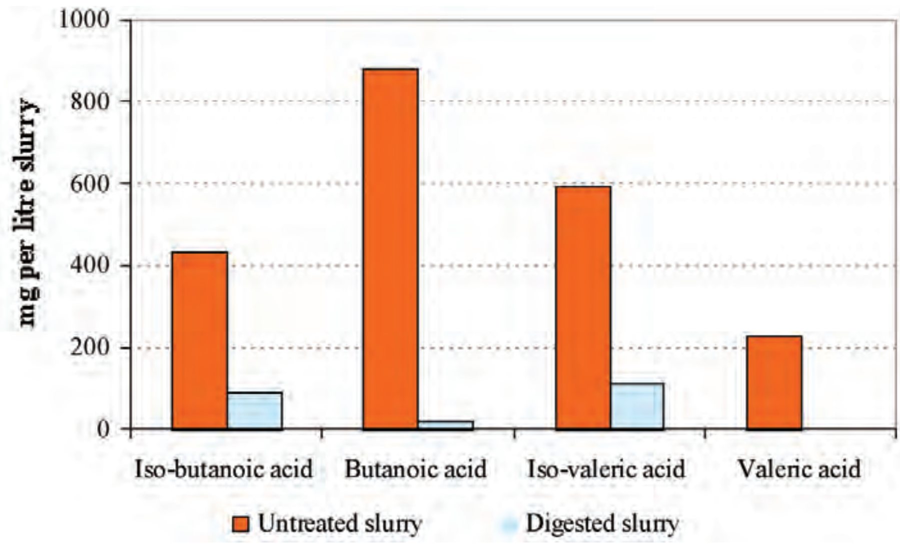

Figure 2. *Concentrations of four very bad-smelling volatile fatty acids in untreated and digested slurry. Source: Hansen et al., 2004A.*

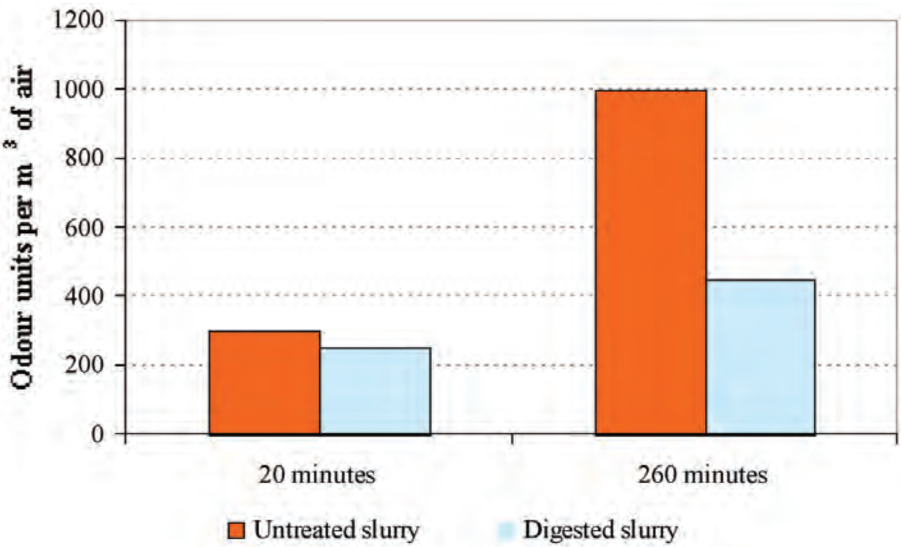

Figure 3. *Odour concentrations in air samples collected above untreated and digested slurry spread on a field. Source: Hansen et al., 2004.*

7. CONCLUSIONS

The agricultural and environmental advantages of digesting slurry and organic waste are so many and various that digestion should be given a much higher priority. It is a paradox that only about 4% of all animal manure in Denmark is used to produce biogas.

Some of the reasons for this relatively low percentage are the poor and unstable economy and a large administrative workload in the period of establishing biogas plant (these are typically planned and established by farmers and it often takes 3-4 years from inception to operation).

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FATE OF NITROGEN IN PIG AND CATTLE SLURRIES APPLIED TO THE SOIL-CROP SYSTEM

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SUMMARY

Animal manure may be a valuable source of nitrogen (N) in crop production, but it also causes environmental problems such as nitrate leaching, ammonia volatilisation, and greenhouse gas emissions. The first-year N fertiliser value of slurry is approximately equivalent to the ammonium content when N losses are low after application. Most of the organic N remains in the soil after the first year and is released slowly over many years. The residual N is also released in periods without crop growth and, under North European conditions, there is a higher risk of nitrate leaching from this N pool. After anaerobic digestion (AD), slurry contains a higher proportion of mineral N and less decomposable organic matter. It means that the first-year fertiliser value is higher and that less organic N is left in the soil after the first growing season, which also reduces the long-term residual N effect and the long-term risk of nitrate leaching. After AD, the emission of greenhouse gases is reduced, but slurry pH is higher and attention should be directed at limiting ammonia losses from digested slurry.

1. INTRODUCTION

Animal manure is an important and valuable source of nitrogen (N) in crop production. However, the manure nutrients may also cause environmental problems such as pollution of surface- and groundwaters by nitrate leaching and phosphorus run-off. The manure also causes eutrophication of natural ecosystems by ammonia deposition and emission of greenhouse gases (GHG) such as methane and nitrous oxide.

A consequence of the concentration of livestock production into larger specialised units is that livestock density is increasing in some regions. The challenge is to adapt manure management and technology to the change in agricultural practice, otherwise structural changes will exacerbate the environmental problems.

In Denmark, the utilisation of nutrients in manure has been significantly improved during the last 25 years. The export of N from the farm in plant and animal products has thus increased from about 20% of input in 1980 to 37% in 2004 (Kyllingsbæk and Hansen, 2007). Mineral N fertiliser use has been reduced by about 50% in the same period and nitrate leaching from agricultural land has declined, but still there is scope for improvement.

Anaerobic digestion (AD) of manure creates energy in the form of biogas that can be used to substitute for fossil fuels. The digestion can also be expected to reduce GHG emissions by reducing methane emission from slurry storage and nitrous oxide emission in the field (Sommer et al., 2004). The digestion influences the N composition of the manure and significantly reduces the C content; it can therefore be expected to influence the utilisation and losses of manure N.

In this paper, we give an overview of the fate of N applied in slurry. The effects of AD of manure on N cycling are also discussed and evaluated on the basis of experiences from northern Europe.

2. METHODOLOGIES FOR MEASURING THE FATE OF MANURE N

Traditionally, the utilisation and losses of manure N are measured indirectly by the difference method. This means that N uptake or losses are measured on field plots amended with animal manure and compared with similar measurements on plots that received no manure or only mineral fertiliser. The plant utilisation of manure N is often related to that of mineral fertiliser by comparing crop N uptake on plots receiving animal manure with plots receiving increasing amounts of mineral N fertiliser. The measurement expresses how much mineral N can be replaced by a certain amount of manure N and is sometimes called the mineral fertiliser replacement value (MFRV). It is normally expressed relative to the amount of manure N applied (Schröder, 2005). The fate of manure N can also be measured directly by using 15N-labelled manure. In experiments with 15N-labelled manure, it is also important to have a reference treatment with 15N-labelled mineral N. All methods have advantages and drawbacks. The isotope method gives more precise results, but it is expensive and difficult to produce homogeneously labelled manure (Sørensen and Jensen, 1998). Moreover, data from isotope experiments are sometimes difficult to interpret due to isotope substitution effects (Jenkinson et al., 1985).

3. THE FATE OF SLURRY N AFTER APPLICATION TO SOIL

In cattle slurry, 40-70% and in pig slurry, 60-80% of N is typically in ammonium-N form, while the remaining N is in organic form. Organic N generally has to be mineralised before it can be used by plants in the form of nitrate and ammonium-N (Fig. 1). Within the first days of application to the soil, a significant microbial immobilisation of ammonium-N takes place (Kirchmann and Lundvall, 1993). At the same time, organic N compounds are mineralised to ammonium-N (Sørensen, 2001). Initially, more N is immobilised than is mineralised, but after some weeks, mineralisation is nearly equal to immobilisation (Kirchmann and Lundvall, 1993; Sørensen and Amato, 2002). The relationship between mineralisation and immobilisation is influenced by manure composition, the distribution in soil, and soil type (Sørensen and Jensen, 1995). The ammonium-N in the soil is quickly nitrified to nitrate, usually within days or weeks. During the nitrification process, a minor proportion of N is lost to the air as nitrous oxide and elemental N. If there is excessive precipitation in the period after manure application, much of the nitrate can be lost by leaching to deeper soil layers.

In the days immediately following application, significant losses of ammonia may occur. This loss is very dependent on weather conditions (rain and temperature), application method, and manure composition (Sommer and Hutchings, 2001). Under unfavourable conditions, more than 40% of the ammonium in slurry can be lost by volatilisation.

Some ammonia loss is unavoidable following slurry application. However, ammonia loss can be much reduced by rapid incorporation or by direct injection of the slurry. Incorporation by harrowing is not as efficient a method of reducing ammonia losses as direct injection or ploughing (Huijsmans et al., 2003).
The crop takes up most of the mineral N left in the soil after the initial weeks of intensive N mineralisation-immobilisation turnover if an appropriate N application rate has been applied. That means that the N fertiliser effect of the slurry is roughly equal to the ammonium content when manure N losses are low after the application.

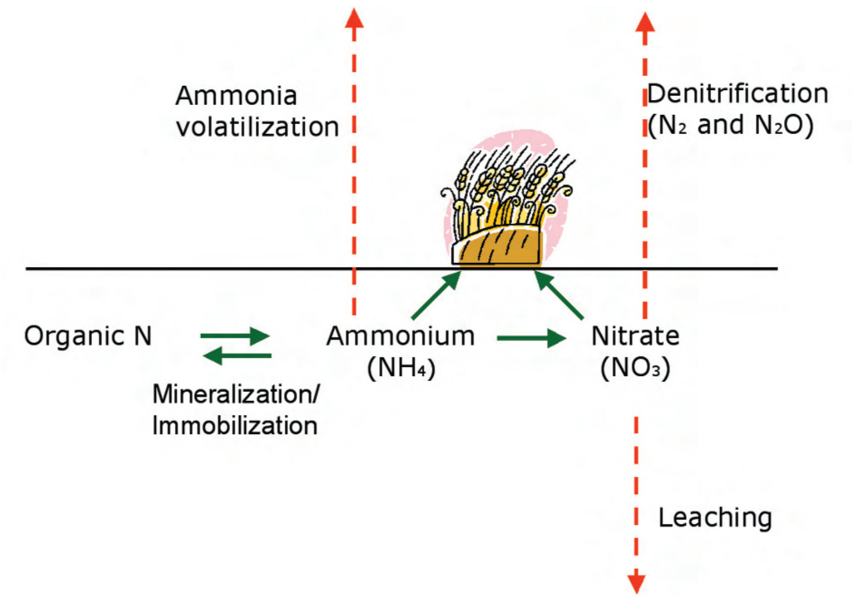

Figure 1. *The most important N transformations and losses after application of animal manure to soil.*

Most of the organic N remains in the soil after the first growing season. Figure 2 shows that about 40% of the labelled N could still be found in the soil 15 mo after application of 15N-labelled pig slurry. The N remaining in the soil after the first year is released slowly. A crop uptake of 2.5-6 % of 15N in applied manure has been recorded in the second year after application (Fig. 2; Christensen, 2004). In the third year, the release rate is even slower (Sørensen and Amato, 2002). The release of residual manure N will continue for many years. The residual effect of a single application of slurry is insignificant in the year after application. However, the accumulated effect of repeated manure applications is significant and should be accounted for in N fertiliser planning (Berntsen et al, 2007; Schröder et al, 2007).

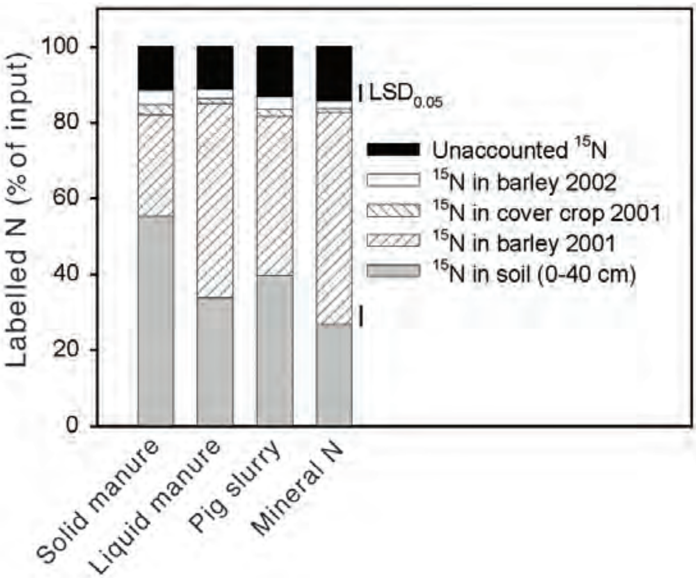

Figure 2. *Recovery of ^{15}N in crops and soil 15 months after incorporation of ^{15}N-labelled mineral N and ^{15}N-labelled separated and unseparated pig slurry applied to a barley crop in 2001. The slurry was separated by centrifugation into solid and liquid fractions (data from Sørensen and Thomsen, 2005).*

If slurry is applied in the spring, N leaching losses from slurry are normally low and comparable with those from a similar application of mineral N in the first year. Since more total N is applied with manure than with mineral fertiliser, total nitrate leaching is also higher with manure than with mineral fertiliser. In a lysimeter study with 15N-labelled ruminant slurry, Thomsen et al (1997) found that 22-25% of slurry N was recovered in the crop and 3-5% was leached during the first year (Fig. 3). In the second year, 3-4% of slurry N was taken up by the crop, whereas 1-3% was leached, depending on the soil type. Thus, the proportion of leaching compared with plant uptake of manure N was higher in the second and following years. The organic manure N was released by mineralisation, which takes place most of the year.

That means that N is also released during periods without plant uptake. Therefore, the mineralised N is susceptible to nitrate leaching. Growing a crop or a cover crop during autumn can be an effective way to reduce the leaching of mineralised N (Christensen, 2004).

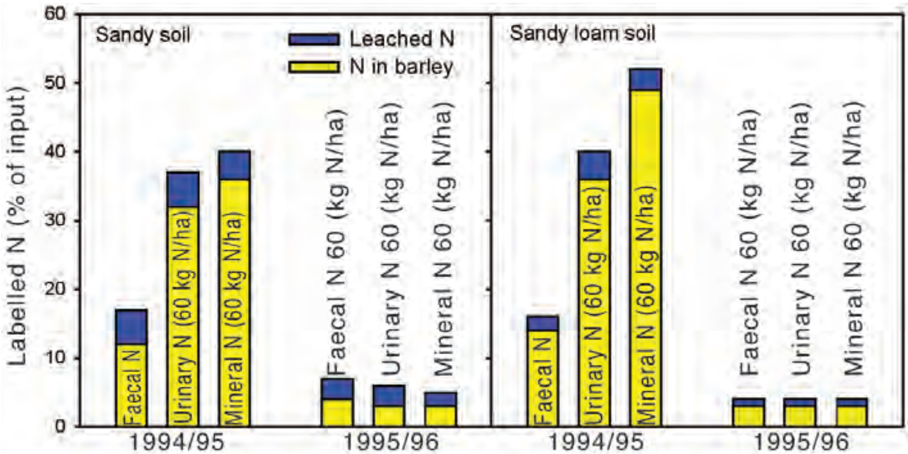

Figure 3. *Crop uptake and nitrate leaching of labelled N in the 2 years following the application of ^{15}N-labelled faeces and urine from ruminant slurry and mineral ^{15}N to lysimeters in spring 1994 (based on data from Thomsen et al. 1997).*

If animal manure is applied in autumn or winter to bare soil, a significant part of the mineral manure N can also be lost by nitrate leaching in the first year.

4. EFFECTS OF ANAEROBIC DIGESTION ON THE FATE OF SLURRY N

During AD, organic matter in the manure is converted into biogas consisting mainly of methane and carbon dioxide. This process mineralises part of the organic N to ammonium-N. Thus, the digested manure contains less organic N and less dry matter, whereas pH is increased by about 1 unit by the process (Sommer and Husted, 1995). The easily decomposable compounds such as volatile fatty acids that cause N immobilisation after the application of slurry to soil are also decomposed during the treatment. Normally, slurry is co-digested with other energy-rich organic wastes to obtain higher energy production and thereby a better economy. It is therefore normally difficult to make a direct comparison between the properties of digested and undigested slurry under practical conditions.

Figure 4 shows the results from a study comparing the release of mineral N in soil after the application of untreated slurries and the corresponding digested slurries. In this study, no other wastes were added to the slurry before digestion. After 12 wk, of incubating soil with slurry at 10 °C, the net release of mineral N from undigested pig slurry was equivalent to 70% of the slurry N, while 90% was released from the digested pig slurry. The digestion of cattle slurry resulted in an increase of mineral N release from about 40% to about 60% of total manure N. Lower N immobilisation occurred within the first week as also observed by Kirchmann and Lundvall (1993). A flow system was used in the experimental anaerobic digester and some settling of dry matter occurred. The dry-matter-rich fraction of the cattle slurry was sampled from the digester at the end of the experiment, and the release of mineral N from this fraction was also higher than from the undigested slurry. The results indicate that an extra amount of N equivalent to 15-20% of the slurry N is plant-available within the first growing season after AD of the slurry.

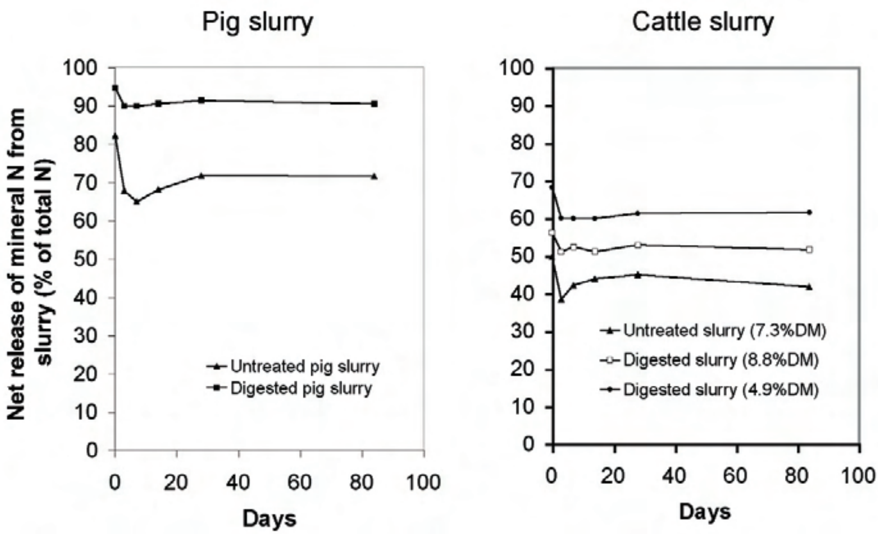

Figure 4 *Net release of mineral N in soil after application of digested and the corresponding undigested pig and cattle slurries to a loamy sand soil. Mineral N released in unamended soil was subtracted. The slurry was digested under thermophilic conditions (50-51°C) in a pilot flow digester. The digested cattle slurry with the high dry matter content (8.8% DM) was sampled at the bottom of the digester and contained extra sedimented solids. (Sørensen and Møller, unpublished results).*

The results of the incubation experiment are in accordance with the findings of other Danish field experiments where the MFRVs of pig slurry, cattle slurry, and digested slurry were measured (Fig. 5). The digested slurry used in these experiments consisted of a mixture of pig and cattle slurries supplemented with other organic wastes before the digestion. Figure 5 shows an average MFRV of 57% of total manure N for injected cattle slurry, 74% for injected pig slurry, and 82% for injected digested slurry. When the slurry was applied by surface banding in a wheat crop, the MFRV was generally lower owing to a higher ammonia volatilisation. The MFRV for the digested slurry was only 64% after surface application. Even though the digested slurry has a better soil infiltration that reduces ammonia volatilisation due to a lower dry matter content, the higher pH still resulted in a significant ammonia volatilisation after surface application. Therefore efforts should be made to reduce ammonia volatilisation from digested slurry both during storage and after application.

The reduced content of decomposable organic matter in the digested slurry also reduces the potential for denitrification after application to soil (Petersen, 1999). This means a reduction in the emission of nitrous oxide, which is a strong GHG.

The lower content of organic N in the digested slurry also means that the potential long-term nitrate leaching losses from mineralised N can be reduced and that the residual fertiliser N effects in the years after application are lower (Schröder et al, 2007).

In fertiliser planning, it is important to take into account the higher N availability of the digested manure in the first year. Otherwise, it could result in increased leaching losses due to an excess of plant-available N.

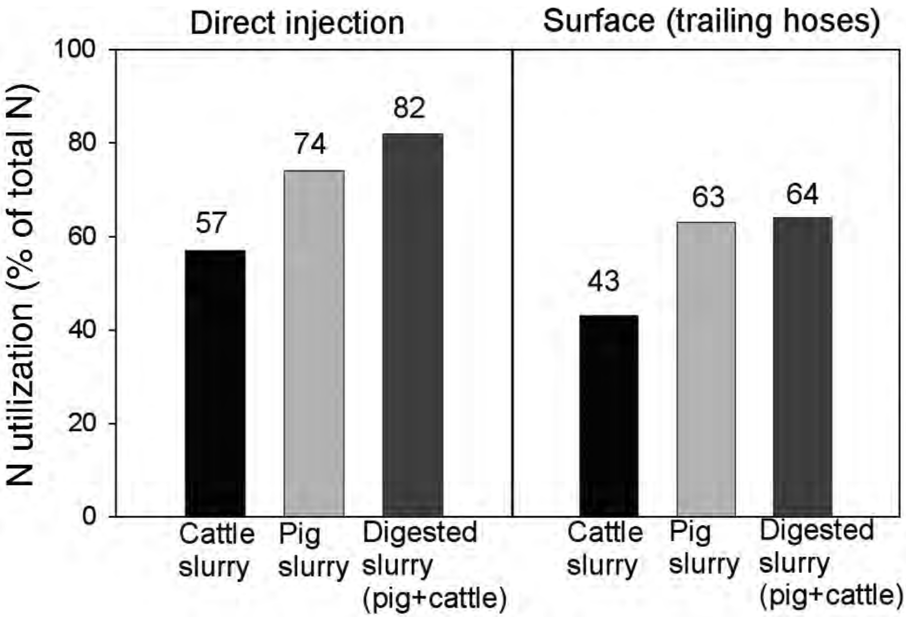

Figure 5. *Mineral fertiliser replacement value of cattle slurry, pig slurry and digested slurry applied to winter wheat by direct injection or surface banding. Average of 12 years' on-farm experiments in Denmark (data from Pedersen, 2001).*

5. CONCLUSIONS

The first-year N fertiliser value of slurry is approximately equivalent to the ammonium content when N losses are low after application. Most of the organic N remains in the soil after the first year and is released slowly over many years. The residual N is also released in periods without crop growth and, under North European conditions, there is a higher risk of nitrate leaching from this N pool. After AD, slurry contains a higher proportion of mineral N and less decomposable organic matter. It means that the first-year fertiliser value is higher and that less organic N is left in the soil after the first growing season, which also reduces the long-term residual N effect and the long-term risk of nitrate leaching. After AD, the emission of GHG is reduced, but slurry pH is higher and attention should be directed at limiting ammonia losses from digested slurry.

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POTENTIAL AND LIMITATIONS OF THE MODELS OF NITROGEN FATE IN SOIL-CROP SYSTEMS AT DIFFERENT SCALES

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SUMMARY
This paper demonstrates the incorporation of knowledge from experiments into simulation models, with special emphasis on soil organic matter modelling. Subsequently, the modelling of crop-soil interactions is outlined. The challenges of moving from topsoil measurements to modelling of the whole soil profile are also presented.
When utilising the agro-ecosystem model complex FASSET, an essential aspect of environmental assessment in agriculture turns out to be the timescale, an element often overlooked.
Two examples of model-based environmental assessment of biogas treatment of slurry are provided. Finally, the main lessons learned are given.

1. DYNAMIC SIMULATION MODELS
Technically, the kind of dynamic simulation models described here represents an integration of a large number of differential equations that cannot be solved analytically. Such dynamic models are, in many cases, the only way at hand to answer questions of great concern-e.g. expected levels of nitrate leaching by different policies and regulations. We cannot wait for 10–100 field experiments with a duration of 5–50 years for the answers; we need them here and now. The price is the associated

uncertainties, but providing no answers still leaves us in a much worse position.
As one of numerous examples, the climate projection of the future of the earth is carried out by simulation models.
Dynamic simulation models may be very helpful tools. On the other hand, the large numbers of parameters involved and the level of complexity may, in the worst case, cause the models to give non-optimal results.
To take advantage of the full potential of dynamic simulation, both the models and their results should be analysed carefully and critically, and the models tested and further improved to the largest possible extent.

2. MODELLING SOIL ORGANIC MATTER

The turnover of organic matter in the soil is central in many agroecological issues, as it is intimately connected with nitrate leaching and greenhouse gas emissions. In most soil-plant models, the combined carbon (C) and nitrogen (N) turnover in the soil is on focus, where the turnover of C can roughly be considered the driving force for N turnover. So in order to model N turnover, one has to be good at modelling C turnover.

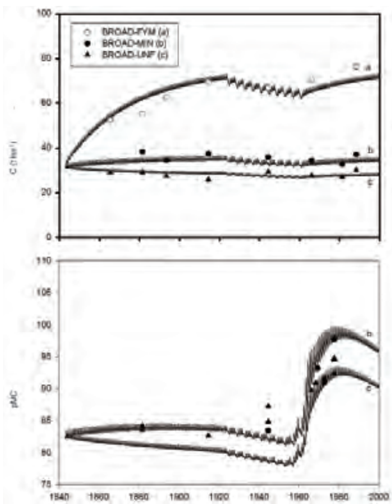

Figure 1. *Measurements (symbols) and simulations (lines) from the Broadbalk continuous wheat experiment. Soil C (top) and ^{14}C content in % modern (bottom) from 0-23 cm depth from unfertilised (BROAD-UNF), mineral-fertilised (BROAD-MIN) and farmyard manure-fertilised (BROAD-FYM). From Petersen, et al. (2005).*

For the development of the soil organic matter model CN-SIM (Petersen, et al., 2005; Petersen, et al., 2005), a large dataset was utilised for calibration and validation, consisting of 22 long-term field treatments and 43 different short term laboratory treatments. Isotope information (^{15}N, ^{13}C, ^{14}C) was utilised whenever available. CN-SIM was coupled with a parameter optimisation software with a multiple criteria target function, a database with all experimental results, and a software with automated graphical representation routines. This setup allowed the estimation of parameters on a statistical basis and the assessment of parameter confidence intervals. Figures 1 and 2 show examples of long-term and short-term simulations, respectively. Generally, the simulations of the short-term data may be characterised as acceptable to fair, despite the large effort, whereas the long-term data simulations were good to excellent. So the modelling of short-term C and N dynamics represents an even greater challenge than long-term dynamics.

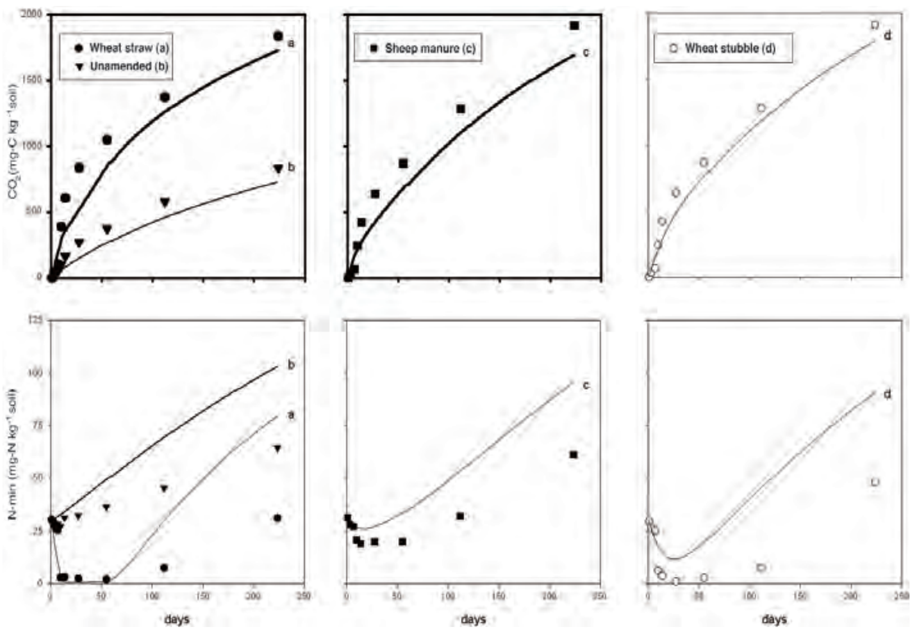

Figure 2. *Measured (symbols) and simulated (lines) CO_2 evolution and mineral N from an experiment with unamended soil, wheat straw, and sheep.*

3. MODELLING PLANT-SOIL INTERACTIONS

FASSET (www.fasset.dk) is a farm model with a focus on the turnover of N, which as an important part includes a dynamic field model. FASSET contains detailed soil and crop models, described elsewhere (e.g., Berntsen, et al., 2003). Briefly, the crop model simulates daily dry matter accumulation and N uptake based on light interception by green leaves. Daily dry matter produced is translocated to the roots and aboveground biomass. A fraction of the root matter is lost by rhizodeposition (Berntsen, et al., 2005), which, together with top and root residues, constitutes organic C and N input for the soil organic matter model. Specified amounts of animal manure may also be added. Daily dry matter production can potentially be limited by nitrogen or water stress. The soil model simulates daily changes in water, temperature, and transport of solutes. The turnover of mineral N in the soil is coupled to the C and N turnover in the soil organic matter submodel, as outlined in Figure 3.

When implementing the developed soil organic matter model in the FASSET model, N leaching in the initial tests turned out to be beyond the realistic level (Petersen, 2007). This was quite puzzling, as this model was intended to represent a state-of-the-art improvement. But, putting into context the whole soil-plant-atmosphere systems with realistic contents of C and N in the soil profile, it failed to simulate realistic N-leaching levels. As the simulation of N leaching is a very important part of FASSET's purpose, this was quite unsatisfactory.

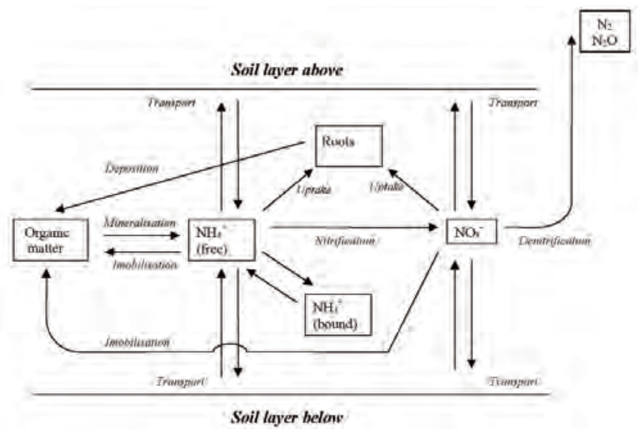

Figure 3. *Modelled net processes of the N turnover in one soil layer in FASSET.*

The available measurements from almost all the long-term experiments are results of the balance between the input and the decay of organic matter from the *topsoil*. And almost all the organic matter models are based on a paradigm of no interaction between soil layers. However, there is clear evidence from isotope studies that there is a substantial downward transport of organic matter (e.g., Bruun, et al. 2007).

Thus a significant proportion of the apparent decay from the topsoil may in reality just represent transport to the subsoil. With few exceptions, models of organic matter do not take this fully into account. The process of resolving mechanisms and setting parameters for yet another, further improved organic matter model that accounts for the issues of the whole soil profile will probably be quite time-consuming. To be able to utilise the improved organic matter within FASSET in the meantime, two coarse assumptions (Berntsen, et al., 2005) were made:
1. The “real” turnover rate of the “active humus” pool is 50% of that in CN-SIM because 50% of the apparent decay is assumed to be transported to deeper soil layers.
2. The “passive humus” content of the subsoil is set to 70%, rather than the assumed 40.5 % in the topsoil, as judged from various subsoil ^{14}C measurements.

The adjustment resulted in lower N mineralisation and realistic N leaching levels. So we are a bit further–in my view–but there is still work to be done.
This also is a good example of the need to recognise that modelling of the soil is still a comparatively young discipline, with pitfalls remaining.

4. COMPARING SIMULATED LEACHING WITH SIMPLE N BUDGETING

The following outlines a modelling study, where a crop rotation purely based on mineral fertiliser input was changed into intensive pig slurry application. This was done according to Danish regulation rules, where 100 kg nitrogen in slurry is assumed to have the same fertilisation value as 75 kg from mineral fertiliser (the substitution value). The focus was on the change in N leaching rather than the absolute level of leaching. Two model approaches were compared: a simple, total N budgeting approach (N balance model) with the inclusion of N losses from denitrification, and the FASSET dynamic model.

Table 1. *Additional leaching (kg N ha^{-1} y^{-1}) under different Danish conditions by utilising 120 kg N ha^{-1} y^{-1} pig slurry applied every year*

Soil	Climate	FASSET (50 years)	Balance model	FASSET rise in leaching compared to the balance model (cummulated over 50 years)	FASSET rise in leaching compared to the balance model (cummulated over 200 years)
Sandy	Dry	7.3	20.7	35%	64%
Sandy	Wet	8.4	20.7	41%	70%
Sandy loam	Dry	3.2	18.3	18%	42%
Sandy loam	Wet	5.7	18.3	31%	58%

As seen in Table 1, after 50 years, the dynamic modelling predicts a rise in leaching level of only 18-41% of the balance model prediction; even after 200 years, the cumulative rise in leaching predicted by the budget model is far from the level predicted by the dynamic model.

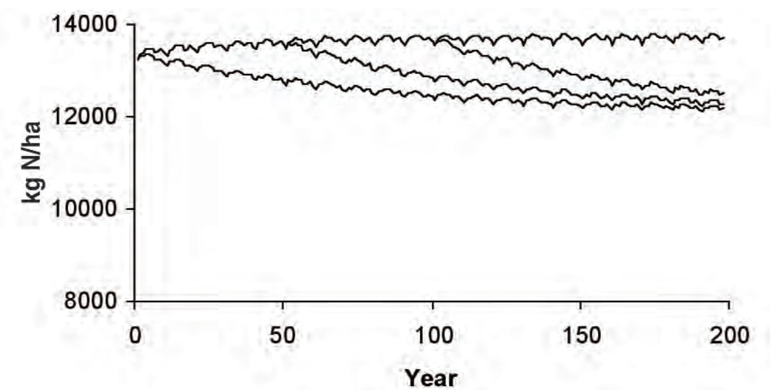

Figure 4. *Development in organic soil N for sandy loam, wet climate. Lower curve is mineral fertilised, and upper curves are slurry applications.*

By the end of the 200-year simulation of slurry application, a fairly large amount of organic matter has been lost from the mineral fertilised scenario (lower curve, Fig. 4), relative to the scenario with slurry application. The soil N accumulated in the slurry treatment, relative to the mineral fertilised, can of course not be lost as leaching. More importantly, during this period, a fairly large difference in N mineralisation evolves.

The big amounts of N exchanged with soil organic matter and its timing, have a bearing on the N dynamics, as seen in Figure 5.

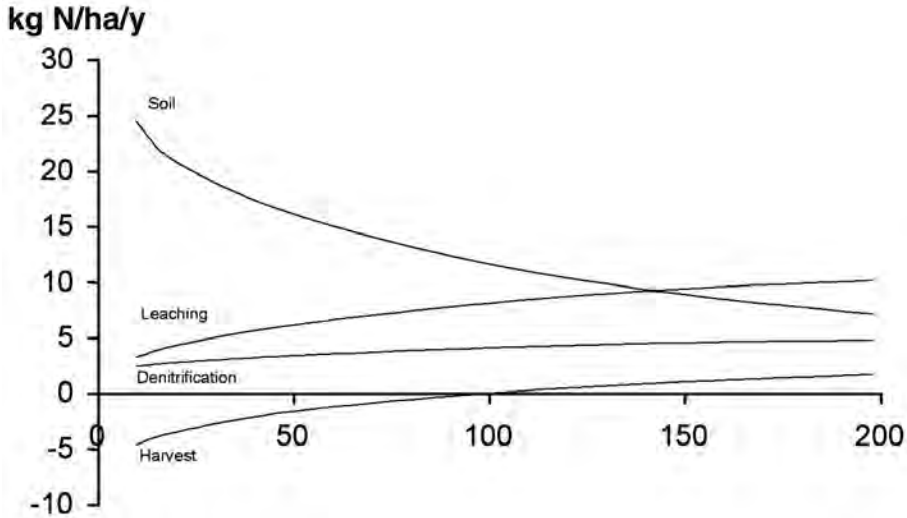

Figure 5. *N entries (sandy loam, wet climate). The curves are cumulated differences between permanent slurry application and mineral fertilisation, calculated with the FASSET model, divided by the number of simulated years.*

The substitution value of N in slurry for crop utilisation depends on the time frame and, according to the model, the assumed 75% (Danish legislation) are first reached after 100 y (Fig. 5). Also, note the development in N leaching due to growing mineralisation differences.

The initial difference in N leaching increase calculated by simple N balances and dynamic modelling, respectively, was quite big. Even after 50 years, only in the order of one-third of the expected increase in leaching was simulated.

The budget model was carefully tuned and, over an infinite period, results would have been quite similar.

When dealing with changes in agricultural practice that have significant effects on the soil N pool, this example stresses *the need to explicitly state a time frame* within the political and administrative system. The consequences judged over, for example, a 10-year period, may be very different from the consequences judged over a very long period. In this example, these differences were up to a factor 4-5 in estimated leaching.

5. BIOGAS SCENARIOS

The total Danish energy consumption in 2005 was 845 PJ, out of which biomass energy constituted 89 PJ. Two scenarios were made to investigate the consequences of a comprehensive biogas production:

1. Utilise 75% of the total animal manure in Denmark for biogas production, yielding 19 PJ extra.
2. Combust 75% of the fibre fraction from the residual of biogas, yielding 2.5 PJ extra.

The consequences for soil C were modelled over a 50-year period at the national level.

- Utilising animal manure for biogas production (19 PJ y-1) decreases the topsoil C in Denmark by 3.2%.
- Combusting the fibre fraction (2.5 PJ y-1) decreases the topsoil C in Denmark by 1.3%.

The results are additive, so these two actions will decrease the topsoil C content by 4.5%. The effect will not be equally distributed, so some soils may lose considerably more organic matter.

Note that the decline in C, relative to the energy gained, is markedly made larger by the fibre combustion. This is due to the lower net energy efficiency of this combustion.

So there is a trade-off between the energy gain by fibre combustion and the ease of handling the residues versus the additional loss of soil fertility that needs to be evaluated.

The effects of biogas production were also modelled at the farm level, as outlined in Table 2.

Table 2. *Soil C and nitrate leaching from a pig farm applied 120 kg manure-N ha^{-1}. Accumulated effects over 50 years, simulated with the FASSET model.*

	Raw manure	Biogas treated manure	Biogas treated, adjusted application of mineral fertiliser	Biogas treated, fibres combusted, adjusted application
Soil carbon change (kg C ha^{-1} y^{-1})	78	-7	-7	**-80**
Nitrite leaching (kg N ha^{-1} y^{-1})	57	**60**	54	52

With *unchanged* application of N, the N leaching estimated with FASSET has *increased* slightly when using biogas-treated manure. Only when adjusting the supplementary mineral N to obtain the same amount of harvested N as before does the leaching decrease.

Why does leaching rise with unchanged levels of N input?
Two major reasons may be given:

- Pollution substitution, as atmospheric N losses decrease when applying biogas-treated manure.
- Reduced buildup of soil N when applying biogas-treated manure, caused by less total organic matter in the digestate.

Judged from the present FASSET model parameter settings, the larger availability of N then causes both plant uptake and leaching to increase.

6. CONCLUSIONS

- Measurements from the field plot and laboratory can, as exemplified in this paper, by the use of simulation models be projected up to the field, farm, or even national level.
- Simulation models are very useful tools and for many issues the only tools at hand. Structure, parameters and results should be examined critically–but one should acknowledge the overall usefulness also.
- When looking at changes in pollution from agriculture, the time frame frequently is the thing to consider.

- Biogas production may cause soil organic matter content in the soil to decrease markedly, especially if the fibre fraction is combusted.
- Treating manure in a biogas plant and spreading the residues with the same amount of N per hectare as before probably increases N leaching slightly, or at least does not decrease leaching. To get considerable environmental benefits, the amount of supplementary mineral N should be decreased.

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FERTILISATION WITH DIGESTED MANURE FROM BIOGAS PLANTS: A METHODOLOGICAL PROPOSAL AT THE DISTRICT SCALE

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SUMMARY

The hypothesis described in this paper is that the manures obtained as a by-product from large anaerobic digestion (AD) plants are best managed at the district scale. We envisaged a management scheme for digested manures that maximises agronomic, environmental, and economic benefits. We also described the research steps required to put it into practice. In our hypothesis, the digestion plant and the machinery for manure distribution are managed by a central entity. A nutrient management plan is set up using the information contained in a geographic information system incorporating all relevant information about cropping systems and animal production systems in the district. Using manure nitrogen concentrations estimated with near infrared spectroscopy (NIRS) sensors,

the results of the plan are translated into amounts of manure to be distributed. Field application of manure (with soil incorporation) is then carried out using machinery equipped with sensors that update the information system with data about the operation carried out. We finally describe the operational, agronomic, economic, and environmental advantages of this management scheme.

1. INTRODUCTION

Farmers in Europe are oriented toward anaerobic digestion (AD) as a means to recycle animal manure and other biomass, and to integrate their profits. In Italy, its diffusion is particularly encouraged due to public economic incentives. Besides biogas, AD produces "digested manures," which are organic fertilisers. However, the knowledge of various aspects of the use of digested manures as fertilisers is still incomplete and requires attention. This paper aims to propose an agronomic management scheme for digested manures produced by large-scale AD plants, describe the knowledge needed for the application of that scheme; and identify research needs.

2. THE FACTS

Many AD plants are large. A recent survey in Italy (Piccinini et al., 2008) has shown that 26% of existing plants in Lombardia have an electrical power higher than 0.8 electric MW. To avoid nutrient excesses, an agronomic-based management of digested manures produced by these plants requires wide cultivation areas. An example can be the case of a digestion plant with a power of 1.2 electric MW. On a daily basis, the digestion plant uses 70 t of silage maize (containing about 273 kg N) and 40 t of pig liquid manure (containing about 100 kg N). If we assume the absence of losses in the digestion plant, we expect that 373 kg N are found in the digested manure daily, corresponding to 124,000 kg N per year (with 333 days of activity). If this amount of N is applied to soils at a rate of 250 kg N ha^{-1}, 500 ha are required. However, the area needed can be higher if the application rate is lower, which is the case for crops (as winter cereals) that do not have high crop N uptake. The conclusion is that it is difficult to use digested manures only in the farm where the plant is located.

Therefore, a district-scale approach is needed, with biogas-farms producing the manure, and other farms receiving it. This type of approach makes it possible to obtain economic advantages (for the farmers receiving the manure) and environmental benefits (as the concentration of high nutrient loads on small areas is avoided). As an example of the economic benefit, the current economic value of an application rate providing 250, 132, and 247 kg ha^{-1} of N, P_2O_5, and K_2O is of about 450 € ha^{-1} (calculated with actual costs of inorganic fertiliser). Another issue of interest for the management of digested manures is their high compositional variability. The concentration ranges of several nutrients, measured during a survey carried out in 2007 in northern Italy, are reported in Table 1. The data clearly show that variability is high owing to sampling problems (in particular for the solid fraction), to changes in the amount and type of input materials used to feed the digestion plant, and to irregular separation efficiency.

Table 1. *Compositional range of raw digested manures and of their fractions, northern Italy (unpublished results, T. Maggiore and M. Negri, Department of Crop Science, University of Milano, 2007).*

Variable	Digested manure	Solid fraction	Liquid fraction
Total N, kg t^{-1}	4 - 6	2 - 16	4 - 6
P_2O_5, kg t^{-1}	0.3 - 1.5	3.0 - 6.0	0.2 - 2.5
K_2O, kg t^{-1}	0.6 - 5.0	1.0 - 3.4	1.5 - 3.2
Ca, kg t^{-1} DM	12 - 43	2 - 23	9 - 57
Mg, kg t^{-1} DM	5 - 12	2 - 19	7 - 25
Na, kg t^{-1} DM	2 - 31	0.1 - 6	1 - 13

Therefore, it is necessary to propose a management scheme that fulfils these objectives:

i) maximise agronomic efficiency (crop recovery) of nutrients contained in the digested manure;
ii) minimise nutrient losses;
iii) minimise management costs (storage, transportation, distribution); and
iv) make it possible to monitor and record composition and application date of the digested manure.

3. PROPOSAL FOR A DISTRICT-SCALE MANAGEMENT SCHEME

Our proposal is based on the following principles. First, a recognised legal entity should supervise the entire management process. In our opinion, this entity is necessary to take care of the management and maintenance of the digestion plant, of the machinery used to transport and distribute the manure, and of the associated computer information system. In addition, this entity should look after the periodic innovation of the machinery. Finally, it should supervise the agronomic distribution of the manure, which needs to be carried out by respecting existing agronomic and environmental regulations. This entity can be represented, for example, by the owner of the digestion plant or by a contractor (owning the machinery and working for a group of farmers).

Second, the size of the storage tanks needed to collect the digested manure has to be carefully defined. This is a decision to be taken in agreement with the cropping systems surrounding the digestion plant, as the periods when the digested manure can be applied are relatively limited and strongly depend on the sowing and harvest dates of the various crops sown, and on their surface area. It is also important to study the dynamics of the composition of the manure that occurs during storage, as relatively little information is available on this subject.

The third principle is that manure should be separated into a liquid and a solid fraction, with eventual removal of ammonia. Research is needed on this aspect, as the efficiency of ammonia removal is not known. In addition, potential enrichment with phosphorus (P) of soils should be evaluated. Fourth, a geographical information system needs to be established as a support to the preparation of nutrient management plans. This information system (such as that described by Bergamo et al., 2007 and by Bechini and Castoldi, 2006) should contain georeferenced data about chemical and physical properties of the soils surrounding the digestion plant; crop rotations adopted; date and parameters for each agronomic operation (tillage, fertilisation, sowing, irrigation, pesticide treatment, harvest); expected final crop yield; residue management; and animal production systems. All these data are used to prepare a nutrient management plan for each single field receiving the digested manure. A nutrient management plan is a technical document prepared by an agronomist describing dose, date, type, and application method of fertilisers. The nutrient management plan is prepared by taking into account soil properties, climate, crops, rotations, and type of fertilisers available. Therefore, it represents a state-of-the-art methodology for soil fertility management in production agriculture and makes it possible to respect many existing agronomic, economic, and environmental ties. In our hypothesis, the nutrient management plan would be prepared with a (semi)-automatic procedure. In other words, a computer program linked to the database would prepare a first version of the plan, which could be later checked, modified, and approved by a professional agronomist. In preparing the nutrient management plan, the most urgent issue is the knowledge of crop nitrogen recovery of digested manure under different pedological, climatic, and management conditions. Another aspect that should be the subject of innovative research is compiling the plan with due consideration to various economic, environmental, and agronomic limitations at the district scale-i.e., by looking at the limitations of many fields (potentially hundreds of them) and their interactions simultaneously. Once the amounts and dates of field application of digested manures are established, an appropriate working chain for manure spreading is needed. We believe that, due to great compositional variability, the first element of this chain is an automatic sensor for real-time manure analysis installed on the storage tank. The installation of the sensor on the storage tank (as opposed to the installation on the machinery for field application) would prevent it from damages. The feasibility of such a sensor should be investigated with a specific research project. Laboratory results show that several chemical properties of dairy and pig liquid manures can be estimated using near-infrared spectroscopy (NIRS) and electrical conductivity. Examples of NIRS estimates taken from the literature are reported in Table 2.

Table 2. *Examples of the root mean squared prediction error of NIRS for the estimation of properties of liquid animal manures.*

	Dry Matter	Total N	NH_4-N	C	P	K
	g kg^{-1}					
De Ferrari et al., 2007 (liquid dairy manures)	9.5	0.32	0.18	3.7	0.13	0.67
Sørensen et al., 2007 (liquid pig and dairy manures)	6.1	0.43	0.37	3.1	0.16	0.64

In addition, the possibility of developing simplified NIRS instruments for on-farm use was reported by De Ferrari et al. (2007).

Here, the research need is to establish adequate calibrations for digested manures, using large sets of samples describing different production conditions.

Once the nutrient concentrations of the digested manure are estimated and the amount to be distributed is calculated according to the nutrient management plan, there is a need for an appropriate machinery to carry out application in the field. Research projects recently carried out in northern Italy have produced prototypes of manure spreaders that can provide the requested amount of manure per unit area. Other features of these prototypes are the presence of a global positioning system and the capability of incorporating the manure in the soil immediately after application.

Finally, we believe that the information system should be regularly updated with all information about each crop management operation until harvest. This would make it possible to track additional fertiliser applications (e.g., topdressed inorganic N fertilisers) and final crop yield. These elements facilitate the preparation of the nutrient management plan for the subsequent year. Monitoring of crop management operations is already feasible using equipment such as those developed by Mazzetto et al. (2006). These systems individually identify the tractor or the operating machine using sensors and register its position over time. All these data are collected in a server, and their analysis makes it possible to understand the type of operation carried out, to calculate its duration, and to identify the field(s) where it was done. In addition, the amount of fertiliser applied per unit area can be calculated and inserted into the database for further integration into the nutrient balance. Maps can also be generated to better represent the operations done.
Some estimates of manure distribution costs are reported in Table 3. These estimates include fixed and variable costs (fuel, lubricants, manpower, mortgage, maintenance) and are carried out by assuming that the machinery used for manure distribution (73 kW tractor + 15 m^3 tank spreader) is intensively used over the year by the management entity mentioned before. The result is that fixed costs are shared by a large number of users, and therefore estimated total costs are not excessively high. In addition, the difference in average annual cost between the “completely on farm” scenario and those “completely outside” is not very high. These data show the convenience of using a single equipment over many hectares of land.

Table 3. *Estimated total costs of field application of liquid manures for different scenarios of distance between storage tank and fields.*

Scenario of farm fields	Average distance (km)	Operative time (h)	Average annual cost € ha^{-1}
All on-farm	1.1	1250	129
Half on-farm, half off-farm (near)	0.8 2.0	1163	122
Half on-farm, half off-farm (far)	0.8 5.0	1375	141
All off-farm (near)	2.0	1190	124
All off-farm (far)	5.0	1613	162

4. ADVANTAGES FOR THE FARMERS

The farmers joining this management system would obtain a number of advantages. First, they would benefit from an administrative simplification, as all their crop management data would be stored in a relational database and could be easily extracted once needed for purposes other than the nutrient management plan. In addition, they would receive a technically correct nutrient management plan, prepared by a professional agronomist using up-to-date information about nutrient dynamics and relatively inexpensive data about the specific cropping system analysed (cropping system management and crop yields). This would make it possible to reduce the expense for fertilisers. Besides, the use of shared machinery among many users would keep distribution costs low and would guarantee that a precise and correct manure application is carried out (i.e., at the right dose, with incorporation into the soil, thus minimising ammonia losses). Moreover, even if distribution errors occur, technical supervision based on updated data would be available to set up appropriate remedy measures. Finally, the information system can be used to identify fields available for the distribution of digested manures (i.e., belonging to non-animal farms) and therefore could help match the “demand” and the “offer” of soils for manure application.

5. RESEARCH REQUIREMENTS

The management system described above is based on the hypothesis that several issues are solved with appropriate research projects. First, a rational nutrient management plan can be set up only if crop recovery of N contained in digested manures is known for different crops in various pedo-climatic conditions. This means that appropriate fertilisation experiments need to be carried out over several years to measure N recoveries in various conditions for raw and separated digested manures. These experiments, conducted in the field or with the use of lysimeters, should be coupled with laboratory incubations aimed at determining the parameters of the mineralisation of organic C and N of these materials. Later, the application of simulation models and nutrient balances to the experimental data can help to estimate these parameters also for other conditions not explored experimentally. Once parameterised, simulation models may also help establish regional-scale scenarios for the use of digested manures. Second, NIRS calibrations are needed for quick and cheap estimates of the nutrient concentrations of digested manures, raw and separated. Third, optimisation algorithms at the district scale that simultaneously maximise agronomic, environmental, and economic benefits need to be developed. Such algorithms need to identify the size of the storage tanks, and the amounts, dates, and fields where digested manure will be applied. Fourth, a comprehensive estimate of economic costs for the entire management process is needed (from storage to field distribution). Fifth, the energy balance of the digestion plant needs to be assessed to ensure that more energy is obtained after digestion compared with the energy used to produce the input biomass and to manage the entire process (including direct and indirect costs). Finally, further research is needed to ascertain the consequences of removing crop residues on the maintenance of soil organic carbon. This is important because the increasing prices of dedicated biomass (mainly maize) underline the importance of providing secondary biomass for the production of energy.

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THE NITRATES DIRECTIVE: DEROGATIONS IN EUROPE AND PROSPECTS FOR ITALY

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SUMMARY

The Commission has granted Member States numerous derogations from the obligation not to exceed the limit of 170 kg ha^{-1} of nitrogen from the application of livestock effluent in nitrate-vulnerable areas. Such derogations have, however, only been granted for cattle and almost exclusively for grassland. On 6 November 2007, a novel form of derogation was granted to the Flanders Region of Belgium, which might be of great significance to Italy. This was indeed the first time that the Commission had been prepared to consider derogation for pig slurry and for arable land. This paper illustrates the contents of the derogation granted in Flanders, the conditions imposed by the Commission, and finally, gives an the outline of the contents of a possible application for derogation, which could be used by Italy for the regions of the Po River valley.

1. THE DEROGATIONS GRANTED BY THE COMMISSION

By its decision taken on 6 November 2007 in Brussels, the Nitrates Committee, the consultative body of the European Union Commission, created a precedent of potential use for Italy. It decided to approve a request for derogation to the limit of 170 kg ha^{-1} per annum for livestock nitrates in nitrate vulnerable zones presented by the Flanders Region of Belgium–all the land covered by the Region has been designated as being nitrate vulnerable.

This marked a new departure because, up to now, derogations have only been granted for cattle and almost exclusively only for grassland. A brief review of the derogations granted up to now, prior to the Flanders derogation of such potential interest, reveals the following picture.

1.1 Derogation granted to Denmark
Only cattle farms are covered and the permitted effluent may be up to 230 kg of N ha-^{1} per year. The conditions for the derogation can be summarised as follows:

- at least 70% of the UAA must be permanent or temporary grassland or other crops intercalated with grassland;
- leguminous crops are not permitted (with the exception of grassland with a maximum of 50% clover).

1.2 Derogation granted to the Netherlands
The farms affected are those rearing cattle and other pasture animals, the permitted effluent may be up to 250 kg of N ha^{-1} per year. The conditions for the derogation are as follows: at least 70% of the UAA must be permanent or temporary grassland. For arable land, a winter cover crop is obligatory.

1.3 Derogation granted to Germany
The farms affected are cattle farms and the maximum quantity of effluent permitted is 230 kg of N ha^{-1} per year on "intensive production grassland".
The conditions are summarised as follows:

- by "intensive production grassland" is meant a permanent or temporary grassland (for at least 4 y) with at least four cuts or three cuts plus one episode of pasturing;
- an "intensive production grassland" must not contain legumes. A mixed grassland is, howeve,r permitted with a maximum of 50% of clover.

1.4 Derogation granted to Austria
The farms affected are cattle farms and the maximum quantity of effluent permitted is 230 kg of N ha^{-1} per year. The conditions for the derogation can be summarised as follows:

- at least 70% of the UAA must be permanent or rotated meadow. For arable land, a winter cover crop is obligatory.
- leguminous crops are not permitted (with the exception of grassland with a maximum of 50% clover).

1.5 Derogation granted to Ireland

The farms affected are cattle farms and the maximum quantity of annual effluent is 250 kg N ha^{-1}. The conditions for the derogation can be summarised thus:

- at least 80% of the UAA must be permanent or rotated meadow;
- leguminous crops are not permitted (except of grassland with a maximum of 50% clover).

1.6 Derogation granted to Poland

The farms affected are cattle farms and the maximum quantity of effluent permitted is 230 kg of N ha^{-1} year in parts. On other crops, the maximum N dose is 115 kg ha^{-1}. The conditions for the derogation can be summarised as follows:

- at least 80% of the UAA must be permanent meadow;
- leguminous crops are not permitted (with the exception of grassland with a maximum of 50% clover).

1.7 Derogation granted to Flanders

The documentation presented by Flanders in support of its application was extremely detailed and dealt with aspects of both agricultural and environmental nature with regard to the state of water resources and the strict regional regulations limiting the use of phosphorus.

The application requested permission for livestock farms specialising in crops with high N requirements and extended growing season (grassland, maize followed by a second crop in the same year, autumn/winter cereals followed by a second crop with the function of recovering excess N that has not been taken up, sugar and forage beet) to increase the dose of livestock N to apply on the basis of the following scheme:

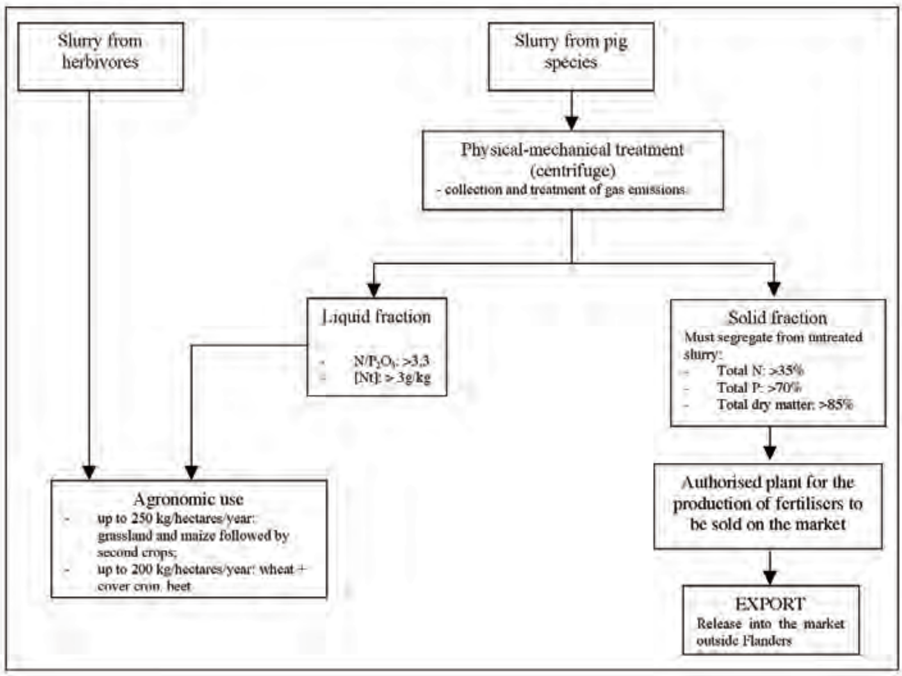
- a maximum of 250 kg N ha^{-1} per year for permanent or temporary grassland and maize followed by a second crop;

- a maximum of 200 kg N ha^{-1} per year for autumn/winter cereals followed by a second crop, sugar or forage beet.

The Commission imposed a series of particularly rigid conditions on its acceptance of the Flanders application:
a) <u>Conditions for the application of the derogation on livestock slurries</u>
Pig slurries must be subjected to physical-mechanical treatment to obtain two fractions:

- a solid fraction containing at least 35% of the total N, 70% of total phosphorus, and 80% of the suspended solids in the untreated slurry. This fraction must then be sold to industrial plants with authorisation to process it. It will be processed to enhance its quality, identifying it as an organic-based fertiliser to be sold in the market, thus removing it from vulnerable areas. The controlling authorities will be required to check that the amounts of the solids produced by all the farms covered by the derogation is compatible with the processing capacity of the authorised plant;
- the clarified fraction must be set aside for storage and subsequent agronomic use without further processing. This means that it cannot be subjected to subsequent processes of a biological or chemical/physical nature designed to reduce N content. Proof that such N reduction treatments have not been applied is obtained from the total N level, which must not be less than 3 g L^{-1}. A further condition is that the N-P_2O_5 ratio is greater than 3.3, demonstrating that removal of phosphorus from the clarified fraction has been highly efficient;
- in addition, ammonia, methane, and compounds responsible for odours developing during the separation treatment, must be captured and treated in such a way as to eliminate their atmospheric impact. The solid/liquid separation must thus be effected in a closed, slightly depressurised environment and the extraction air must be treated with chemical or bio-scrubbers or passed through bio-filters for the biological reduction of odours and ammonia;
- the separation treatment, however, is not obligatory for herbivores. The slurries of these animals can be applied in derogation to the 170 kg N ha^{-1}, even in untreated form.

The following diagram summarises the conditions that the Commission laid down for the grant of the derogation to Flanders.



B) <u>Conditions for the application of slurries on the land</u>

- The derogation applies to single areas in individual farms. This means that there may be some pieces of land in the same farm on which derogation could be applied and other parts where it could not;
- the maximum limit of livestock N ha^{-1} per year is increased, as requested in the application, to 250 kg ha^{-1} for maize with a dual crop cycle and grassland and to 200 kg ha^{-1} for beet and winter cycle wheat followed by a cover crop. In addition, a compulsory total maximum N dose has been established (thus including that contained in any chemical fertilisers used, that obtained from the atmosphere, that derived from organic fertilisers applied during the previous year etc.). This dose amounts to 300 kg ha^{-1} per year for grassland, 220 kg ha^{-1} for sugar beet, 275 kg ha^{-1} for wheat followed by cover crop, by forage beet and dual crop maize;

- it will be necessary to draw up an agronomic fertilising plan (AFP) every year for the whole farm (and hence also for those areas not benefiting from the derogation). The AFPs are not dissimilar to those requested by Italian regions in the action programmes for vulnerable zones;
- it will be necessary to carry out analyses of the contents of N and phosphorus in the soil at least once every 4 y for the pieces of land affected by the derogation. An analysis is required for each 5 ha of UAA under the derogation;
- it will be necessary to analyse the concentration of nitrates in the profile of the soils affected of at least 25% of the farms benefiting from the derogation once a year in autumn (a sample must be taken from at least 5% of the land cultivated with the crops indicated above);
- the slurry may not be applied in the autumn preceding the planting of the meadow;
- at least 2/3 of the livestock N must be applied before 15 May each year.

C) <u>Conditions for management of land coming under the derogation.</u> The farmers benefiting from the derogation must observe the following restrictions:

- the grassland must be pure graminacea. Grassland including leguminous crops or crops, which fix atmospheric nitrogen, will not be permitted;
- the grassland may only be ploughed in the spring. The ploughing of the grassland must be followed by the immediate planting of a crop with a high N take-up. No fertilisers of any kind must be applied over the first year following the ploughing of a permanent meadow;
- crops following wheat must be sown immediately after harvest and, in any case, no later than 15 Sep;
- the crops referred to above will have the function of ensuring autumn-winter cover and recovering the nitric form of N not taken up by the cereals, which might otherwise leach down into the ground water and/or be whased out in the flow of surface waters. The green manuring of these crops, if effected at harvest, may not be carried out before 15 Feb of each year.

D) Conditions for the slurry produced and its transport

In the Flanders region, there is already a decree in force fixing the maximum number of animals that can be kept on each farm. One of the conditions allowing the maintenance of the regime in derogation of the 170 kg ha^{-1} per year limit is that no Flanders farm, including those not subject to the derogation, is authorised to carry out enlargements leading to an increase in the number of animals currently authorised. Another condition is that the transport of slurry, contracted out to third-party businesses listed in a specific register, is recorded on GPS. Before its transport to other farms, a sample of the slurry will have to be taken and analysed at authorised laboratories. The results of such analyses have to be communicated to competent authorities and the farm receiving the slurry.

These conditions are supplemented by rigorous monitoring, checking, and recording plans to be carried out by the supervisory authorities whose main aspects are worth analysing. With respect to monitoring, the competent authorities will be required to identify at least 150 sites corresponding to the same number of farms, representing different types of soil, manuring practices, and crops in which data on N and P concentrations in the soil imbibition water and mineral N in the profile have to be collected to calculate the corresponding losses of N and P to the groundwater and surface water. These measures will cover the whole locality, whether or not the areas concerned are affected by the derogation.

The checks must, however, be effected in the individual farms covered by the derogation. They involve checks on formal compliance with conditions, examination of the analyses that these farms will be required to carry out (see B above) and the correctness of the documentation that must be used to accompany transport. A field inspection programme must then be carried out involving at least 5% of the exempted farms to check the correct application of the Nitrates Directive overall. The competent authorities will be required to send the Commission a report containing information on the treatment of slurry in the exempted farms, including deliveries to authorised plants, the results of the field inspections and the checks on documentation, together with all other matters envisaged by the monitoring and control plans no later than July in each year.

2. PROSPECTS FOR ITALY

How much of these rigorous and complex derogation, conditions, and checking structure would possibly be transferred to the Italian livestock context?

Before replying to this question, it is important to note that no application for derogation would be accepted during the ongoing proceedings concerned with the infraction of Articles 3 and 5 of the Nitrates Directive. Neither will it be easy to make such an application, even after the infraction proceedings have been closed in the light of the fact that the Commission has shown itself to be very uneasy, even only in the examination of derogation applications when coming from countries that have only declared a part of their territory as vulnerable. Furthermore, the Commission appears much more likely to grant derogation if it is in the context of stringent national environmental protection legislation. This does not play in Italy's favour, given the total absence of provisions concerning phosphorus in the Italian regions' action plans, even though it is the nutrient which is responsible, together with N, for the eutrophication of large bodies of water and growing accumulations in the soil.

Notwithstanding these difficulties, the writer is of the opinion, drawn from the experience of participating in a number of meetings of the Nitrates Committee as the Italian Ministry of Agricultural Policies' consultant, including the last one on 6 November 2007, that now is the time for the regions with intensive livestock farming and with extensive areas of vulnerable zones to prepare the documentation required for the grant of a derogation pursuant to paragraph 2 of Annex III of EC Directive 91/676.

The documentation would have to contain an analysis of decreasing trends, both of nitrates in the water table and of N and phosphorus in surface waters. Data on the reduction in livestock number and fertiliser use could be of great help, together with the elaboration of models capable of showing that an increase in livestock N dosage of more than 170 kg ha^{-1} would not prejudice the achievement of the goal of reducing nitrates in water resources and bodies. If this documentary apparatus is rigorously sustained by scientific research and technical reports, it could be used as the basis for the formulation of an application for

derogation, taking account of the fact that the first condition required to obtain such a derogation is to be able to show that it will be concerned with crops with a long growing season and a high N absorption capacity. Paragraph 2 of Annex III of the Nitrates Directive is unequivocal on this point.
The application has to be made by the national state to the European Commission, including on behalf of individual regions. What could the contents of such an application be, in the light of what the Flanders region was able to obtain?

3. CONTENTS OF A POSSIBLE APPLICATION FOR DEROGATION ON THE BEHALF OF VULNERABLE AREAS OF THE PO RIVER VALLEY BASIN AND VENETO

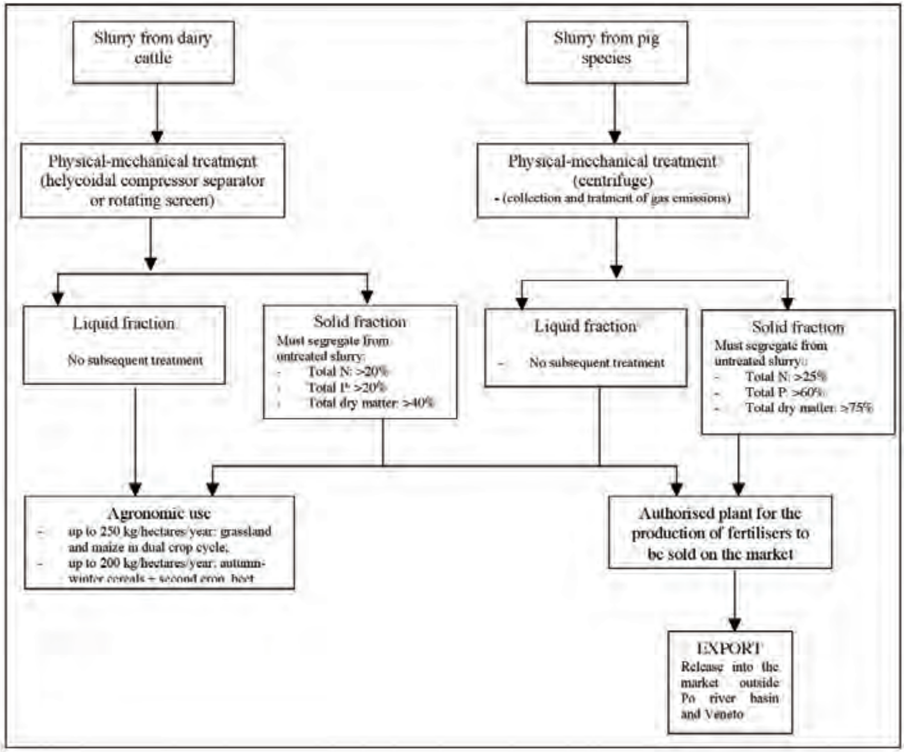
The application could be in the same terms as those presented by Flanders with respect to crop type and livestock N levels exempted from the 170 kg ha^{-1} limit, with a possible extension to all autumn-winter cereals (thus not limited to wheat alone). In effect, the application could cover the following:

- permanent or temporary grassland with only graminacea or with mixtures of leguminous crops and graminacea where the latter is prevalent. Derogation up to 250 kg ha^{-1};
- maize grown with a second autumn-winter cycle crop such as rye grass or other herbaceous species to be harvested green or as hay or used in silage in the spring: derogation of up to 250 kg ha^{-1};
- autumn-winter cereals (wheat, barley), followed by the sowing, after harvest, of a winter cycle crop to be used as green manure or harvested in spring, derogation of up to 200 kg ha^{-1}.

The conditions for slurry application and agronomic management of the land could be the same as those laid down for Flanders at points B) and C). The conditions for transport out of the farm could also be the same (point D), except perhaps for the extremely onerous and complex requirement for the analysis of every load leaving the farm.

Perhaps, the most sensitive part-although a proposal dealing with this in the Italian context would undoubtedly be necessary-relates to the conditions for the treatment of the slurry. Some restrictions applied by the Commission on Flanders (point A) appear to be impracticable to apply to Italy, particularly in relation to the very different characteristics of the slurries and of pig slurry in particular.
Unlike the situation in Flanders, where dry matter concentration averages about 9% and may reach 10-11%, in Po valley pig farming, with liquid feed and little attention to wasting water, the average concentration of dry matter in slurry is about 2.5%, with levels of around 5-6% only in the most developed systems. The separation treatment in these conditions, even with the use of efficient processes like centrifuges, would not be able to obtain the high performance levels demanded of operators in Flanders. Thus, in the Italian context, it would appear impossible to achieve segregation in the solid fraction of 35% of total N contained in the untreated slurry and a level of 3 g kg^{-1} of N in the liquid fraction. The Commission would thus have to take into account the specific local conditions with a consequential adjustment of the level and type of requirements.

A measure that might reasonably be required to lessen N levels in Italian vulnerable areas is a treatment line for slurry from dairy cows involving the separation of a solid fraction to be sent for processing for sale on the fertiliser market. It should be noted in this regard that Italy lacks the infrastructure for the production of this type of fertiliser. The fertiliser industry has always shown very little interest in the use of livestock materials (with the exception of chicken manure) for the production of organic fertilisers for quite understandable business reasons. A change in this attitude to a more advanced approach and to increased use of these materials appears to be an essential requirement if a derogation is to be obtained along the same lines as that granted in Flanders.
In line with what has been stated above, the following diagram sets out possible conditions for slurry treatment with changes that take into account the specific nature of the slurry produced in the Po valley regions.



4. CONCLUSIONS

The proposed contents for an application for derogation to the 170 kg ha^{-1} per annum livestock N limit imposed by the Nitrates Directive in the vulnerable zones of the Po River basin and Veneto should only be seen as the basis for discussion for the affected regions with a view to having a proposal that can also be supported by the farming community. This would make it possible, once the infraction proceedings have been closed, to begin a procedure similar to that successfully completed by Flanders. It will of course be necessary to verify the difficulties posed by and the sustainability of the whole scheme underlying the derogation granted to Flanders. The conditions imposed as a result of the derogation are indeed extremely onerous, representing the price farmers are required to pay to ensure that the environmental protection objectives set by the Directive are observed.

The techniques described for the treatment of slurry appear to be simple, well-tried, and not requiring particular skills from farmers. For a strategy of this kind to become consolidated practice, it will be necessary to initiate a process in which the Italian fertiliser industry equips itself to enable to use the solid part of livestock slurry as the basis for new lines of organic fertilisers.

Plant using helicoidal compression for cattle slurries

Centrifuge plant for the separation of the solid fraction from pig slurries

Distribution of covering slurries using low volatile N emission techniques

REFERENCES

Literature is available online at www.crpa.it

RENEWABLE ENERGY FROM ANAEROBIC DIGESTION. COMPARISON OF DIFFERENT TECHNOLOGIES-KEY POINTS FOR SUCCESS

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SUMMARY

In view of a rising global energy demand and the serious problem of global warming, a shift toward a more sustainable energy supply is urgently needed. On this background, in Bavaria, the supply of energy from biomass, particularly by anaerobic digestion (AD) of agricultural waste and energy crops has experienced a tremendous growth. In 2006, the production value of electricity from biogas already exceeded that of potato, hops, and sugar beet. The process stability and performance of biogas plants in practice are influenced by a number of factors-quality and mix of input materials, particularly nutrient content and microbial availability, design of the treatment process, and mastery of the operator. Continuous monitoring is required to prevent process instabilities and the consequent economic losses. The production of electricity from biogas has a considerably smaller climate footprint than the current

grid mix and can be further minimised by technical measures and management. To improve overall efficiency of energy supply from biogas, the utilisation of the surplus heat needs to be maximised. A further environmental benefit derives from the sanitary effect of the AD process.

1. BACKGROUND

Following the definition by the United Nations, Brundtland Report, 1987, sustainable development means:

…"development that "meets the needs of the present without compromising the ability of future generations to meet their own needs". It relates to the continuity of economic, social, institutional and environmental aspects of human society, as well as the non-human environment."…

Concerning the aspects of energy distribution and energy demands, a tremendous conflict is arising (Fig. 1).

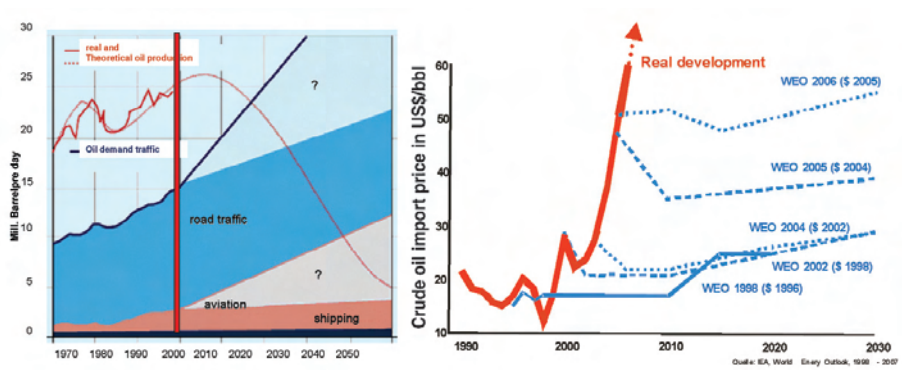


Figure 1: *Prognosis of worldwide demand for crude oil and real production.*

According to the prognosis of various institutions, global oil demand for aviation will increase up to 2050, compared with 2005: 2.7 to 9.4 times (for road traffic: two times). At the same time, a rising concentration of CO_2 in the atmosphere urges the world to significantly reduce the emission of greenhouse gases (Figure 2).

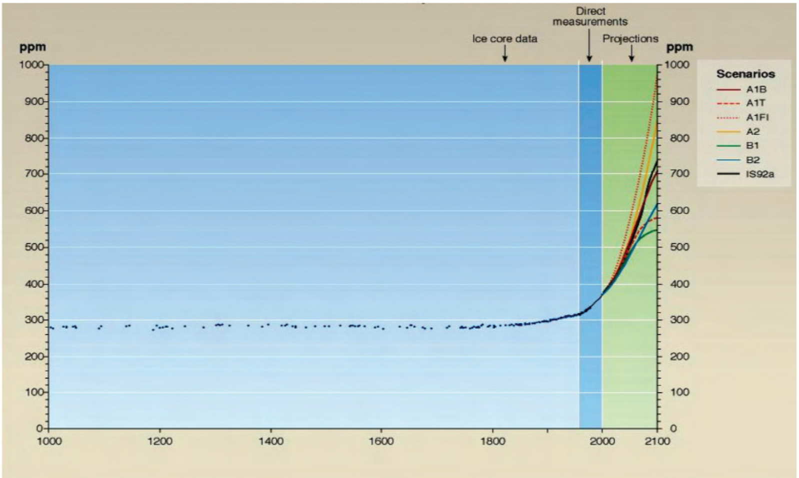


Figure 2: *CO_2 concentration in the atmosphere (IPCC, 2002).*

As a consequence, the European Commission has defined milestones for the use of renewable energy sources as documented in the "White Paper on Renewable Sources of Energy":

- Increasing the share of renewable energies from 6% (1995) to 20% (2030)
- Biomass to contribute more than 80% of the total additional RES contribution by 2010
- Biogas (livestock, sewage treatment, landfills) to contribute 15 Mtoe in addition to the current contribution estimated at 1-2 Mtoe (see Fig. 3)

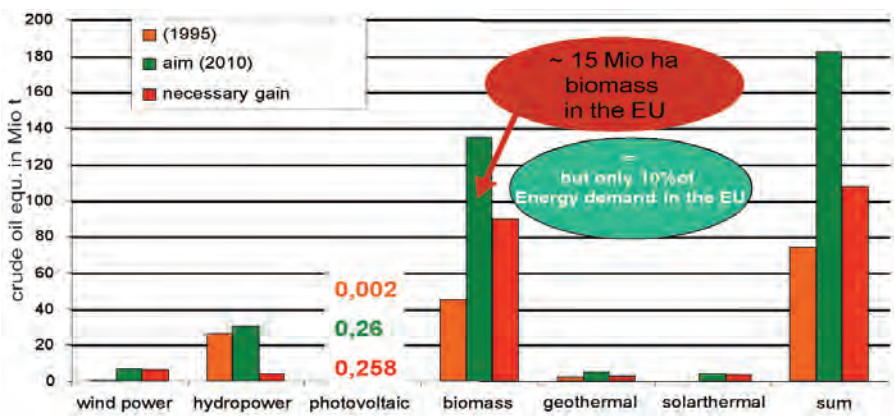


Figure 3: *Potentials of Renewable Sources of Energy in the EU (EC 1998: White Paper on Renewable Sources of Energy).*

In this context, a tremendous development of energy production from biomass took place in Bavaria. The generation of biogas from anaerobic digestion (AD) of agricultural waste and energy crops experienced a disproportionate growth (Fig 4.).

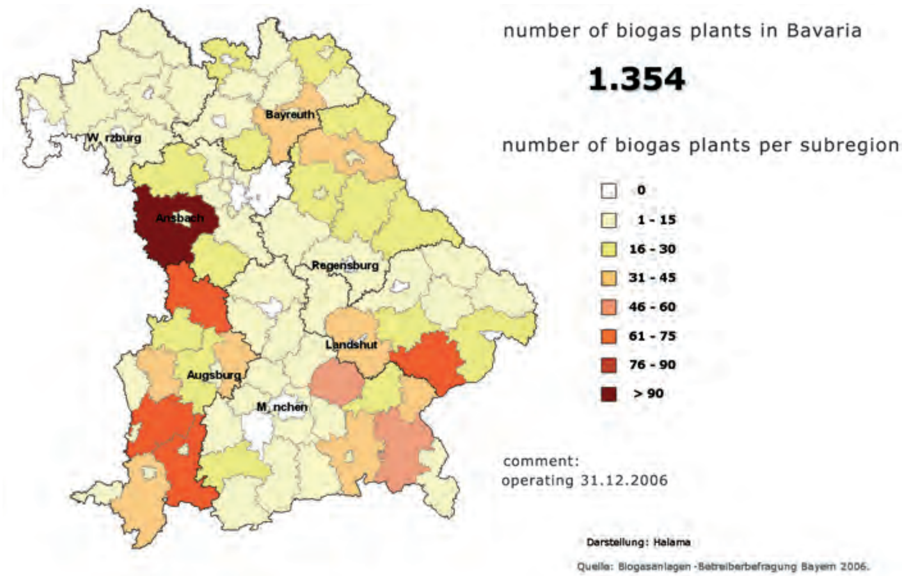


Figure 4: *Number of operating biogas plants in Bavaria.*

Studies evaluating the actual situation and potential of biogas production in Bavaria still predict a large potential for future growth (Fig. 5).

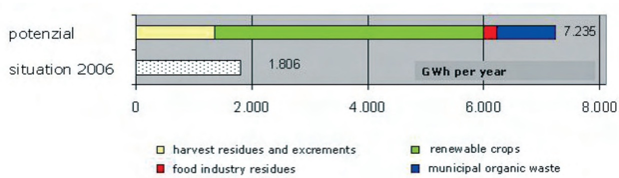


Figure 5: *Electricity production from biogas in Bavaria in 2006 and potentials of various sources.*

Also, the production value of electricity from biogas in 2006 exceeded that of potato, hops, and sugar beet (Fig. 6).

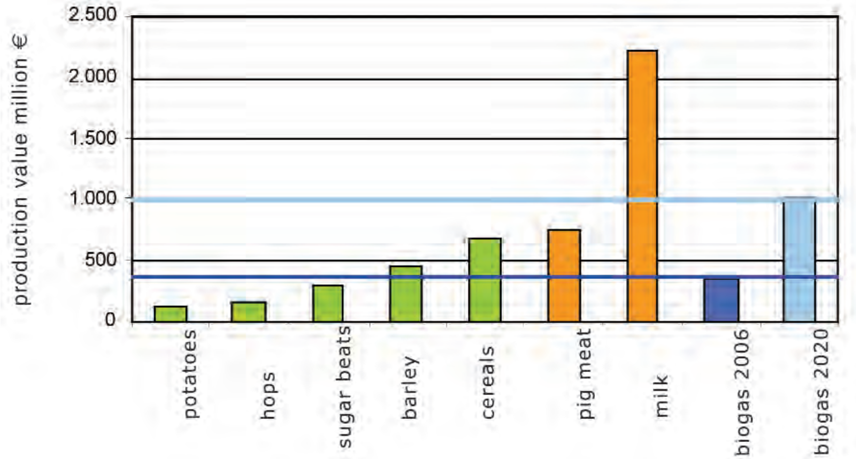


Figure 6: *Production value of agricultural products in 2006 in comparison with current production value of biogas.*

2. RESEARCH ON BIOGAS PRODUCTION IN BAVARIA

At the Bavarian Research Center for Agriculture (LfL), a key activity for biogas research was started in 2005. This involved nine institutes of LfL and several external research institutions. As to research concerning microbiology, technology, and biochemistry, various laboratory-scale digesters have been developed and are now used (Fig. 7).

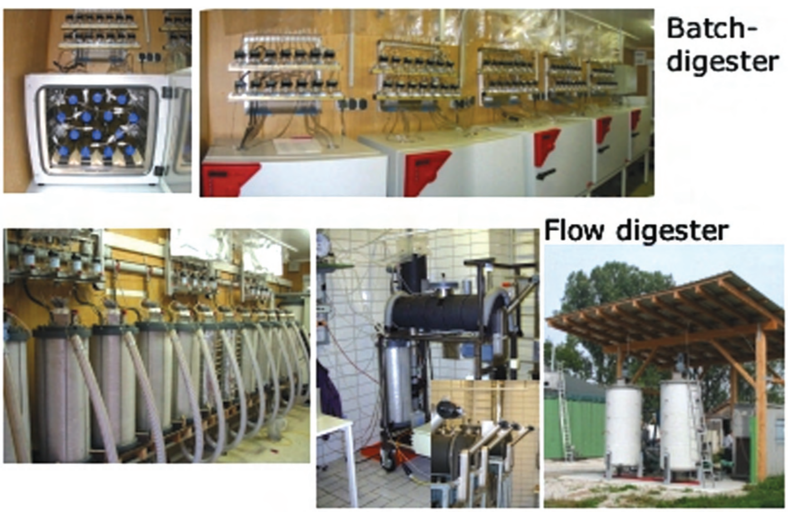
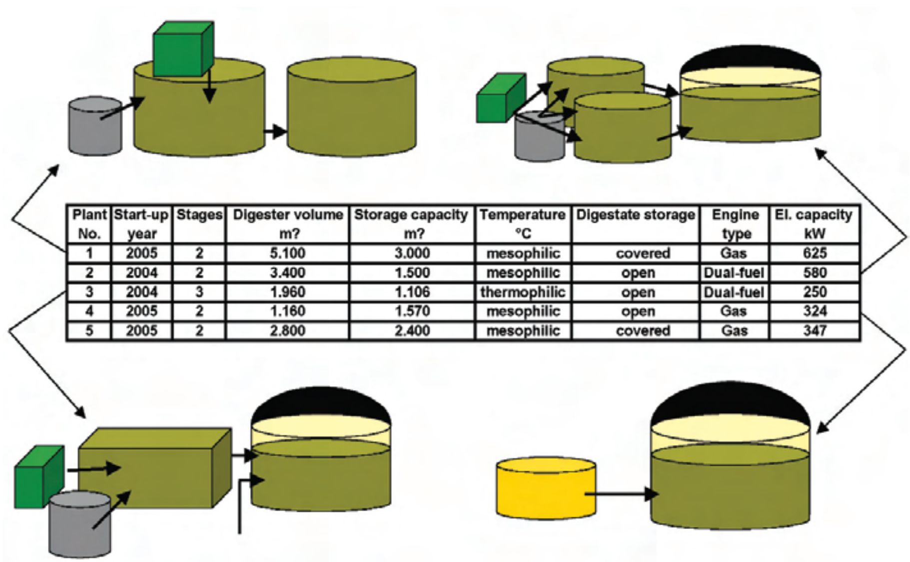


Figure 7: *Lab-scale and bench-scale experimental digesters at the LfL (228 batch; 72 flow).*

To verify the scientific results in practice, monitoring and data screening are in progress at 42 biogas plants in Bavaria. The focus of this monitoring project is to assess efficiency and evaluate the different technologies and to look into their maintenance. The main objectives are:

- Creation of a data pool concerning efficiency, functionality, and reliability of agricultural biogas plants;
- Improvement of concepts applied in practice to increase biogas yield from renewable primary products (RPP), organic residues, and manure;
- Evaluation of applicability of different technologies for the digestion of energy crops.

The biogas plants monitored can be classified into four specific groups (technological systematisation) (Fig. 8).



Plant No.	Start-up year	Stages	Digester volume m?	Storage capacity m?	Temperature °C	Digestate storage	Engine type	El. capacity kW
1	2005	2	5.100	3.000	mesophilic	covered	Gas	625
2	2004	2	3.400	1.500	mesophilic	open	Dual-fuel	580
3	2004	3	1.960	1.106	thermophilic	open	Dual-fuel	250
4	2005	2	1.160	1.570	mesophilic	open	Gas	324
5	2005	2	2.800	2.400	mesophilic	covered	Gas	347

Figure 8: *Systematisation of biogas plants in Bavaria connected to the monitoring project of LfL.*

3. PARAMETERS EVALUATED AND RESULTS FROM THE BAVARIAN BIOGAS MONITORING PROJECT

3.1 Measuring equipment/process monitoring

- Continuous online data monitoring
  - * Weighing of input material
  - * Biogas flow meter
  - * Biogas analyzer (CH_4, O_2, H_2S; possibly CO_2, H_2)
  - * Electric meter for generated electricity + own electricity
  - * Demand
- Regular sampling for chemical analysis
  - * Quality control of input : DM, oDM, (total C, N)
  - * Projection of methane yield: Weender, van Soest
  - * Digester content: DM, oDM, individual volatile fatty acids (alternatively: total organic acids + alkalinity), NH_4-N, (pH)
  - * Digestate: DM, oDM, (total C, N, total organic acids)
- Individual economic data evaluation (costs and income)
- Pathogen analysis.

3.2 Exemplary results from the biogas monitoring project

3.2.1 Weighing of input material

Estimation of input mass is faulty: continuous weighing is required (Fig. 9).

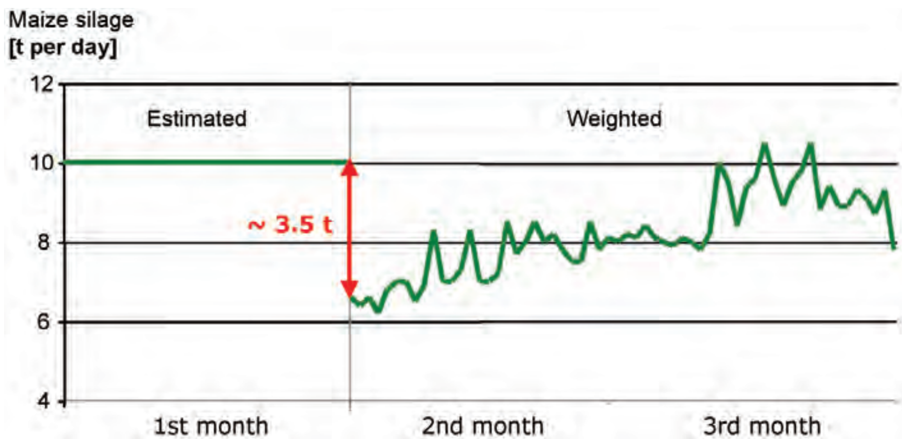


Figure 9: *Errors from estimating the mass input (t d-1) in comparison with weighing.*

3.2.2 Influence of fodder ingredients/quality and mass input on process stability.

Different fodder exhibits different biodegradability, methane potential, and nutrition quality for microorganisms. In practice, the mix and quality of input materials showed great variability (Fig. 10).

Process stability was influenced by numerous factors such as content of nutrients and their microbial availability, and the concentrations of intermediary products such as volatile fatty acids.

Process efficiency and overall energy yield are connected closely. Various examples have shown that discontinuous feeding and varying the organic loading rates caused fluctuations in the methane content and biogas production rate. Consequently, the power output fluctuated considerably.

Figures 11 to 13 show an example of process monitoring by chemical analysis of digester samples and continual data logging.

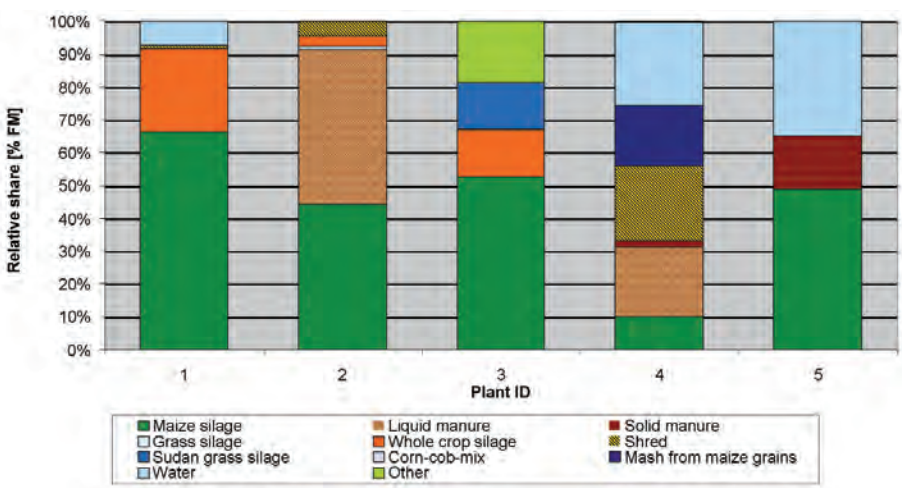


Figure 10: *Mix of input materials for five sample biogas plants.*

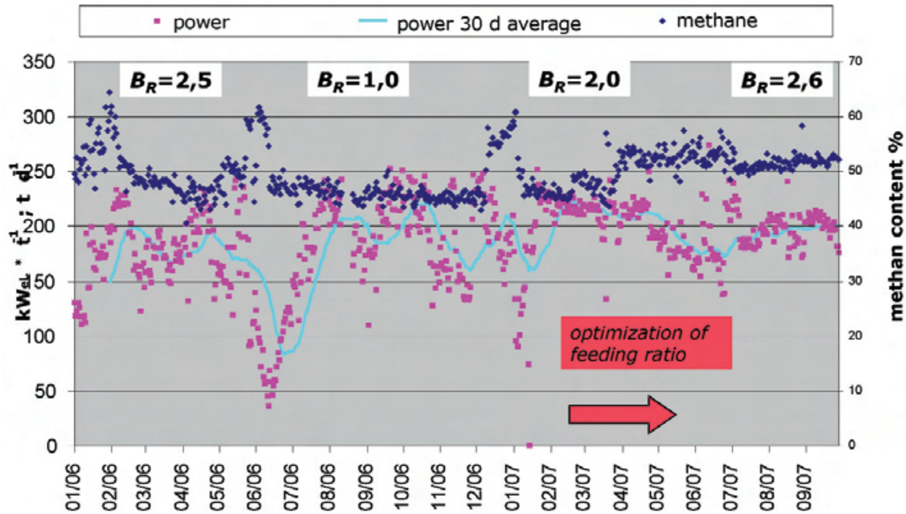


Figure 11: *Example from practice: Variation of electrical power output, fodder input per day, and methane content in the biogas (BR = organic loading rate in kg per m^3 digestor volume and day).*

Up to the point when an optimised feeding took place, the concentration of fatty acids increased several times (red arrows in Figure 12). The increase of propionic acid indicates the start of the acidification process and the inhibition of acetate and methane formation. In the end, daily energy production could be increased stepwise (Fig. 13); from an average daily electricity input into the grid of 4300 over 5800 up to 7150 KWh d^{-1}). Bared on tariffs in Germany, this results in an increase of cash flow from 800 over 1100 up to 1300 per day.

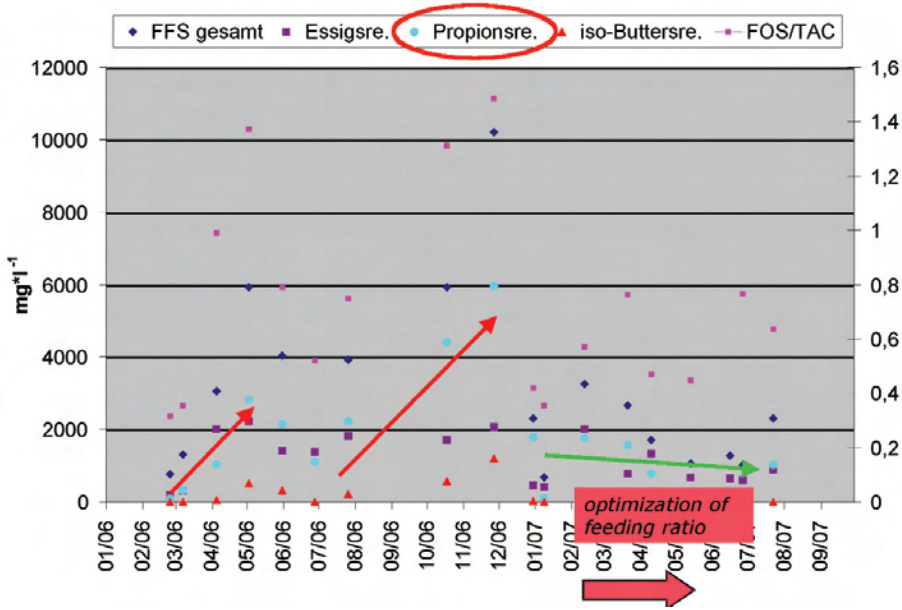


Figure 12: *Development of fatty acid concentrations in the digester samples.*

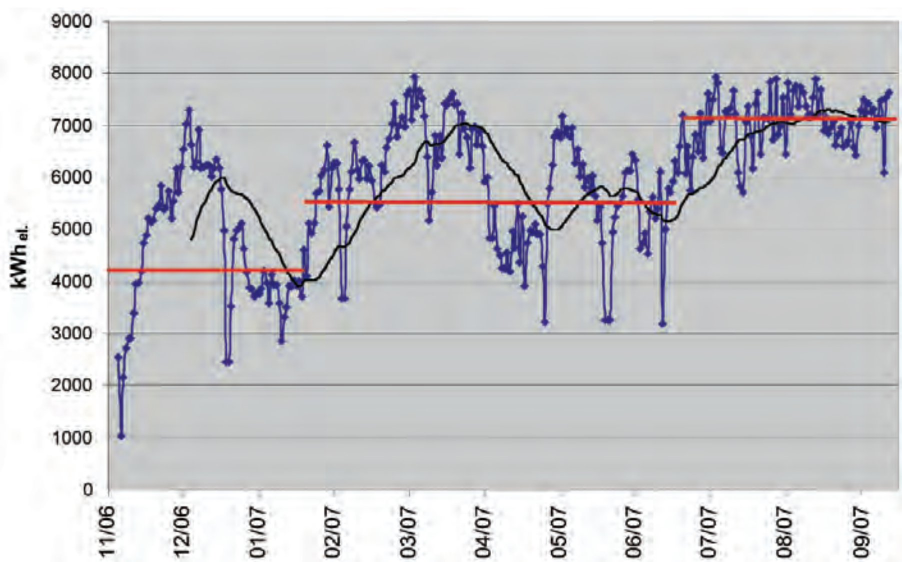


Figure 13: *Increase of energy yield (electricity due to optimised feeding of the digester).*

3.2.3 Influence of different biomass on biogas yield.

The high variability of biodegradable organic matter caused high variation in potential biogas yield. The content of carbohydrates, proteins, and lipids and their biodegradability define the amount of biogas that can be expected (Fig. 14).

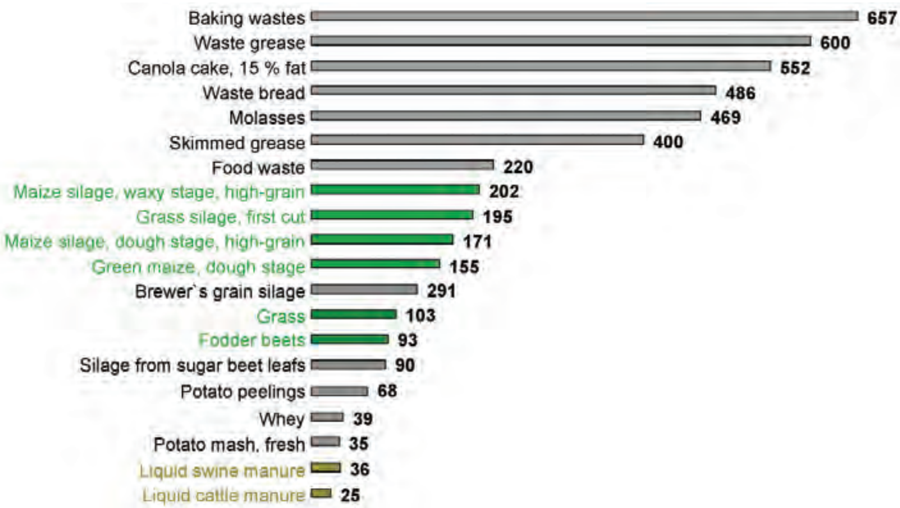


Figure 14: *Biogas potential of different biomass (m^3 gas per tonne fresh matter).*

3.2.4 Economic benefits

As the evaluation of three exemplary plants in Bavaria showed, there was high variability of investment cost (Fig. 15). The integration of biogas installation in an existing farm plays an important role. The largest investment is needed for the installations and infrastructure, followed by investment on technical installations and the cogeneration unit. As shown in Figure 16, investments related to installations and structure can be minimised for farm integrated plants. The startup period can also affect the cost efficiency of a biogas plant (Fig. 17). A difference of 84.000 € gross income showed dramatically how important additional investments for analytical consultancy can be.

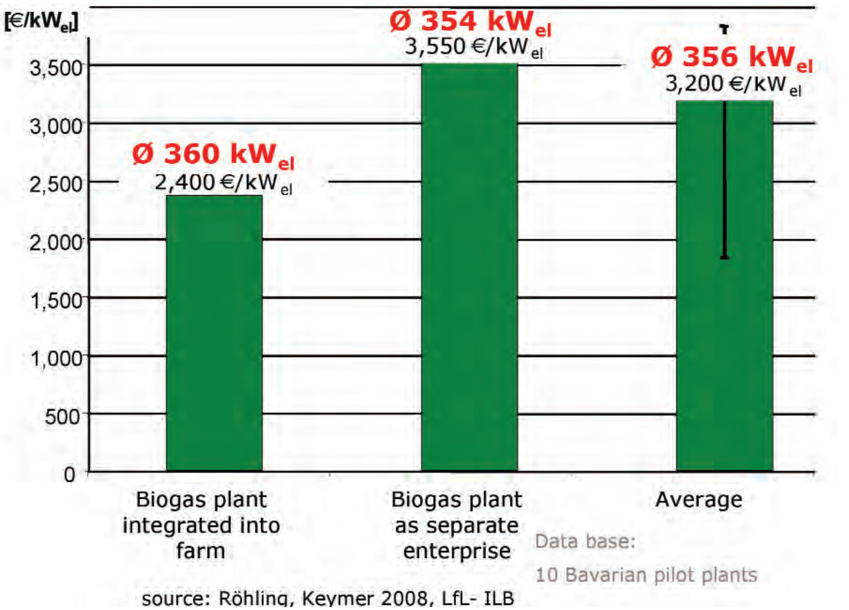


Figure 15: *Comparison of three exemplary biogas plants: specific investment costs.*

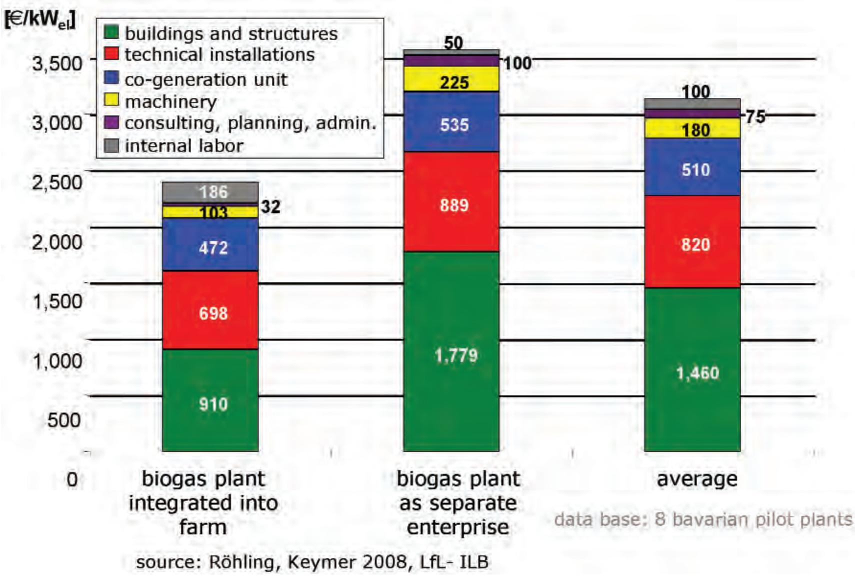


Figure 16: *Comparison of three exemplary biogas plants: specific investment costs – differentiation of cost factors of the digester.*

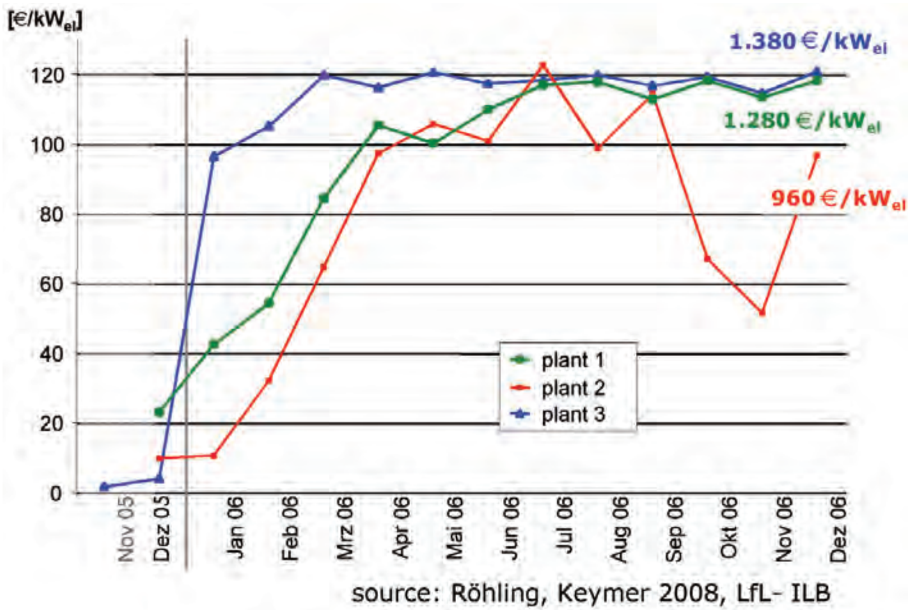


Figure 17: *Comparison of three exemplary biogas plants: variation of specific income during startup and initial period of operation.*

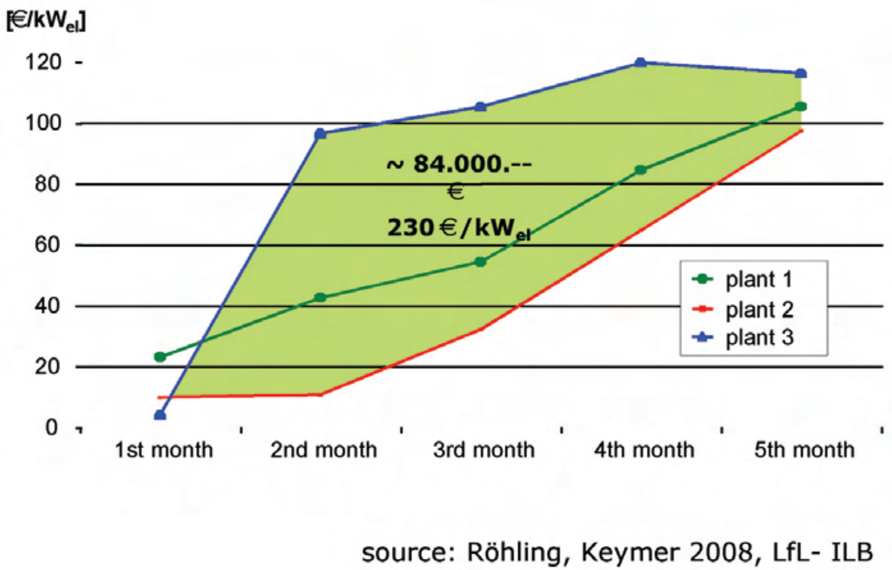


Figure 18: *Comparison of three exemplary biogas plants: influence of variation of startup quality on specific gross income.*

3.2.5 Greenhouse gas emissions from biogas production-evaluation of emission reduction.

To evaluate and compare different concepts and installations of biogas plants with respect to GHG emissions, several sectors have to be analysed and balanced. The main sectors are energy inputs for the installation and inputs for the production of renewable crops. On the other hand, methane emissions during slurry storage are avoided by anaerobic treatment. Own-energy consumption of the plant and methane emissions (21 times higher CO_2-equivalent) have to be included in the calculations. If the biogas plant distributes heat, the substitution value of the heat also has to be included. With all the relevant factors considered, the GHG balances for individual plants can be calculated and compared (Fig. 19).

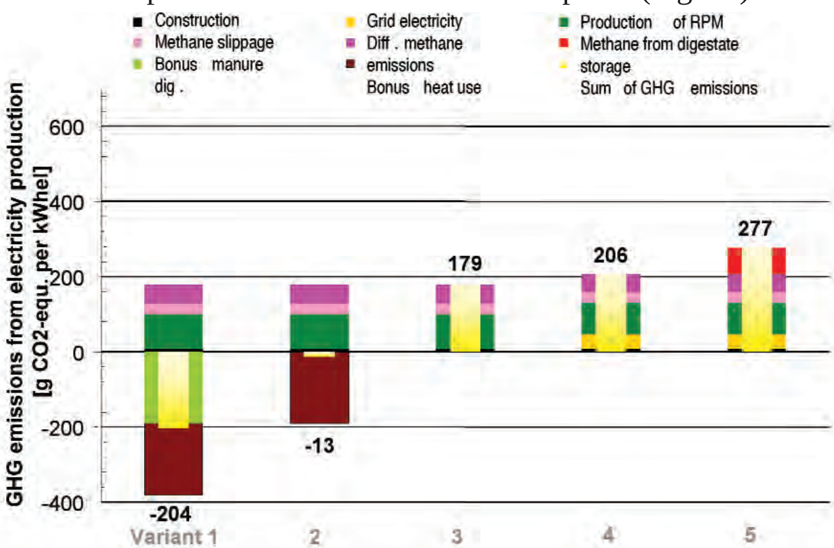


Figure 19: *Comparison of five scenarios: variation of greenhouse gas emissions (CO_2 equivalents from several sources).*

Variant 1:

- 1/3 of organic dry matter input from animal manure,
- Feed-in of surplus electricity only,
- Gas recovery during digestate storage,
- 65% utilisation ratio for off-heat

Variant 2: 100% renewable primary products (RPP) as input
Variant 3: No heat use
Variant 4: Plant electricity demand supplied from grid
Variant 5: Open digestate storage.

Production of energy crops causes CO_2 emissions due to energy consumption and N_2O-emissions (GWP: 310). GHG emissions for five biogas plants in practice are shown in Figure 20.

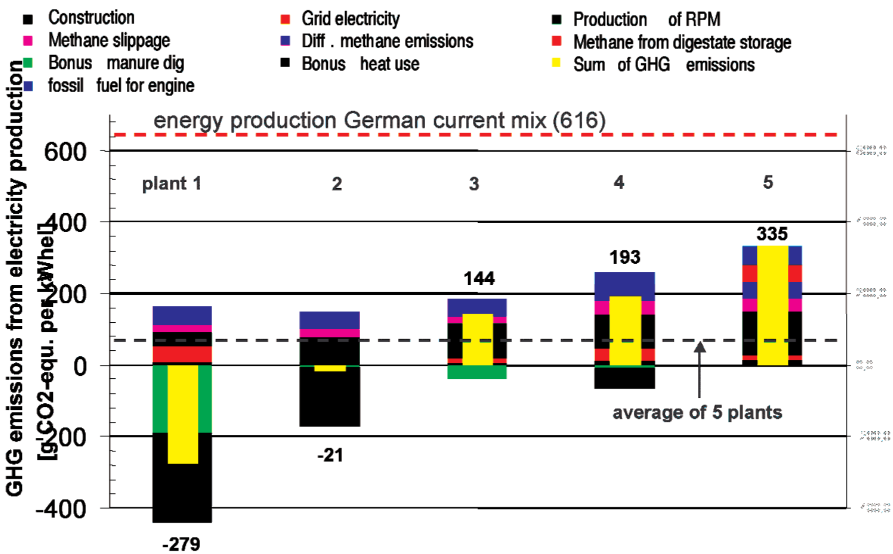


Figure 20: *Comparison of five biogas plants in Bavaria: variation of greenhouse gas emissions (CO_2 equivalents) from several sources.*

The data showed that specific GHG emissions of electricity production from biogas (RPP + manure) were significantly below current German grid emissions. Different measures are available to effectively reduce GHG emissions of agricultural biogas plants. A main target is the reduction of leakiness of biogas installations. Also, the biogas produced during digestate storage must be collected. The electricity demand of the plant should be satisfied from its own production. Additional measures to reduce GHG emissions are efficient heat use and digestion of animal manure. Still, there is a high demand for research on N_2O emissions from energy crop production.

3.2.6 Sanitary effects of anaerobic digestion

Anaerobic digestion can also improve the hygienic status of the organic fertiliser. Based on investigations at a three-stage (mesophilic-thermophilic-mesophilic) biogas plant digesting liquid dairy cattle manure, it is proposed that in sensitive areas with respect to (drinking) water management, thermophilic AD (4 h, 55 °C) should be applied to treat manure before soil application. A reduction of relevant pathogens in the digested manure of up to 99.99% or 4 log units was achieved (Fig. 21). To improve the bathing water quality in the catchment area, even mesophilic AD will be helpful.

Parameter	Reduction (^{10}log) Berbling (8-9h, 55°C)	$T_{99.99}$ (h) thermophilic Berbling / literature	score
Fecal coliforms	4.8 - 6.0 < bathing water direc[illegible]	0.12 - 1.6	
Enterovirus sp.	not detect[illegible]	0.12 - 0.36	
Thermophilic campylobacters	> 1 (3 CF[illegible]	0.04 - 0.15	
Yersinia enterocolitica	[illegible]	0.27 - 2.04	
Rotavirus sp.	[illegible]ted	0.48 - 1.2	
Norovirus (Gg1+2)	[illegible] detected	(ca. 4?)	
Coliforms / *Serratia marc*[illegible]	3.5 - 5.6 [illegible]bathing water directive	n.a.	
Cryptosporidium parvu[illegible]	> 5	< 0.8 ~~[8.9 [illegible]]~~	
Intestinal enterococci	> 2.5 - 3.0	4 - 6.8 (1. phase)	
Bacillus cereus group	0	3298 - 400000	
Clostridium perfringens	0 - -0.5	10629 - 400000	

more sensitive at thermophilic conditions, too: all relvant agents of viral epizootics (M. Hoferer, 2001)

MGRT: > 4 h (8 - 9 h) at ≥ 55°C

Figure 21: *Reduction potential of thermophilic (55 °C) anaerobic digestion for minimal guaranteed retention time (MGRT) > 4 h.*

4. KEY POINTS FOR SUCCESS

Overall, several factors are responsible for the successful operation of a biogas plant:

- Realistic economic projections
- Utilisation of heat energy
- Reasonable construction costs, particularly for smaller plants
- Flexible design to facilitate extension
- Cost, quality, and mix of input materials
- Well-dimensioned technical installations
- Integration into local infrastructure (logistics + heat usage)
- Process monitoring and control

- High engine utilisation ratio (target: ≥90% 7900 operating hours per year)
- Low residual methane potential (target: <3% of input) or closed digestate storage, including gas utilisation
- Promotion of additional ecological benefits such as sanitation of manure.

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Literature is available online at
http://www.lfl.bayern.de/arbeitsschwerpunkte/as_biogas/12229/

STATE-OF-THE-ART BIOGAS PRODUCTION IN ITALY

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SUMMARY
The CRPA carried out a survey of all operational anaerobic digestion (AD) plants in Italy in the livestock and agro-industrial sector to create an archive capable of providing a complete picture of the dimensions of this sector in Italy and of the main plant characteristics. In October 2007, 185 biogas plants were identified to be working with livestock effluents, energy crops, organic residues, waste from the agro-industrial sector, and the organic fraction of urban refuse. This figure includes those plants still waiting for authorisation and those still under construction. The majority of the plants surveyed (154) operate with livestock effluent, agricultural waste, agro-industrial residues, and energy crops. There are now 115 examples of active plants using livestock effluents. This represents an increase of about 43 units since the last survey in 1999 (+60%). When those still under construction are considered, this is an increase of 78 units (+108%). This confirms the strong expansion of the AD sector in Italy.

1. INTRODUCTION

In Europe, the development of the anaerobic digestion (AD) process began in the sector of civil sewage treatment plants. Aimed primarily for the stabilisation of sludge, current estimates put the number of operational digesters at more than 1600. As things stand at the moment, this technique is considered one of the best treatments of wastewater from agro-industrial complexes with high organic content. As early as 1994, there were about 400 business and consortium biogas units; today, more than 3,500 anaerobic digesters operate using livestock effluent in all countries of the European Union. The highest number is in Germany, followed by Denmark, Austria, Sweden, and Italy. There are currently about 450 active plants for biogas recovery from MSW landfills with a high concentration in Great Britain. This type of treatment is being increasingly supplemented in recent years by the treatment of the organic fraction derived from the differentiated collection of municipal waste (biowaste), digested with other organic industrial waste and livestock slurries. In Denmark alone, 20 centralised co-digestion plants of this type exist, treating about 1,750,000 tons of livestock slurry and 450,000 tons of organic industrial and biowaste.

A recent survey showed that about 130 AD units are treating the organic fraction of urban refuse coming from both differential collection and mechanical sorting, following collection and/or organic industrial waste.

It is estimated that, for 2006, the production of biogas by European countries was about 5,347 ktoe (ktoe = kiloton of oil equivalent). Of this figure, about 60% came from the recovery of biogas from urban waste tips (EurObserv’ER 2007). EurObserv’ER forecasts 2010 biogas production in the vicinity of 8,600 ktoe. Organic refuse produced yearly by European Union countries amounts to about 2.5 billion tons, of which about 40% is livestock effluent and agricultural waste and the remainder being made up by urban and industrial waste, sewage sludge, and wood-cellulose waste from forestry (the only part that could not be used in AD (source IEA Bioenergy task 37, www.iea-biogas.net). The country where AD has been most developed over the last 10 years is Germany, particularly in its livestock sector.

This is the result of a policy incentive adopted by the national government, which, in addition to contributing toward investment, pays a price for electrical energy from biogas, which may reach 0.215/kWh over a period of 20 years. At the end of 2006, according to data produced by the German Biogas Association, there were about 3500 active units, with primary production of energy from biogas of 1923 ktoe.

The situation is different in Italy where EurObserv’ER estimates that biogas production in 2006 stood at 353.8 ktoe (about 4 TWh). Of this, about 80% comes from the recovery of biogas from urban waste tips.

In the context of a research project into AD of cattle slurry financed by the Region of Emilia-Romagna, CRPA surveyed all active AD plants in Italy in the livestock and agro-industrial sectors to set up a database of the sector dimensions in Italy and the main plant characteristics. The sector is strongly expanding, both in terms of construction of new plants and founding new companies or business areas interested in the construction of a complete plant and/or related components. This may mean that the data collected in October 2007 are not complete or exhaustive.

2. THE SURVEY

The survey method made use of a questionnaire aimed at gathering the main information relating to the business, the technical characteristics of the plant, the substrates used, and the energy conversion of the gas. Data collection was done through visits to some of the larger plants while sending the questionnaires to plant businesses of the sector, requesting their collaboration in providing some plant details. In addition, a number of people identified as key figures were interviewed, contacts were made with a number of public administration staff, together with professional firms working in this area and agricultural associations.

3. THE RESULTS

As at October 2007, 185 biogas plants were identified to be operating with livestock effluent, energy crops, organic residues, discharges from the agro-industrial sector, and the organic fraction of municipal solid waste. This number includes plants awaiting authorisation and those under construction. Majority of the units surveyed, that is, 154 (Table 1) operate with livestock effluent, agricultural waste, agro-industrial residues, and energy crops. No account has been taken (as this was not covered under the project) of AD plants for the stabilisation of civil and industrial sewage sludges, for the most part constructed within large urban civil and industrial sewage treatment work. Based on an earlier survey (Gerli A., Merzagora W., 2000), it was estimated that there were more than 120 large-scale plants in this category.

The recovery of gas from urban waste tips was also significant. Here, there are about 113 operating plants and about 164 MWe installed (data GSE as of 30 Jun 2007) representing another important source of biogas from biomass.
Of the plants using livestock effluent, 115 were active (Table 1). This number represents an increase of about 43 units (+60%) with respect to the 1999 survey and 78 units (+108%) if one takes into account those still under construction. This confirms that anaerobic digestion is expanding strongly in Italy.

Table 1 - *The age of biogas plants operating with livestock slurry.*

Age of operating plant	**Plant (numbers)**
> than 16 years	10
Between 5 and 15 years	59
Less than 5 years	31
Data not available	15
Total operating	**115**
Under construction	22
Under authorisation	17
Total	**154**

Figure 1 shows a map of Italy with the number of plants identified by the survey in each region. The plants have been constructed mostly in the northern regions. The areas most affected are those with the highest concentration of livestock farms-Lombardy, Emilia-Romagna, and Veneto. Some plants are being constructed in areas where significant quantities of waste and organic by-products are produced by the agro-industrial sector. These will be used in co-digestion, becoming a part of a management solution to recover this waste.
Plant number was significantly small in central and southern Italy. On the other hand, the number of plants present in the province of Bolzano is influenced by its proximity to Austria and Germany, in addition to the extensive policy of incentives adopted by the provincial administration.

Figure 1 - *Breakdown of biogas plants, by region (154, of which 115 were operational, 22 were under construction, and 17 were waiting, for authorisation) processing livestock effluent, agricultural and agro-industrial waste, and energy crops.*

Table 2 shows an analysis of the surveyed plants in terms of type of substrates processed. The number of plants using only pig slurry is note worthy. Some of these were simplified biogas plants mainly constructed in the early 1990s, with a plastic covering fitted to a slurry storage tank and/or a lagoon. Subsequently, there has been increased interest in Italy as well in the co-digestion of livestock slurries mixed with other biomass such as energy crops and organic waste.
In seven of the cases surveyed, chicken manure was used: in four plants, this substrate was processed in a mixture with other livestock effluents and/or organic waste, while in three plants (two still awaiting authorisation), chicken manure was used in a mixture of only organic waste and/or energy crops without pig and/or cattle slurry.

Table 2 – *Number of plants, per type of substrate.*

Type of sub-strate processed	Plant (numbers)
Only pig slurry	44
Only cattle slurry	38
Pig and cattle slurry	5
Pig and/or cattle slurry and/or chicken manure + organic waste + energy crops	35
Pig and/or cattle slurry and/or chicken manure + energy crops	20
Energy crops and/or organic waste	9
Chicken manure + organic waste and/or energy crops	3
Total	**154**

With reference to the type of reactor (Table 3), the most common by some distance was that of the stirred and insulated tank with vertical walls (CSTR = completely stirred tank reactor) in the majority of cases constructed in reinforced concrete. There was only one plant (see "Other"), that used dry fermentation of biocells. The piston-driven horizontal flow reactor (PFR = plug flow reactor) was used in 40 of the surveyed plants, this type being particularly prevalent for the processing of pig slurry.

Table 3 – *Plants classifield according to reactor type.*

Reactor type	Plant (numbers)
Vertical sided tank (CSTR)	77
Anaerobic lagoon	3
Piston-driven horizontal flow reactors (PFR)	40
Other	1
Data not available	33
Total	**154**

In the majority of cases, the digester volume (Table 4) was between 1,000 and 5,000 m^3. There were only 20 plants bigger than this range.

Table 4 – *Plants classified according to total reactor volume.*

Total volume of digester	Plant (numbers)
< 500 m^3	24
Between 500 and 950 m^3	17
Between 1,000 and 5,000 m^3	47
> 5,000 m^3	20
Data not available	46
Total	**154**

Tables 5 and 6 show a breakdown of biogas plants according to process temperature and their hydraulic retention time (HRT). The temperature most commonly used in the plants was between 30 and 40 °C (mesophilia). It should be noted, however, that eight plants work at temperatures over 50 °C (thermophilia). Even though this figure represents only 9% of the 97 plants for which information was available, it was nonetheless significant. With regard to HRT, plants with an average time between 16 and 25 days are the most common.

Table 5 – *Plants classified according to process temperature.*

Process temperature	Plant (numbers)
Psychrophilia	8
Mesophilia	81
Termophilia	8
Data not available	57
Total	**154**

Table 6 – *Plants classified according to hydraulic retention time.*

Process temperature	Plant (numbers)
< 15 days	3
Between 16 and 25 days	45
Between 26 and 35 days	9
> 36 days	37
Data not available	60
Total	**154**

As far as the use of biogas is concerned, in those plants using livestock effluent co-generation is the most common model. Only eight plants, generally connected to cheese-making dairies for the production of "Grana Padano" or "Parmigiano-Reggiano," burn the biogas directly in a boiler solely for heat production (the real value is probably greater).

Of the 154 plants processing livestock effluent, agricultural and agro-industrial waste, and energy crops, 44 have installed electrical power of less than 100 kWe and 14 of more than 1 MWe (Table 7); this came to a total of about 49 MWe installed for the plants for which data were available.

Table 7 – *Plant classified according to installed electrical power.*

Electrical power	Plant (numbers)
< 100 kWe	44
110 - 500 kWe	28
110 - 1,000 kWe	19
>1 MWe	14
Biogas burnt in boiler	8
Data not available	41
Total	**154**

During the research, information was provided by sector businesses concerned with plants that only process agro-industrial wastewater–it was possible to obtain information on the main points of interest from 22 plants.
Seven plants were also identified that process the pre-sorted organic fraction resulting from the differentiated collection of urban waste (biowaste), either on its own or mixed with sewage sludge. There were two plants that process the organic fraction resulting from mechanical sorting mixed with sewage sludge.
Of the plants using livestock effluent, another four (one of which was under construction and one awaiting authorisation) process biowaste together with slurry, chicken manure, agro-industrial sludge, and energy crops.
To complete the picture, Table 8 shows the number of biogas plants in each region, by category, including those that do not process materials of an agricultural or agro-industrial origin. Plants for the recovery of biogas from MSW landfills have been excluded.

Table 8 – *Regional distribution of biogas plants, by category (not including plants for the recovery of biogas from urban waste tips).*

Region	Livestock Effluent +organic waste + energy crops(1)	Civil sewage sludge(2)	Agro-industrial waste	Biowaste + sewage sludge	Total
Lombardy	48	12	2	1	**63**
Emilia- Romagna	30	21	7	1	**59**
Trentino-Alto Adige	34	8	0	1	**43**
Veneto	17	11	3	3	**34**
Piedmont	6	21	0	1	**28**
Tuscany	1	10	1	1	**13**
Puglia	0	11	1	0	**12**
Campania	1	5	3	0	**9**
Sardinia	7	0	0	1	**8**
Marche	0	7	1	0	**8**
Lazio	0	5	1	0	**6**
Liguria	0	5	0	0	**5**
Friuli-Venezia Giulia	2	3	0	0	**5**
Umbria	2	2	0	0	**4**
Basilicata	2	0	1	0	**3**
Abruzzo	1	0	1	0	**2**
Valle D'Aosta	2	0	0	0	**2**
Calabria	1	0	0	0	**1**
Sicily	0	0	1	0	**1**
TOTAL	**154**	**121**	**22**	**9**	**306**

(1) Organic waste: agro-industrial waste and biowaste.
(2) Gerli A. and Merzagora W. (2000).

Figure 2 – *Regional distribution of biogas plants in operation and/or under construction in Italy (306), excluding plants for the recovery of biogas from urban waste tips:*

- *154 plants: livestock effluent + organic waste + energy crops*
- *121 plants: civil sewage treatment sludge*
- *9 plants: biowaste*
- *22 plants: agro-industrial waste.*

4. CONCLUSIONS

Over the last 10 years, AD has become established in many European countries. These were constructed not only for the purpose of recovering renewable energy or biogas, but also to control the emission of unpleasant odours and to stabilise biomass prior to their agronomic use.

In Italy, the law on auto-production of electrical energy from renewable sources (green certificates) has given rise to renewed interest in biogas. It could be given greater impetus by developing environmental policies concerned with the sector of energy enhancement of biomass, initiated following the Kyoto Conference on the reduction of atmospheric pollution from greenhouse gases. Further emphasis on the recovery of biogas may come from EC Regulation 1774/2002 on by-products of animal origin, identifying AD and composting as two biological processes, permitting their exploitation as an energy source and recycling as fertiliser. The new Common Agricultural Policy also provides incentives for energy crops. The combination of problems such as the greenhouse effect, the improved exploitation of organic waste, and the requirement for a greater contribution from renewable energy is thus bringing to light new opportunities that the agricultural world might be interested in taking advantage of. In particular, the livestock sector could be the driving force for the development of AD on a larger scale, something that is already happening in Germany, Denmark, Sweden, and Austria. The incentives to follow such a path are numerous: an improvement of the farms' "environmental sustainability," an additional source of revenue from "green energy," a reduction of environmental problems connected to atmospheric emissions and odours, and an improved agronomic use of the fertilising elements present in slurry.

These are the reasons that make it important to strengthen and rationalise systems that exploit anaerobic co-digestion processes for different kinds of biomass.

For these opportunities to be exploited in full, however, it is necessary that authorisation procedures underlying the construction of biogas plants, connection with national electricity grid, and use of various materials be made clearer and easier to satisfy compared with those currently in force. It is also essential to ensure the agronomic use of the digestate even when livestock slurries are co-digested with energy crops and selected organic waste.

The contribution that AD can make toward sustainability in energy terms of processing plants to reduce N levels in livestock slurries produced in vulnerable zones (pursuant to the Nitrates Directive) is also important. Finally, the construction of biogas plants may have good prospects for the future if biogas use is made easier (after purification for a methane content of 95-98%) in motor transport and in the natural gas distribution network.

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BIOGAS IN ITALY: TECHNOLOGIES AND OPPORTUNITIES

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SUMMARY

Biogas production from animal slurries in Italy is not something new. Since the late 1970s, its application had already been proposed as a possible solution to environmental problems connected with intensive pig farming. The experience gained, later on, turned out to be very fruitful in terms of coming up with a design of simplified anaerobic digestion units "tailored" for agriculture, which, together with economic feasibility, showed good odour control efficiency as well. Today, agricultural energy production has good development prospects, a consequence of the economic incentive system included in the normative framework. Because of the rising costs of oil and natural as, more and more countries have now passed laws aiming to enhance the use of renewable energy sources. The issue of different sets of rules in favour of the innovation technology is actually hoped for in the development of an Italian suite of integrated technologies which, besides supporting biogas production, would also allow farmers to achieve the proper nitrogen-SAU ratio.

1. INTRODUCTION

In the whole European Union (EU), primary energy production from biogas (including the one from landfills) had markedly increased in 2006-13.1% growth with respect to the 2005 production. In 2 years, there had been a significant increase in biogas produced by agricultural plants; this increase is mainly done by co-generation (through a combined heat and power process–CHP). Among EU members, the United Kingdom

and Germany are the leader countries in this regard (Fig. 1): the latter one, in particular, has this role as a result of a very effective incentive policy given to farmers. They produce electricity from small farm methanisation units involving CHP. With reference to the primary energy production in the EU, Italy has 88% of its production provided by landfill gas and only 12% from decentralised agricultural plants, municipal solid waste methanisation plants, and centralised co-digestion plants.
First estimates made by ENEA (Italian Agency for Energy, the Environment and New Technologies) indicate that the production of primary energy and electricity from biogas increased by 3% in Italy in 2006. Biogas plants using vegetal and organic wastes are recognised by the GRTN (Italian power grid manager) as being able to participate in the national green certificate system. In the Italian system, producers and importers use these certificates to prove that they have fulfilled their legal obligations to supply a certain percentage of electricity with renewable origin (2.7% in 2006). The mean price of a green certificate in Italy has been constantly increasing, reaching 13.91 c/kWh in 2006.

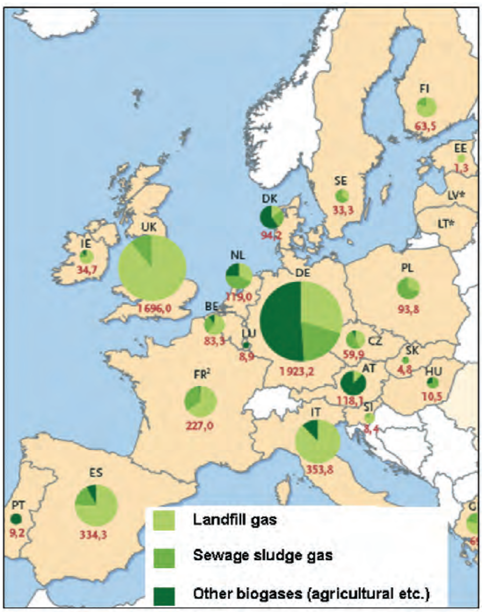

Figure 1: *Estimation of the primary biogas production (in ktoe) of the European Union in 2006 (Eurobserv'ER, 2007).*

2. ANAEROBIC DIGESTION IN ITALY: THE ORIGIN

When thinking of the origin of biogas production in Italy, we must go back to the 1970s when the Italian government passed environmental laws (e.g., law no. 319 of 10/05/1976, and 650/1979) whose main purpose was to address the environmental impact of large intensive animal farms (swine farming, in particular).

In 1980, a research project called "Biogas" was carried out in Emilia Romagna by CRPA, ENEA, ENI, ENEL, and a university. The result is the establishment of five demonstration and three experimental biogas units. The final document, entitled *"Production and Use of Integrative Energies in Zootechnics,"* then concluded that, with respect to slurry management techniques available, producing biogas was not worth it from the point of view of energy recovery. Nevertheless, it was claimed that biogas technology should be supported as well because of additional advantages that may lead to improvements in the balance sheet, a factor that could raise farmers' interest. Unfortunately, some of the predicted advantages turned out to be fallacious: first, slurry purification was found to be not feasible because of the stages needed to complete the process. The increase in fertilising power of the digested slurry was more theoretical than real and, considering agricultural practice in Italy at that time, the conversion of organic N into a readily available form turned out to be a disadvantage.

The remaining advantages were anything but secondary benefits of odour and pathogen reduction. At that time, these results could not justify the high investments required to put up biogas plants as they could be better achieved with simpler technologies?e.g., those not designed for energy recovery (aerobic intermittent treatment with low power requirements).

With this research, it was pointed out that

- anaerobic digestion had inadequate purification efficiency (as per limits for surface water discharge (Tables "A" and "C" of the Merli Law n. 319 of 10/05/1976),;
- the complexity and high cost of applied industry technologies made them inadequate for zootechnics;
- running any biogas plant for farmers would entail incentives that, besides partly covering the building and design costs (as mandated by law at the time), would increase the value of the produced energy;
- farm slurry alone had inadequate energy content and this cannot justify the cost of a very complex biogas plants for energy conversion.

3. RENEWABLE ENERGY SOURCE INCENTIVE PROGRAM

In the green certificate market, the sellers are the renewable energy source (RES) owners, who obtain certificates for each unit of electricity produced and supplied to the electric network. The government or a regulatory body authorised by the government sets as quantitative index a desired share of electricity to be produced by RES: buyers (either electricity consumers or electricity supply companies) are therefore obliged by law to buy the number of certificates that make up the set share of their electricity consumption.

The renewable energy incentive scheme provisions created interest toward biogas production in zootechnics by making it economically feasible. For this purpose, the very first legislative action, the so called CIP 6/92 (decision of the Interdepartmental Prices Committee n. 6 of 29 Apr 1992), established that the price for selling the produced electric power to the Italian National Energy Board (ENEL) should be about double that of the price of energy produced by that board. As a matter of fact, CIP 6/92 increased electrical power production from renewable sources and encouraged biogas utilisation with co-generation. This provision has been in force until the enactment of the "Bersani decree" (Italian law decree n.79/1999), which acknowledged in Italy EU Directive 96/92/CE unfreezing the energy market.

In the green certificate market, demand is represented by the obligation for energy producers and importers to offer a yearly amount of energy produced by RES: this amount had been fixed at 2% of the total amount of energy from conventional sources both produced and imported the previous year. From 2004 to 2006, that share increased annually at 0.35 percentage points (art.4 comma 1 del D.Lgs. 387/2003), whereas for the 3-year periods of 2007–09 and 2010–12, the set share had been established by the Italian Ministry of Economic Development at 3.05% with an increase of 0.75 percentage point per year until 2012. On the other hand, supply is represented both by the green certificates issued in favour of biogas producers which received IAFR qualification (Qualifica Impianti a Fonti Rinnovabili) from the "Gestore Servizi Elettrici" (GSE) and by the green certificates that the GSE issues on its own favour in account for the energy produced by six CIP plants.

Actually, the 2006-07 Italian financial law gave a very big impetus to biogas production because electric power production was at last defined as an activity related to farming. Moreover, the provisions about electric power production from renewable sources (e.g., D.lgs 387/2003, Del. AEEG n.34/2005, Italian laws 222/2007 and 244/2007), together with simplifications in authorisations and other incentives (e. g., a price for energy from renewable sources of 0.30 per kWh for biogas plants with less than 1 MW), helped achieve the economic feasibility of this activity. The introduction of these economical incentives, together with the selection of agronomic use of slurry as the best available option for slurry disposal, made AD of biomass interesting again because of its environmental importance (slurry stabilisation plus odour and emission reduction). Provided that biogas plant production is economically feasible, this was the starting point in the development of new, low-cost simplified biogas production technologies.

4. THE EVOLUTION OF BIOGAS PLANTS WITHIN ITALY

In Italy, at the end of the 1980s, a new generation of biogas plants started being introduced in the country. At first, these were extremely simple and with low realisation costs, mainly consisting of a plastic cover placed over the slurry storage tank. These units were set up not only for energy production purposes but for slurry stabilisation and odour control. Figure 3 illustrates the scheme of a very simplified "first-generation" biogas plant without the heating system equipment: by using such biogas plants, the estimated biogas production was about 15 m^3 y-1 of biogas per 100 kg of live weight (25 m^3 y-1 of biogas).

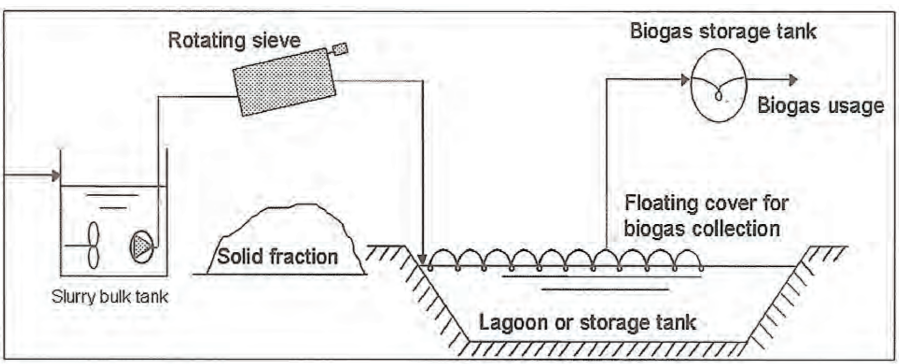

Figure 2: The *scheme of an "first-generation" simplified biogas plant without a heating system (from Piccinini, 2004).*

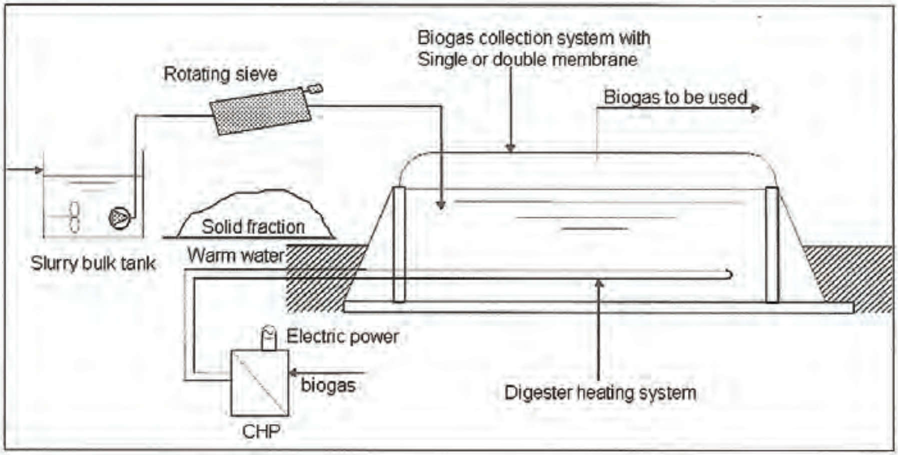

Figure 3: *The scheme of an "intermediate-generation" simplified biogas plant equipped with anaerobic digester heating system (from Piccinini, 2004).*

Thanks to co-generation with the CHP process, the subsequent heat availability stirred interest toward mesophilic AD as well.

On the other hand, as shown in Figure 3, taking advantage of co-generation allows farmers to produce both warm water to heat the biomass inside the anaerobic digester and electrical power that can be subsequently sold to the National Electric Company or used to cover farmers' needs. With such biogas plants, methane yield is about 23 m^3 y^{-1} per 100 kg of live weight (35 m^3 y^{-1} of biogas). With the introduction of the new provisions on the green certificates, interest in electric power production from RES increased and attention was focused on the German experience, as this was the country where biogas production remarkably increased as a consequence of the addition of agricultural biomass in the anaerobic digester to such an extent that farmers are driven to leave zootechnics to specialise on on-farm electric power production.

For this purpose, various types of biomass can be used (fodder cereals, green forages, grains, siomais, crop residues, etc.) and all these can be defined as raw materials of vegetable origin (in Italian, this is defined by the acronym *"MAPROV": (Materie Prime di Origine Vegetale)*. Nowadays, the main features of Italian biogas production units, despite being directly taken from German agricultural biogas facilities, are distinctiveness in the higher dimensions, automatic feeding of the digester, presence of in-line checking of biogas quality devices, constant use of slurry and, last but not least, existence of agricultural biogas plants using slurry only. With this framework, it is clear that the introduction of anaerobic co-digestion of vegetable biomasses increases the chance to enhance energetic potential of slurry as putting vegetable biomasses/by-products directly inside the anaerobic digester enables the conversion of their energetic content into biogas. Furthermore, the adoption of co-generation enables differentiation of farmer production by selling the produced energy, while the heat produced during CHP is effectively used to heat the digester or to meet other objectives (e.g., distance heating systems).

To optimise AD efficiency, there is the need for microorganisms to stay 'in touch' with the fermenting biomass and this is ensured by thorough mixing. Achieving a complete mix of the biomass is influenced by many variables (e.g., digester volume, biomass' solid content) and different mixing solutions are actually available on the market, which can be divided into two big categories: hydraulic and mechanical devices. The former device takes advantage of an external pump that redistributes the biomass by means of strategically placed nozzles inside the digester: its main advantage is the complete absence of mechanical devices inside the digester. The latter, in contrast, are characterised by big steel revolving blades placed inside the digester that, with their rotation, keep the biomass thoroughly stirred: these are actually the more frequently installed but they have the disadvantage that, in case of maintenance, the digester must be emptied with a subsequent stop of energy production.

Anaerobic digestion as related to animal farming was proven to have a favourable environmental impact because

- it allows slurry stabilisation to be achieved with a significant reduction of greenhouse gas and odour emissions both during storage and agronomic use of the digested slurry (Clemens et al., 2006; Monteny et al., 2006; Loughrin et al., 2006; Schiffman S. S., 2005);
- it allows good abatement of microbial activity (Albinh et al., 2007; Heinonen-Tanski, 2006; Sahlstrom, 2003; Coté et al., 2006; Juteau, 2006);
- it reduces slurry solid content and the homogenisation rate achieved allows better agronomic use because of nutrient and N availability, together with a reduced C-N ratio (Loria et al., 2007; Massé et al., 2007);
- the energy produced can be effectively used to reduce the N load of the livestock unit (Marti et al., 2007; Uludag-Demirer et al., 2008; Waki et al., 2007).

The mixing of different products allows compensation for seasonal variations in slurry composition, helping avoid either overload or insufficient load of the digester and making the process more stable. It thus makes it possible to achieve a better balance among the nutrient and carbon content (Msandete et al., 2004; Parawira et al., 2004; El-Mashad et al., 2007; Lehtomäki et al., 2007) and set up positive interactions among the microbial populations inside the digester (Mata-Alvarez et al., 2000). The vegetable biomass more widely used in co-digestion with slurry comprises energy crops whose production should be set in sustainable rotation (Amon et al., 2007). Organic by-products that can be used for co-digestion come from different sources and have very different chemical compositions and biodegradation ability., food wastes, because of their highly degradable nature, could be an ideal co-digestion substrate (Zhang et al., 2007).

5. CONCLUSIONS

A wider diffusion of biogas plants is likely to happen in Italy, provided the government gives enough incentives to farmers who produce energy from renewable sources. Given that, there should be better coordination among the different authorities involved in the release of production licences for a more clearly regulated and simplified use of agricultural by-products. Furthermore, the development of integrated technologies, which allow farmers to achieve the proper N-SAU ratio, is clearly necessary to force biogas production. As to legal support, a different set of rules for innovation technology promotion is critical to develop a suite of technologies. Other possible developments of this sector can briefly be summarised as follows:

- A wider surface should be left to agricultural used surfaces cropped for energy purpose, considering that 1 ha gives from 3.5 to 5 kW of electric power.
- The biogas plant should not be too far from the energy crop production site; the distance of the biogas plant from the crop area is expected to be short.
- Some energy crops are actually grown for feed: the consequence of this is that their “energy” destination will compete with the feeding route.
- The use of agro-industrial by-products for biogas production can be considered an effective economical-environmental source.

Interest in Italian agriculture and these recent issues fully correspond to the resolution on sustainable agriculture and biogas issued by the EU parliament to fulfil the need to review EU legislation in this area (EU Parliament, 2008). This is in recognition of the fact that biogas is a vital energy resource, highly contributing on one hand to sustainable economy, agricultural and rural development, and environmental protection and being able to reduce, on the other hand, EU's energy dependence on imports. Moreover, with regard to biogas economic viability, it is recognised that further advancement of biogas production and technology is not possible without additional funding for research and development: it is desirable that such European recommendation will help overcome the obstacles related to bureaucratic tape in the release of the needed licences.

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NITROGEN REMOVAL FROM DIGESTATE: CONVENTIONAL AND ADVANCED TECHNOLOGIES

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SUMMARY

More stringent limits on maximum N load for land application of raw and digested animal wastes require sustainable N removal processes. Digested effluents have a higher N-C ratio than raw substrates, as anaerobic digestion (AD) converts carbon to biogas, but not N. However, AD is effective in converting particulate N (proteins) into soluble ammonium. The main processes for the removal of N from the liquid fraction of the digestate are briefly outlined. High efficiency solid/liquid separation is required to achieve a solid product with an acceptable N content for subsequent aerobic treatment and land spreading. The concentrated liquid, rich in N, can be processed by physical and chemical or biological processes. The latter are far cheaper and do not pose problems of by-product disposal, as N is converted into molecular N2 gas released to the atmosphere. Novel processes that bypass the conventional conversion into nitrates or that make use of recently discovered bacterial strains are also briefly described.

1. INTRODUCTION

Nitrogen removal from digestate is one of the key options to face the more stringent limits for land application of manure in Italy (DMPAF 209/06, G.U. 120 12/05/06) and in Lombardy (Regional Council Decree

3439/2006). In fact, if compared with previous limits and considering the worst case scenario (sensitive land areas and cattle breeding), a reduction of the N load up to 1/3 is required or, alternatively, a larger land surface area for manure spread is needed to fulfil regulations. The "nitrogen problem" is sometimes, but incorrectly, considered as an "anaerobic digestion problem", as though the need to reduce N arises from the anaerobic digestion (AD) of manure and livestock wastewater. Although the AD process does not reduce significantly the overall N load of the feed, the thermal and electrical energy produced with biogas and the relevant revenues can support the requirements and costs of N removal technologies.
In case of co-digestion of manure with organic substrates (energy crops, agro-industrial waste, etc.) the application or disposal of the digestate should also take into account the additional N of the co-substrate. In this regard, the ratio of N to volatile solids (N/VS) in the raw substrates provides preliminary information on the expected producible biogas increase and on the expected N increase in the digestate (Table 1).

Table 1 – *Average content of total (TS) and volatile solids (VS) and N concentration (from Navarotto, 2006).*

Substrate / Component	TS (%		VS (%		n (asTS%		N (kgt_{ww}^{-1})
	min	max	min	max	min	max	
Cow wasterwater	8	11	75	82	2.0	6.7	4.4
Piggery wasterwater	7	-	75	86	6.0	18	-
Cow manure	25	-	68	76	1,1	3,4	5.6
Piggery manure	20	25	75	80	2.6	5.2	8.8
Poultry manure	32	-	63	80	5.4	-	-
Silage maize	20	35	85	95	1.1	2	4.3
Whole rye	30	35	92	98	4.0	-	13.0
Sugar beet	23		90	95	2.6	-	6.0
Silage grass	25	50	70	95	3.5	5.9	19.5

Nitrogen in livestock wastewater and energy crops is mostly present in the reduced form (N^-), bound to proteins and other organic compounds or as ammonia (ammonium ion NH_4^+ in equilibrium with dissolved free ammonia NH_3). The distribution between the soluble (ammonia, amino acids, simple proteins, etc.) and particulate forms (proteins, inorganic precipitates, etc.) provides preliminary and useful information on the removal efficiency achievable by mechanical separation of the particulate matter, while the ratio ammonia to soluble or total N is related to the maximum removal efficiency achievable by most N removal processes, incapable of removing directly N bound to proteins and organics compounds.
Typical ranges of N forms in anaerobic digesters fed on raw and fresh manure are the following: particulate N-soluble N ratio: from 25/75 to 40/60, ammoniacal N/total N: 40 to 60%. The longer the storage time before entering the AD, the higher will be the soluble forms and the ammonia fraction due to hydrolysis of particulates to soluble forms and ammonification. During AD, depending on hydrolysis efficiency, bound N will be converted to ammonia and a) a certain amount of ammonia will escape with the biogas; b) a certain amount of soluble ammonia will precipitate as inorganic ammonium salts (struvite, etc...) or will be incorporated in the bacterial biomass. The extent of these phenomena depends on process pH and temperature, alkalinity and ionic composition of the feed, degree of mixing, biogas recirculation, and others. Although they might not be negligible (struvite and other ammonium salt precipitates are well recognised in many digesters), they are site-specific and cannot be evaluated and calculated in general terms. Therefore, it is usually assumed that no net N removal takes place inside the reactor.

2. NITROGEN REMOVAL TECHNOLOGIES

Particulate N removal can be achieved by solid-liquid separation, while ammonia removal from concentrated streams can be achieved with a wide range of chemical/physical (liquid/gas stripping and condensation in mineral acid; evaporation; precipitation) and biological processes (autotrophic nitrification–heterotrophic denitrification; biological autotrophic nitritation–heterotrophic denitritation; biological autrotrophic deammonification).

Other options are theoretically applicable, such as membrane separation, reverse osmosis, electrodialysis, and ion exchange; but, to date, they do not appear sufficiently established or convenient from a technical/economic point of view.
As for solid-liquid separation devices, Table 2 shows the removal efficiencies obtainable with centrifuges and screw presses on raw manure and digestate. Both the length of storage and, thus, the corresponding degree of hydrolysis affect removal efficiency, reducing the fraction of N in the separated solid phase. Centrifugation can achieve relevant removal efficiencies (even more than 30%) because it is effective on particles as small as 10^{-3} mm (micrometer), while more simple devices such as screens and screw-presses hardly achieve 10% removal.

Table 2 – *Dry matter (DM), total phosphorus (TP), nitrogen (TN) and COD removal on raw manure and digestate with different separation devices (from Møller, Sommer et al., 2002).*

	Manure no.	Age	Separation equipment	Liquid flow rate (l/h)	Energy consumption (kW h/ton)	Removal efficiency (	
						DM	TP
Pig manure	1a	2 weeks	Centrifuge	750	6.01	60.48	62.28
	1b	1 month	Centrifuge	1189	4.32	48.28	60.43
	2	21 days	Centrifuge	1036	4.60	62.10	63.56
	3	28 days	Centrifuge	709	6.30	32.77	65.89
Cattle manure	4	2 weeks	Centrifuge	983	5.10	65.17	82.00
	5	1 month	Centrifuge	1189	4.30	59.00	77.80
	6	4 months	Centrifuge	1050	7.30	55.02	78.74
Anaerobically digested	7	Fresh	Centrifuge	869	5.61	68.55	90.95
	8	Fresh	Centrifuge	ND	5.00	65.07	64.21
	9	Fresh	Centrifuge	2000	2.50	59.70	83.33
	10	Fresh	Centrifuge	1433	3.10	53.50	52.35
Pig manure	1a	2 weeks	Screw press	2594	0.90	27.25	7.12
Cattle manure	4	2 weeks	Screw press	1868	ND	29.94	15.46
	6	4 months	Screw press	3456	1.10	13.12	7.97

Most of these processes are well established in their operating principles and a lot of knowledge and experience has been gained from many years of full-scale application to several streams (contaminated groundwater, municipal wastewater, landfill leachate, agro-industrial effluents, etc.). Until now, N removal from manure and animal wastes was usually required when they were to be discharged directly into sewers or surface waters (Rozzi & Malpei, 2003). Biological processes are usually cheaper than physical and chemical processes and they close the N cycle, converting ammonia into gaseous N2, which is released into the atmosphere. Physical and chemical processes transfer the ammoniacal N from the liquid phase to a gaseous (NH_3) stream or into salts (such as ammonium sulphate ($(NH_4)_2SO_4$). A post-treatment to abate ammonia from exhausted gaseous streams or to recover ammoniacal salts (possibly as a commercial product) is required. In this regard, although ammonium recovery is in principle a valuable option, it is frequently not effective because of the complexity of the processes involved, the high content of impurities of the resulting product, and the low cost of conventional industrial ammonia production.

3 MAIN PHYSICAL AND CHEMICAL PROCESSES

Among the available options, those that are more established for digestates are ammonia stripping and precipitation. These techniques will be briefly discussed hereafter.

Stripping and condensation

The total ammoniacal N content (TAN) of a digested effluent can be reduced by transferring it to a gaseous stream. The efficiency of this process depends, in primis, on the fraction of TAN that is under its unionised and volatile form (free ammonia, NH_3), since its conjugated acid (i.e., the ammonium ion NH_4^+) cannot be transferred to the gas phase. This fraction is directly proportional to both temperature (T, in °C) and the suspension pH, according to the dissociation equilibrium equation

$$\frac{[NH_3]}{[TAN]} = \frac{10^{pH}}{\exp\left(\frac{6334}{273+T}\right) + 10^{pH}}$$

As an example, free ammonia accounts for 0.4% of TAN at 20 °C and pH=7; it increases to 28% by raising the pH to 9 and to 84% if temperature is also increased to 60 °C. This normally requires a conditioning step of the N-rich liquid to pH levels up to 11-12 or temperature up to 80-90 °C to enhance the stripping rate. For this purpose, an alkaline reagent is dosed, which causes the flocculation/precipitation of a residual chemical sludge (inorganic salts + coagulated organic matter). The second factor affecting the stripping efficiency is the available interface between the gas and liquid phases. The hydrodynamics of the stripping column is therefore conceived to maximise the interfacial surface area-e.g., by adopting a counterflow packed-bed configuration. Figure 1 shows a typical layout of a stripping stage downstream an anaerobic digester. To avoid plant clogging and fouling, a preliminary and efficient liquid-solid separation step is needed. The exhausted vapour is brought into contact with an acid solution and an ammonium salt is possibly recovered for N reclamation. Finally, the treated effluent is recarbonated and neutralised by dissolving carbon dioxide from biogas. Among the advantages of this technique, the most relevant is the very low ammoniacal N content of the treated and the applicability to toxic wastewaters. However, reagent requests (dependent on the alkalinity and temperature of the incoming stream), foaming and scaling problems in the stripping column, sludge production, and the low quality of reclaimed N are the main drawbacks. The economic sustainability is very dependent on the quality of the wastewater (N content, alkalinity, organic content) and on the feasibility to recover residual heat from electricity generation/cogeneration from biogas.

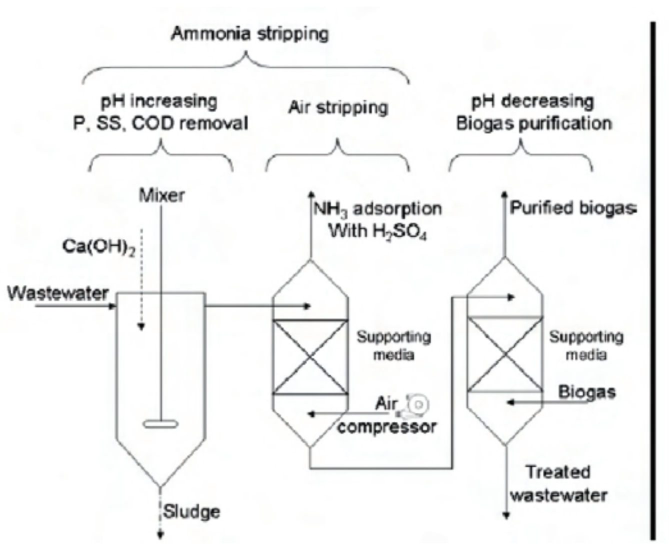

Figure 1: *Main features of a stripping unit (from: Lei, Sugiura et al., 2007).*

Struvite formation

Chemical precipitation is a well-known process for inorganic ion removal from liquids, accomplished by addition of appropriate chemicals to favour salt precipitation. An interesting ammonium salt that can be removed by precipitation is ammonium and magnesium phosphate, also known as struvite ($MgNH_4PO_4 \cdot 6H_2O$) whose solubility has its minimum at pH around 9-10.5. This mineral is a very good slow-release fertiliser for its high N and phosphorus content. A typical process layout for struvite precipitation is depicted in Figure 2 (process Phosnix®UNITIKA). After a preliminary efficient solid separation, the clarified supernatant is fed to a precipitation unit where the pH is controlled to optimum by adding alkaline (as a mixture of sodium and magnesium hydroxide, the latter cation being normally below the stoichiometric request in the influent streams). The presence of preformed struvite granules enhances the precipitation of newly formed salts. Struvite granules are then removed from the bottom of the reactor and, according to their dimension, returned to the reactor or sent to a struvite hopper for final storage. Process simplicity, limited chemical request, and the fertilising properties of struvite are among the most notable advantages. However, N removal efficiency is limited by the availability of phosphate and is defined by the mass ratio of phosphorus to N in the digestate. Further refining stages are required to achieve sufficiently high quality for its marketability.

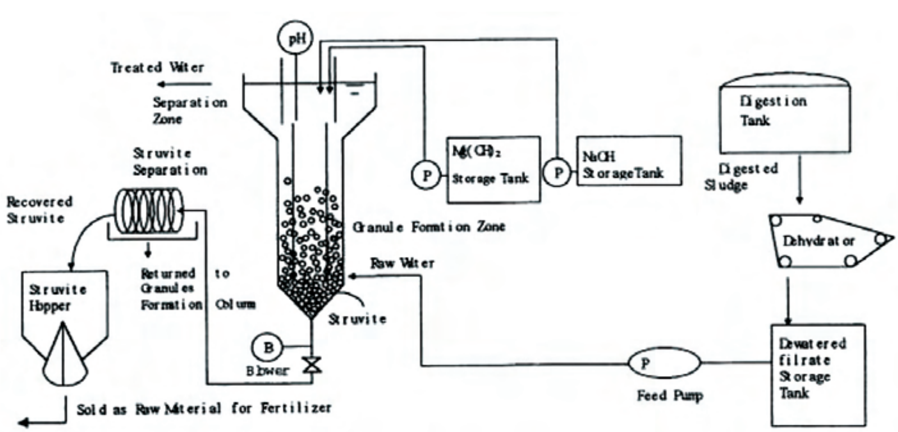

Figure 2: *Struvite precipitation: process layout (Phosnix®UNITIKA).*

4. CONVENTIONAL AND ADVANCED BIOLOGICAL PROCESSES FOR N REMOVAL

Conventional biological N removal is a well-established two-step technology: oxidation of ammonia to nitrite and nitrate by autotrophic bacteria under aerobic conditions and reduction of nitrate to nitrogen gas by heterothrophic bacteria under anoxic conditions. It is commonly adopted for urban wastewater treatment and many successful applications to livestock wastewater can be found in the literature (inter alia Tilche, Bacilieri et al., 1999; Zhang & King, 2006).

Advanced biological processes have been recently studied and developed to remove N from concentrated streams, relying on the same bacteria active in the conventional process but operating in different conditions and/or on the exploitation of recently discovered bacterial strains. Less energy requirements, as well as less oxygen and less organic carbon requirements, are the key features of these processes, with a substantial decrease in investment and operational costs.

4.1 Processes based on nitrite-arrested oxidation

The liquid fraction of digestate is often warm, as it comes from mesophilic (35 °C) or thermophilic (55 °C) AD. This makes it easier to apply nitrification processes arrested to the nitrite step, which is performed by ammonium-oxidising bacteria (AOB). The growth of these bacteria is favoured over nitrite oxidising bacteria at temperature > 30 °C. These processes allow a reduction of up to 25% of oxygen requirements (Surmacz-Gorska, Cichon et al., 1997) and up to 40% of carbon requirements if compared with conventional full nitrification-denitrification processes (Abeling and Seyfried, 1992).

Conventional biological nitrogen removal

Full nitrification:

$2\ NH_4^+ + 4\ O_2 \longrightarrow 2\ NO_{3^-} + 4\ H^+ + 2\ H_2O$ (biomass negligible)

Denitrification:

$2\ NO_{3^-} + 8\text{ g COD} + 2\ H^+ \longrightarrow N_2 + 3\text{ g biomass (sludge)}$

Overall reaction:

$2\ NH_4^+ + 4\ O_2 + 8\text{g COD} \longrightarrow N_2 + 2\ H^+ + 3\text{ g biomass (sludge)}$

Nitrite-arrested biological nitrogen removal

Nitritation:

$2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 4\ H^+ + 2\ H_2O$ (biomass negligible)

Denitrification:

$2\ NO_2^- + 4.8g\ COD + 2\ H^+ \rightarrow N_2 + 1.8g$ biomass (sludge)

Overall reaction:

$2\ NH_4^+ + 3\ O_2 + 4.8\ g\ COD \rightarrow N_2 + 2\ H^+ + 1.8\ g$ biomass (sludge)

Kinetics are faster as they occur at higher temperature values if compared with conventional processes, and this allows savings in space and investment costs.

4.1.1 SHARON Process

The acronym SHARON (Hellinga, Shellen et al., 1998; Van Loosdrecht and Jetten, 1998) stands for "single-reactor high-activity ammonia removal over nitrite". This process occurs in a once-through completely mixed reactor at a retention time of 1.5–2.5 d and T = 30-40 °C. In this temperature range, the minimum required retention time for the growth of AOBs is lower than that required for NOBs (Fig. 3). As a consequence, if the retention time is sufficiently low, NOBs are washed out from the system and no nitrite can be converted into nitrate.

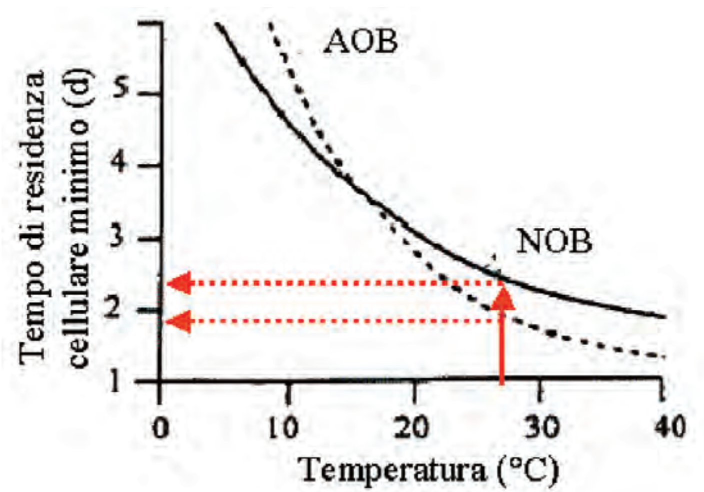

Figure 3 - *In the SHARON process, AOBs grow much faster than NOBs above 30 °C.*

4.1.2 Nitrite-arrested processes at high suspended-solid retention time

Recently, many researchers have shown that nitrite-arrested processes can be operated even at high suspended-solid retention time, with sequencing batch reactors (SBR; Fux, Lange et al., 2004) or membrane bioreactors (MBRs; Canziani et al., 2006). The washout of NOBs can be obtained by combining the effects of very low dissolved oxygen concentration (<0.5 mg/L), high temperature (> 30 °C); also, pH (higher than 7.5) and free ammonia concentration (higher than 1 mg L^{-1}) can play a role in lowering the growth rate of NOBs, causing their complete washout (Jení_ek, Svehla et al., 2004; Balmelle, Nguyen et al., 1992). The SBR option (Fux, Lange et al., 2004) was shown to be cheaper as it produced much less excess sludge than SHARON, required less energy for aeration, and had a more stable and reliable operation. Attention should be paid to avoid excessive temperature values, as ammonia oxidation is strongly exothermal (DH° = -271 kJ per mole of N oxidised). In concentrated solutions (above 1 g L^{-1}), reaction heat can increase the temperature of the mixed liquor of several °C and, if the initial temperature is already around 35 °C, a cooling device should be required to maintain temperature below 40 °C, and avoid negative effects on AOBs.

4.2 ANAMMOX® and combined processes

The ANAMMOX® process (Fux, Boehler et al. 2002; Van Dongen, Jetten et al., 2001) was first observed in denitrifying fluidised bed (Mulder, Van de Graaf et al., 1995) and in a rotating biological contactor treating landfill leachate at Mechernich, in Germany (Hippen, Rosenwinkel et al., 1997). It can be briefly described by the following simplified stoichiometric equation:

$$NH_4^+ + NO_{2-} \longrightarrow N_{2,\ gas} + 2\ H_2O$$

The reaction is performed by autotrophic bacteria that have been classified as Planctomycetales. For these bacteria, oxygen is toxic and their natural habitat is a reducing environment (ORP <-200 mV). Competition with heterotrophic denitrifiers must be avoided, so that a very low C/N (< 0.15) must be maintained. Growth rates are very low (0.065 d^{-1} at 37 °C; Strous et al., 1999), so that it is crucial to avoid any loss of biomass from the system. For this reason, fixed biomass or granular systems or MBRs should be preferred.

As the ANAMMOX® process requires nitrite and ammonium, a partial nitrite-arrested process is necessary prior to the ANAMMOX®. The overall simplified stoichiometric equations are therefore the following:
Partial nitrite-arrested process:

$$2\ NH_4^+ + 1{,}5\ O_2 \longrightarrow NH_4^+ + NO_2^- + 2\ H^+ + H_2O$$

ANAMMOX®: $NH_4^+ + NO_2^- \longrightarrow N_{2,\ gas} + 2\ H_2O$

Overall reaction stoichiometry:

$$2\ NH_4^+ + 1{,}5O_2^+ \longrightarrow N_{2,\ gas} + 3\ H_2O + 2H^+$$

where the produced acid is usually balanced by the ammonium-linked anion (hydrogen carbonate, or sulphide, to yield carbonic acid or hydrogen sulphide).

To obtain a balanced 50% ammonia/50% nitrite effluent, one can operate in two ways. The simplest way is to treat only half of the total flow rate in a nitrite-arrested process and feed the effluent and the remaining half to the ANAMMOX® process. However, if biodegradable carbon is present in the raw influent, rapidly growing heterotrophic denitrifiers may outcompete ANAMMOX® bacteria. A second way is to convert only half of the ammonia loading and oxidising all the biodegradable carbon in a partial nitrite-arrested nitrification process. In this method, a careful and balanced influent feed rate is essential to achieve a stable and reliable 50% conversion; however, the typical value of the ammonium to alkalinity molar ratio of digestate (around 0.5) naturally helps in controlling ammonium oxidation to the desired 50% efficiency.
Compared with a conventional biological nitrification/denitrification process, the combined process partial nitritation and ANAMMOX® is much more advantageous, as

1) it requires no external carbon,
2) oxygen requirements are halved,
3) excess sludge production is reduced to less than one-tenth, and
4) operational costs can be cut by 90% (from about 4 to less than 0.5 € kg^{-1} N removed).

The first industrial-scale ANAMMOX® process has been built at Dockhaven, near Rotterdam (NL). The reactor is filled by biomass in granules and is operated similar to an upflow anaerobic sludge blanket (UASB). A demonstration plant is currently operating in Hattingen

(treated flow rate: 200 m^3 d^{-1}, nitrogen daily load: 120 kgN d^{-1}). As this is a moving-bed biofilm reactor (MBBR) (plastic support filling ratio: 40%), the process safely operates at 20 °C. Partial nitritation is performed in a 104 m^3 reactor at alternate aeration cycles, followed by a second continuously aerated reactor (Gut, 2005).
The two processes can be combined into a unique fixed biomass process called completely autotrophic N-removal over nitrite (CANON) (Hao and Van Loosdrecht, 2003), where the outer part of the biofilm performs the partial conversion of ammonia into nitrite, and ANAMMOX® bacteria operate in the inner layers.

In recent years, the applicability of these advanced processes has been studied in lab-scale installations treating swine manure, mainly in the United States (Vanotti, Szogi et al., 2006; Szogi, Vanotti et al., 2007) and Korea (Dong & Tollner, 2003; Ahn, Hwang et al., 2004; Choi, Eum et al., 2004). The preliminary results are very promising.

5. CONCLUSION

Nitrogen removal from concentrated streams is technically feasible with different processes. Chemical and physical processes may recover the N content as concentrated ammonia salts, but this option is seldom effective due to process complexity and low product quality.
Therefore, in most situations, a further treatment/disposal option for the concentrated solid or gaseous streams must be provided. The biological process is the conventional solution, even for concentrated streams - except for those toxic and highly variable in composition, which may result in unstable operations. Moreover, recent biological processes are able to overcome the need for external carbon source dosage and help to consistently reduce investment and operational costs.
Table 3 reports a comparative evaluation of some of the discussed alternatives, confirming the cost-effectiveness of biological processes.

Table 3: *General comparison of different techniques for N-removal from digested reject-water (STOWA, 1996). Legend: MAP/CAFR: process for magnesium phosphate precipitation with optional recycle.*

	Production chemical sludge	Production biological sludge	Dosage chemicals	Energy requirements	Operation	Cost estimate Euro/kg N
Air stripping	yes	no	yes	average	average	6.0
Steam stripping	yes	no	yes	high	complex	8.0
MAP/CAFR process	yes	no	yes	low	complex	6.0
Membrane bioreactor	no	yes	yes	high	average	2.8
Biofilm airlift reactor	no	low	yes	average	average	5.7
SHARON process	no	low	yes	average	average	1.5

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Book realized from the Prooceding of Conference:
Anaerobic Digestion: opportunities for agriculture and environment.
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Organized by Direzione Generale Agricoltura - Regione Lombardia
in cooperation with ARAL

Printed by
“TIPOGRAF” snc - Crema
September 2009