Alla mia famiglia, a Giovanni e a Maria

Index

1 INTRODUCTION AND GOALS

Urban landfill leachate are highly contaminated wastewater containing a wide range of chemicals contaminant, especially high ammonium concentration (500-3000 mg/l) (Berge et al 2005), along with presence of organic components and trace metals. This organic material is readily biodegradable and its concentration is reduced as it ages, but an high strenght ammonia fraction tends to remain.

Landfills have an elevated post-closure time, since at least 30 years of monitoring are legally required. One of the main parameters to achieve is that the leachate should not contain high concentrations of organics, ammonia, or heavy metals.

Removal of nitrogen from landfill leachate is needed as high ammonia concentration creates problem like oxygen demand and ammonia toxicity thereby requiring treatment of leachate prior to the ultimate disposal. With this regard operating a landfill as an aerated bioreactor has became an acceptable technique to diminish the aftercare period in the landfill, reducing also the costs of the leachate treatment.

To evaluate the best treatment to apply for nitrogen removal it is important to understand the fate of nitrogen, a complex series of chemicals, physical transformations that are often connectedwith each other in a complex circle.

In this study six lysimeters filled with waste collected from a landfill in Germany have been aerated for a long time in order to examine the behavior of nitrogen compounds. Aim of the study is the assessment of a Nitrogen mass balance.

Other purpose of this work is the formulation of a system to examine provided the data set. Many important measurements were incomplete and that led to the attempt of creating a simple Visual Basic tool to evaluate the possible trend of variation of the missing Total Nitrogen and Ammonia values in the collected samples. After that a statistical data analysis approach has been applied, in order to study the obtained kinetics of the examined compounds and the behavior of the Ammonia concentrations inside aerobic and anaerobic reactors.

After this preliminary phase a nitrogen mass balance has been assessed and, through the study of others leachate compounds, the magnitude of heterotrophic denitrification has been evaluated.

The goal of this work are:

- Definition of the major nitrogen pathways in landfill
- Generation of a Visual basic tool in order to evaluate the effects of interpolation of missing values in a poor data set of leachate samples
- Evaluate removal kinetics of Total nitrogen and Ammonia through a Visual Basic tool
- Utilize the obtained kinetics in a forecast model of future Nitrogen compounds release in order to evaluate the feasibility of the calculated values
- Examine the gas and leachate measurement of aerobic and anaerobic Landfill simulator Reactor
- Perform a nitrogen mass balance

2 THEORETICAL BACKGROUND

2.1 Introduction

Landfilling is the most used system for waste disposal worldwide.

There are estimated to be around 120.000 landfills in the 27 European Union member states which landfill 40% of total municipal solid waste [Van Vossen and Prent, 2011]. In 2008 around 93 million tons of MSW were landfilled in EU countries, accounting for about 43% of the total produced. This number decreased by more than 30% compared with ten years earlier. However, the cumulative amount of waste landfilled in EU countries since the year 2000 exceeds 1000 million tons (Wang, 2013).

Problems associated to this practice are various but the discharge of biogas and leachate in the environment are the most severe ones. Nowadays legislation (starting from 1999) gives instructions for the construction and for the minimization of possible pollution through the creation of top and bottom layer. This doesn´t represent a completely safe approach from the long period point of view. After the aftercare period that for landfills is represented in 30 years the possibilities of damage of bottom layers are very high and also the possible contaminations associated. In the last years the strategy for the minimization of landfill´s impacts has been designed "upstream", deciding by laws, which are the waste categories that can be stored. Reduction of biodegradable landfilled waste is the most important directive in this direction (EU directive 1999/31/EC on landfill of waste).

The most relevant problem is constituted by old landfills. Under the category "old landfills" are contained all those waste deposits built before 1980 without any measures to protect the environment. During their activity in the last decades the awareness of the environmental problems associated to the landfilling was not high as nowadays. For this reason the barrier systems are poor where not totally absent (Cossu, 2005). It is easy to understand that these landfills represent the most relevant problem for the environment.

The high content of biodegradable mass inside the old landfills is a potential source of contamination. One of the methods for the reduction of the latter fraction is through the in situ aeration process associated with flushing. Adopting this strategy of remediation is possible to discharge more carbon in the gas phase, reduce leachate concentration and accelerate the biological processes in the landfill [Prantl et al. 2005]. With aeration, the gas produced from the landfill body is almost only carbon dioxide and the presence of methane is around 0,5 – 2 % (Ritzkowski et al., 2006). From the environmental point of view this is absolutely positive because CH_4 has a GWP twenty-five times higher than CO_2. According with various studies a total of 40 to 60 million tons of CH_4 per year is emitted from landfills through anaerobic degradation, between 6% and 14% of global methane emission. Latter one gives values of methane into biogas of 55%-65 % and 35%-45 % of carbon dioxide and these emissions last for decades or even centuries and may result in a significant negative impact on the environment (Ritzkowski and Stegmann, 2007).

Aerobisation process can be used when biogas production is not more suitable and economically favourable.

Another correlated problem is that the final maturation begins after 20 years from the beginning of aftercare which means a reduction of the barrier´s potential. Adopting in this situation the aerobisation of the microbes is able to degrade semi and hardly degradable organics that have not been degraded during the anaerobic process (e.g. cellulose, lignin…) (Ritzkowski et al., 2006).

Aerobic treatment of the landfill body could be seen as the last step of landfill life and the first one of the sustainable landfill concept. In situ aeration permits the reduction of the landfill´s aftercare measures. In an optic of sustainable landfill (Fig.1.) this process permits also a reduction of odours and methane concentration during landfill mining projects (Ritzkowski et al., 2006).

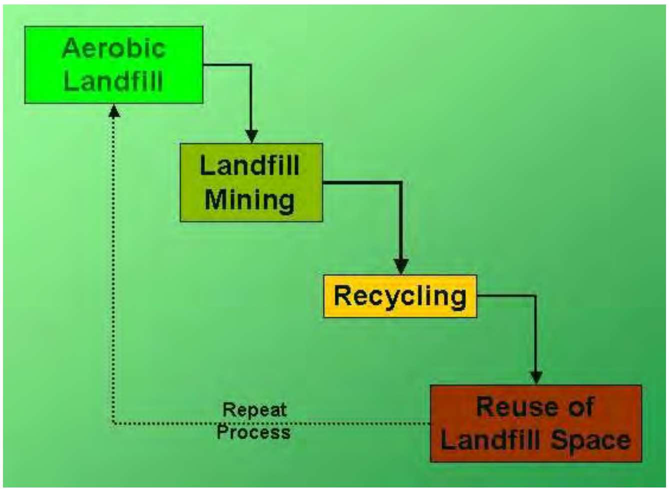


Figure 1 Sustainable landfill concept

Environmental monitoring of a landfill starts the day when the first waste is disposed till when it is possible to say with reasonable confidence that the landfill is not more risky for the environment. This period of time can be very long, in terms of decades if not centuries.

2.2 SUSTAINABLE LANDFILL

Historically, the concept of waste disposal begun with the idea to pit waste or burn it, ignoring the environmental consequences that this behavior could bring. During the twentieth century, the amount of waste incremented exponentially. Associated to it the necessity of a waste management became fundamental. The idea of landfilling waste has been the most used strategy and in many countries is common also nowadays, but an engineering approach has been applied . The basic idea is to pit the waste in an open dump without necessary protection for an environmental contamination as in lining or gas catching dispositives. In this case the degradation pattern is very fast due to the aerobic condition presents. For this reason the landfill is able to reach the emission peak during its operational life. This could be positive because the emissions in the long period would be low but the emissions release would be high and concentrated.

Leachate is a high-strength liquid formed as a result of percolation of rain-water and moisture through waste in landfills. During the formation of leachate, organic and inorganic compounds are transferred from waste to the liquid and pose a hazard to the receiving water bodies. Production of landfill leachate begins with introducing moisture waste into disposal areas and continues for several decades following the landfill closure. Leachate contains high organic matter and ammonium nitrogen. It varies from site to site and its composition depends upon the landfill age, the quality and quantity of waste, biological and chemical processes that took place during disposal, rainfall density and water percolation rate through the waste in the landfill.. If not removed by treatment these contaminants may be toxic to life or simply alter the ecology of receiving streams. Leachate should be treated before reaching surface water or ground water bodies because it can accelerate algae growth due to its high nutrient content, deplete dissolved oxygen in the streams, and cause toxic effects in the surrounding water life (Mahmoudkhani et al., 201).

In the modern landfill management once the site is filled with waste in the majority of the cases landfills are managed as dry tomb or contained landfill without introducing oxygen into the landfill´s body; for this reason the stabilization process runs for decades longer than the aftercare period. The absence of oxygen associated with the low moisture infiltration creates the fundaments for an anaerobic situation with production of harmful bio-products as methane gas. Releases of these substances into atmosphere could be low during the aftercare period but it reaches high and dangerous levels once that this period is terminated. This brings long-term environmental impacts to the landfill area and the increased maintenance costs burdens for municipal and private solid waste management entities (Read et al., 2000).

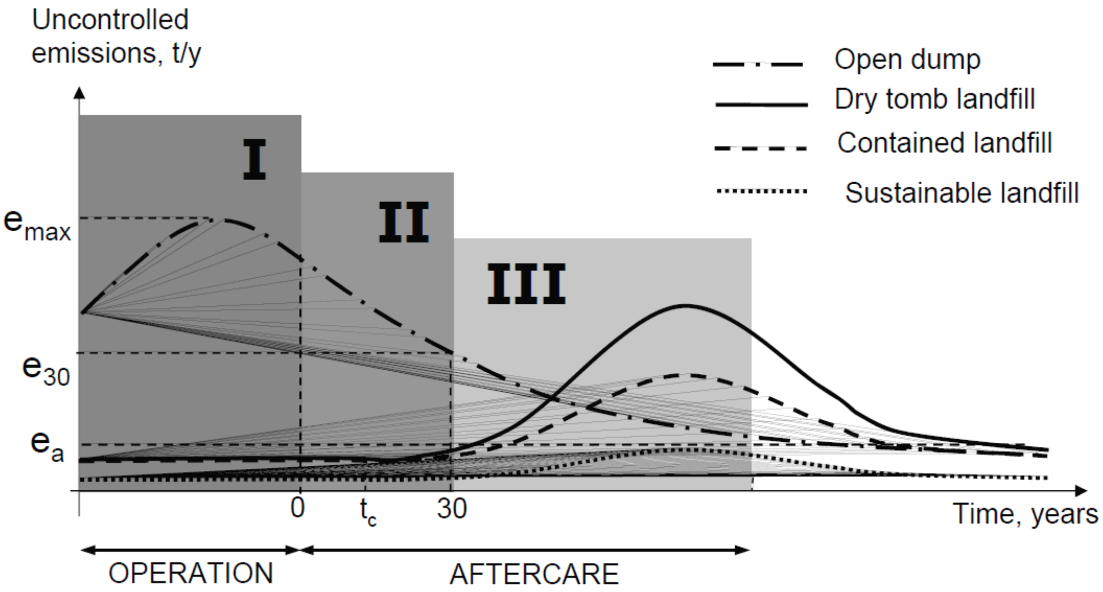


Figure 2 Duration and levels of emission for different type of landfills

In the developed country where the sanitary landfills are the used system for waste disposal, once that the landfill is completely filled different options of management can be applied. Usually, especially in the European countries, where the anaerobic landfills are the only strategy adopted, the practise to leave the body under anaerobic conditions is common. In this way the management concerns only the collections of leachate, caption of methane and control of the seal. The combustion of the produced methane associated with the energy production is also a good income for the landfill owners. The European landfill framework fixes the period where the owner has to have enough capital in order to cover all the costs of the landfill at forty years.

When this period is passed the landfill and its impact on the environmental become a problem extended to other actors as municipality, populations etc. After this aftercare period where the costs are totally covered by the landfill's owner different strategy can be applied. To leave the landfill under anaerobic conditions is the cheaper way but with high environmental costs in the long period.

Nowadays there are different remediation techniques which can be applied after the aftercare period or when the landfill has reached its maximum capacity.

Landfill mining is a technique whereby solid waste which has previously been landfilled is excavated and processed. Processing typically involves a series of mechanical processing operations designed to recover one or all of the following: recyclable material, a combustible fraction, soil and landfill space. In addition, mining and reclamation can be used as a measure to remediate poorly designed or improperly operated landfills and to upgrade landfills that do not meet environmental and public health specifications [Horth, 2006].

2.3 LANDFILL STRATEGIES AND APPROACH

2.3.1 Landfill processes :Aerobic degradation

The reactions that occur in landfill processes can be physical, chemical, and biological. Of these three processes the biological processes probably are the most significant. However, the biological processes are strongly influenced by the physical and chemical processes.

The significant physical reactions in the landfill are in one of three very broad forms: compaction, dissolution sorption and settlement are invariable accompaniments of compression. Similarly dissolution and transport are closely associated phenomena although not to the same degree as compression and settlement. The continuing compression is due to the weight of the waste and that of the soil cover. Settling of the completed fill is an end result of compression. This settling is in addition to the settlement brought about by other reactions (e.g., loss of mass due to chemical and biological decomposition).

The amount of water that enters the fill has an important bearing on physical reactions. Water acts as a medium for the dissolution of soluble substances and for the transport of unreacted materials. In a typical fill the broad variety of components and particle sizes of the wastes provides conditions that lead to an extensive amount of adsorption which is the adhesion of molecules to a surface. Of the physical phenomena adsorption is one of the more important because it brings about the immobilization of living and non-living substances that could pose a problem if allowed to reach the external environment.

Oxidation is one of the two major forms of chemical reaction in a landfill. Obviously, the extent of the oxidation reactions is rather limited in as much as the reactions depend upon the presence of oxygen trapped in the fill when the fill once was made. Ferrous metals are the components likely to be most affected.

The second major form of chemical reaction includes the reactions that are due to the presence of organic acids and carbon dioxide (CO_2) synthesized in the biological processes and dissolved in water (H_2O). Reactions involving organic acids and dissolved CO_2 are typical acid-metal reactions.

Products of these reactions are largely the metallic ions and salts in the liquid contents in a landfill. The acids lead to the volatilization and hence mobilization of materials that otherwise would not be the source of pollution. The dissolution of CO_2 in water deteriorates the quality of the water especially in the presence of calcium and magnesium.

The importance of biological reactions in a fill is due to the following two results of the reactions: First, the organic fraction is rendered biologically stable and, as such, no longer constitutes a potential source of nuisances. Second, the conversion of a sizeable portion of the carbonaceous and pertinacious materials into gas substantially reduces the mass and volume of the organic fraction. The wide varieties of fill components that can be broken down biologically constitute the biodegradable organic fraction of MSW. This fraction includes the garbage fraction, paper and paper products, and “natural fibers” (fibrous material of plant or animal origin).

Biological decomposition may take place either aerobically or anaerobically. Both modes come into play sequentially in a typical fill, in that the aerobic mode precedes the anaerobic mode. Although both modes are important, anaerobic decomposition exerts the greater and longer lasting influence in terms of associated fill characteristics [Nora, 2007].

2.3.2 Anaerobic degradation

The method of anaerobic sanitary landfill for the disposal of municipal solid wastes continues to be widely used in most countries of the world. However, environmental problems generated from anaerobic-type landfills such as high concentrations of TOC and total nitrogen (TN) in leachate, a long stabilization period and a significant generation of greenhouse gases (e.g. methane) are attracting more and more attention. The success of this disposal option is due to easy management and reduced costs. Once the landfill has been filled the waste is covered through the installation of a top cover which minimises both water and air (oxygen) infiltration into the waste. Production of methane is the most important factor that permits a profit from landfilling of MSW.

During anaerobic degradation of organic compounds five different degradation phases occur. The first one is an aerobic phase and consists of the consumption of oxygen by aerobic micro-organism after waste disposal in the landfill. This phase is relatively short and results in CO_2 and H_2O production and a partly degradation of organic compounds. After the oxygen has been consumed the anaerobic processes start. During these phases anaerobic microorganisms which do not consume atmospheric oxygen for cellular respiration but use other compounds (like nitrates or sulphates) as electrons acceptors are dominating. The second phase (*hydrolysis*) is characterized by enzymatic degradation of macro molecules (protein, fats, lipids) into less complex units (e.g. glucose, amino acids). In the third phase (acidic phase) TVA formation leads to a decrease of pH values eventually associated with a mobilization of metals. Moreover, COD reaches a maximum value in this phase. The fourth phase (methanogenic phase) is characterized by the production of methane and carbon dioxide. This production leads to an increase of pH values and consequently a decrease of metal concentration in the leachate. In the last phase (long term phase) the biogas production gradually decreases while methane and carbon dioxide concentrations stay constant [Zanetti, 2008].

Problems associated with this practice start when the gas extraction is not more of economical profit. The anaerobic stabilization of waste is a long term practice and during this period, usually decades, the bottom layer and surface cover system that has a certain period of resistance can be damaged with possible leakages in the groundwater

2.4 Bioreactor landfill Operation

Bioreactor landfills are controlled system in which moisture addition (often leachate recirculation) and/or air injection are used to create a solid waste environment capable of actively degrading the readily biodegradable organic fraction of the waste. Several researchers have documented the benefits associated with bioreactor technology (Murphy et al., 1995; Pohland et al., 1995; Reinhart et al., 1996). One advantage is that increased waste degradation rates characteristic of bioreactor landfills permit the life of a bioreactor landfill to be expanded beyond that of conventional landfills through recovery of valuable airspace. As leachate is recirculated, it is treated in situ, decreasing its organic strength and thus potential impact to the environment. In situ treatment potentially reduces the length of the postclosure care period and associated costs (Reinhart et al., 1998). Additionally, bioreactor landfills stimulate gas production; the majority of the methane is produced earlier in the life of the landfill, allowing for more efficient capture and subsequent use (Berge et al., 2005).

Although the organic strength of the leachate is significantly reduced in bioreactor landfills, ammonia-nitrogen remains an issue. The ammonia-nitrogen concentrations found in leachate from bioreactor landfill are greater than those found in leachate from conventional landfills (Onay et al., 2001). Ammonia-nitrogen tends to accumulate in both system because there is no degradation pathway for ammonia-nitrogen in anaerobic system. However, in bioreactor landfills, moisture addition and recirculating leachate increases the rate of ammonification, resulting in accumulation of higher levels of ammonia-nitrogen, even after the organic fraction of the waste is degraded (Barlaz et al., 2002).

The increased ammonia-nitrogen concentrations intensifies the toxicity of the leachate to aquatic species, potentially inhibiting the degradation processes and necessitating leachate treatment before ultimate disposal to protect receiving waters (Burton et al., 1998).

Because bioreactor landfill environments are different from conventional landfills, there is a potential for a greater number of nitrogen transformation and removal processes to occur and for them to occur to a greater extend than in conventional landfills. System design of bioreactor landfills provides the flexibility in the location and duration of liquid and air injection, allowing for adjustment of pH, oxidation-reduction potential, and moisture content to create an environment conducive to microbial degradation and biological nitrogen removal (Berge et al., 2005).

Liquid addition to landfill has many advantages associated with it. Leachate recirculation involves the collection and redistribution of leachate trough a landfill. Moisture addition and movement are important factors affecting waste biodegradation, resulting in an increase in the moisture content of the waste and distribution of nutrients throughout the landfill, respectively. Optimal levels of moisture content have been found to be between 40 and 70%, on a weight basis (Barlaz et al., 1990).

Air addition has also been used as an enhancement and has been shown to enhance degradation processes in landfills at both the field and laboratory scale (Leikam et al., 1999). Adding air uniformly throughout the waste is also a challenge. Not only waste heterogeneities and compaction affect the air distribution, the presence of moisture does as well. Air will take the path of least resistance; thus, there will likely be areas of an aerobic landfill in which air does not reach, resulting in anoxic or anaerobic pockets within the waste mass (Berge et al., 2005).

Generally, bioreactor landfills undergo the same degradation processes as conventional landfills, just at faster rate and to a greater extend because of the optimization of in situ conditions. However, degradation pathways may vary depending on the operation of bioreactor landfill. Compared with conventional landfills, bioreactor landfills have shown a more rapid and complete waste conversion and stabilization process (Harper et al., 1988).

2.4.1 Anaerobic Bioreactor Landfill

Anaerobic bioreactor landfills are those in which moisture additions is practiced. Sources of liquid may include groundwater, stormwater, infiltrating rainfall, or leachate. Moisture content adjustment results in enhanced methane production, which has been repeatedly demonstraded in several laboratory, pilot, and field scale studies. Because waste degradation is enhanced in anaerobic bioreactors and organic material is returned to the landfill via leachate recirculation, methane is produced at a much faster rate. The total volume of gas produced also increases, as organics in the leachate are recycled and then biodegraded within the landfill. The majority of gas production may be confined to a few years, earlier in the life of the landfill, than traditionally occurs in conventional landfills, allowing for a more efficient capture and subsequent use. (Reinhart et al., 1996).

Anaerobic bioreactor landfills are more effective at degrading the solid waste than conventional landfill. However, when compared to other types of bioreactor landfills, anaerobic system tend to have lower temperatures and slower degradation rates. A disadvantage to operating the landfill as an anaerobic reactor is the accumulation of ammonia-nitrogen. In anaerobic bioreactor landfills, the ammonia-nitrogen present in the leachate is continually returned to the landfill, where there is no degradation pathway for ammonia in anaerobic environments. An advantage of operating the reactors anaerobically when compared with other bioreactor landfill types is that air is not added; therefore the operational cost are less than what would be incurred aerobically and methane can be captured and reused.

2.4.2 Aerobic Bioreactor Landfills

Adding air to landfill has been shown to enhance degradation processes in landfills, as aerobic processes tend to degrade organic compounds typically found in municipal solid waste (MSW) in shorter periods than anaerobic degradation processes (Leikam et al., 1999). Reported advantages of operating the landfill aerobically include increased settlement, decreased metal mobility, reduced ex situ leachate treatment required, lower leachate management and methane control costs, and reduced environmental liability (Read et al., 2001).

Many of the nitrogen transformation and removal process are favored by aerobic processes, including nitrification and ammonia air stripping or volatilization. Air stripping and volatilization may be favored in aerobic bioreactor landfill because of higher pH levels and temperatures that are inherent in an aerobic environment. The additional gas flow associated with air injection may also induce greater masses of ammonia-nitrogen removal (Berge et al., 2005).

During aerobic degradation of MSW, biodegradable materials are converted mostly to carbon dioxine and water. Little, if any, methane is produced, which may be viewed as either an advantage or disadvantage, depending on whether methane collection and use as an energy source is desired or required. Methane is a potent greenhouse gas; thus, if it cannot efficiently controlled and collected in anaerobic landfills, its production can be a local environment concern. Further, the solid waste environment during aerobic degradation has a fairly neutral pH, which decreases metal mobility (Hanashima et al., 1999). Volatile organic acid production is decreased in aerobic bioreactors because the anaerobic fermentation processes are limited. However, volatile acid and methane production may still occur in anaerobic pockets within the landfill (Berge et al., 2005).

The aerobic processes generate a considerable amount of heat, leading to elevated in situ temperatures as high as 66 °C (Stessel et al., 1992). The elevated temperatures increase the evaporation, which results in a significant loss of leachate. As a consequence, there is less leachate to manage. The high temperatures may limit certain biological nitrogen transformation processes from occurring, although no data regarding temperature effects are available. Additionally, the combination of the high temperatures and presence of any air may create a fire potential. However, minimizing methane production and ensuring proper moisture contents, fire potential is lessened (Berge et al., 2005).

2.5 Nitrogen Cycle

The movement of nitrogen between the atmosphere, biosphere and geosphere in different forms is described by the nitrogen cycle which represents one of the most important nutrient cycles found in terrestrial and aquatic ecosystems.

The atmosphere serves as a reservoir of nitrogen and almost all of the nitrogen found in any terrestrial ecosystem originally comes from it. Naturally nitrogen is constantly fixed from the atmosphere either by the action of electrical discharge (lightning) or by biological processes. Nitrogen fixation occurs chemically, to a small extent, when molecular nitrogen (N2) is oxidized to dinitrogen pentoxide (N_2O_5) during electrical storms in the atmosphere. This nitrogen oxide reacts with water and produces nitric acid (HNO_3) which is carried to soil and surface water bodies in the rain where it is finally fixed as nitrate (NO_3-).

On the other hand, nitrogen is also fixed biochemically as ammonia (NH_3) by specialized prokaryotic bacteria called diazotrophs; although ammonia is the first product of biological nitrogen fixation, it is nearly always assimilated as rapidly as it is formed. A variety of free-living prokaryotes fixes nitrogen either under aerobic conditions (e.g., *Cyanobacteria, Azotobacter, Azomonas, Azopirillum, Derxia, Klebsiella* and *Beijerinckia*) or in anaerobic environments (e.g., *Desulfovibrio, Clostridium,* purple sulphur bacteria, purple non-sulphur bacteria and green sulphur bacteria) (Murphy *et al.,*1995).

There is also a group of bacteria working in symbiosis with plants (e.g., *Rhizobium* and *Bradyrhizobium*) that fixes nitrogen only when present in nodules or on roots of specific leguminous plants (Mulder, 2003).

Once nitrogen has been fixed within the soil, it could be transformed into organic nitrogen as plant protein. However, taking into consideration that most of the plants can assimilate nitrogen only in the form of ammonia or nitrate (NO_3-) which occur in soil in only limited concentrations, it is not surprising that nitrogen is often the most limiting nutrient for plant growth. Animals and humans receive the nitrogen they need for metabolism, growth and reproduction by the consumption of living or dead organic matter containing molecules composed partially of nitrogen (plant and animal protein); nitrogen is required in large amounts as an essential component of proteins, nucleic acids and other cellular constituents. In contrast, animals and humans release waste products which contain nitrogen compounds resulting from the metabolic breakdown of proteins (e.g., urea in urine) and appreciable amounts of unassimilated protein (e.g., organic nitrogen in feces).

In most ecosystems nitrogen is primarily stored in living organic matter, but at the end of the life cycle it becomes dead organic matter, which is the starting point for the next step within the nitrogen cycle known as ammonification. Nitrogen from dead organic matter is converted in large measure to ammonium nitrogen by the action of heterotrophic bacteria, under either anaerobic or aerobic conditions, although some dead organic nitrogen can remain as non-biodegradable organic matter (recalcitrant organic matter) and it becomes part of the detritus in water or sediments, or the humus in soils. Ammonium nitrogen can be partially absorbed onto the surfaces of clay particles in the soil, whilst it remains soluble in water.

Ammonium nitrogen can be biochemically altered by a specific type of autotrophic bacteria (*Nitrosomonas*spp and *Nitrospira*spp) into nitrite (NO_2^-). Further modification by another type of bacteria (*Nitrobacter*spp) converts the nitrite to nitrate. Both of these processes involve chemical oxidation under aerobic conditions and they are known as nitrogen nitrification. Nitrate is very soluble and it is easily lost from the soil system by leaching to groundwater and surface water bodies. Under anaerobic (or least anoxic) conditions nitrate can be returned to the atmosphere as molecular nitrogen. This process is called denitrification and it is carried out in soils and waters by many species of anaerobic and facultative heterotrophic proteobacteria, including those in the genera *Achromobacter, Alcaligenes, Micrococcus, Pseudomonas* and *Thiobacillus*. The process of denitrification involves the reduction of nitrate to nitrite and then to molecular nitrogen and nitrous oxide (N_2O) gas (Brock *et al*., 1994).

Recently, a short cut in the denitrification process was discovered (Mulder *et al*., 1995): N2 can be also produced by combining ammonium nitrogen and nitrite directly into molecular nitrogen under anaerobic conditions (van de Graaf *et al.,* 1997).

2.6 Ammonia nitrogen in leachate

The ammonia-nitrogen in leachate is derived from the nitrogen content of the waste; the concentration is dependent on the rate of solubilization and/or leaching from the waste. The nitrogen content of MSW is less than 1%, on a wet-weight basis, and is composed primarily of the proteins contained in yard wastes, food wastes, and biosolids. As the proteins are hydrolyzed and fermented by microorganisms, ammonia-nitrogen is produced. This process is termed ammonification. Researchers report concentrations range from less than detection levels to over 5000 mg/L.(Christens and Stegman 1989)

Leachate composition is quite variable, depending highly on waste composition, moisture content of the waste, and age of the landfill. (fig 3)

	Concentration (mg/L as N)	
Stabilization phase	Conventional landfills	Bioreactor landfills
Transition	120–125	76–125
Acid formation	2–1030	0–1800
Methane fermentation	6–430	32–1850
Final maturation	6–430	420–580

Figure 3 Ammonia-Nitrogen Concentrations in Both Conventional Bioreactor Landfills with Respect to Degree of Landfill Biological Stabilization'

Removal of ammonia-nitrogen from leachate to low levels is necessary because of its aquatic toxicity and oxygen demand in receiving waters. Several researchers have conducted tests to measure the toxicity of leachate, concluding that ammonia-nitrogen significantly contributed to the toxic nature of the leachate (cit Barlaz et al 2002).

In landfill leachate, the vast majority of the ammonia nitrogen species will be in the form of the ammonium ion (NH_4) because pH levels are generally less than 8.0.

Dissolved unionized ammonia (predominant at pH levels above 10) is more toxic to anaerobic degradation processes than ammonium ions but should not be present in significant concentrations in a landfill. Ammonia nitrogen concentration greater than 500 mg/L are inhibitory to the degradation process. (cit Lay, JJ et al 1997).

(in the picture below is indicated the variation of concentration of NH_4-N, NH_3 with the pH, Berge et al 2005)

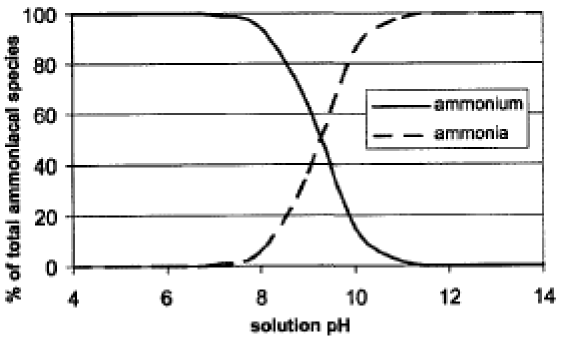


Figure 4 Dominant form of ammoniacal nitrogen in solution at 25°C at various pH levels

Ammonium concentrations between 50 and 200 mg/L have been shown to be beneficial to anaerobic degradation processes in wastewater treatment, while ammonium concentrations between 200 and 1000 mg/L have been shown to have no adverse effect. Concentrations ranging from 1500 to 5500 mg/L have been shown to have inhibitory effects at higher pH levels, and concentrations above 5800 mg/L have been shown to be toxic to some microorganisms (Lay, JJ et al 1997)

However, the effect of ammonium concentrations on landfilled waste degradation has not been reported.

2.7 Nitrogen transformation and Removal

Currently, ammonia-nitrogen is treated in leachate ex situ to the landfill.

Operating the landfill as a bioreactor provides opportunities for in situ nitrogen transformation and removal processes, however, understanding the possible nitrogen transformations is important when considering potential leachate management options. When adding air to landfills, biological processes such as nitrification traditionally found and expected only in landfill cover soils as a result of air diffusion may now occur within the waste mass. Additionally, recirculating nitrified leachate allows for denitrification processes to occur in anoxic areas found in both anaerobic and aerobic bioreactor landfills illustrates the potential nitrogen transformation and/or removal pathways that may occur in bioreactor landfills. (Berge et al 2005)

The heterogeneous nature of solid waste complicates the nitrogen cycle in bioreactor landfills. Because the waste is heterogeneous, portions of the landfill may contain different amounts of nutrients, be at different temperatures, have different moisture levels, and may be at different ORPs. Environmental conditions greatly affect the transformation and removal of nitrogen.

Thus, within one landfill cell, there may be many nitrogen transformation processes occurring simultaneously or sequentially. Processes commonly founding in wastewater treatment processes and in soils, such as ammonification, sorption, volatilization, nitrification, denitrification, anaerobic ammonium oxidation (ANAMMOX), and nitrate reduction, may all occur in bioreactor landfills.

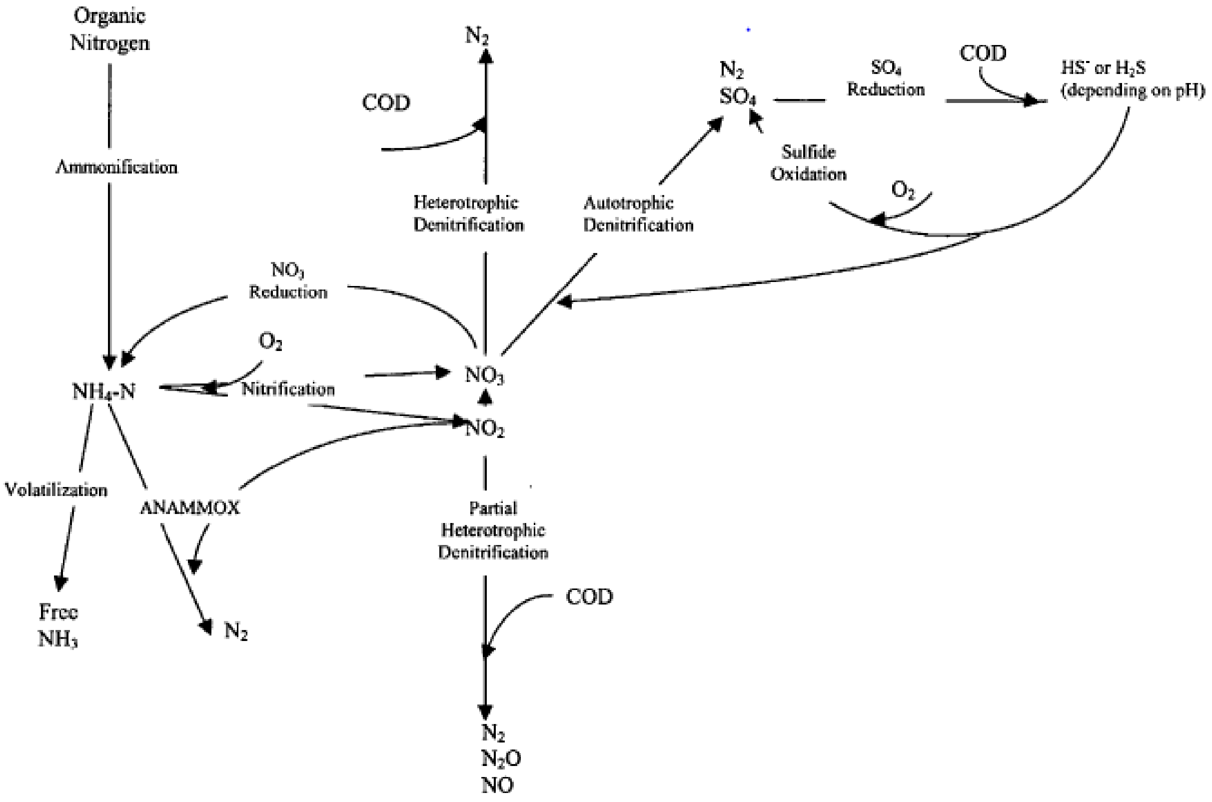


Figure 5 Potential nitrogen pathways transformation and/or removal in bioreactor landfil

Will be discussed how the nitrogen transformation and removal processes found in wastewater and/or soils may also occur in bioreactor landfills based on the current knowledge associated with each process. (Berge, 2005)

2.7.1 Ammonification

Proteins present in the waste are the major source of ammonia-nitrogen.

This conversion of organic nitrogen to ammonia-nitrogen by heterotrophic bacteria is termed ammonification. Ammonification is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing amino acids and the subsequent deamination or fermentation (depending on aerobic vs. anaerobic conditions) of the acids to carbon dioxide, ammonia-nitrogen, and volatile fatty acids. During deamination, amine groups are liberated to form ammonia or ammonium, depending on the pH, and alkalinity (Barlaz et al 2002)

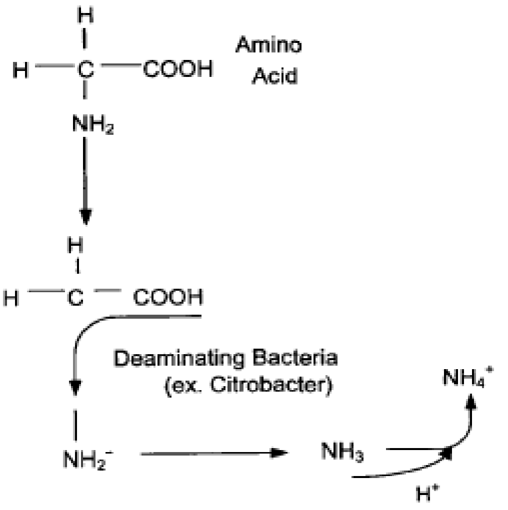


Figure 6 The Deamination proces

Once ammonification occurs ammonia-nitrogen is dissolved in the leachate and is ready to be transformed and/or removed via volatilization, sorption, or biological processes when in an aerobic environment. The pH also increases during ammonification. Any free ammonia that is present is highly reactive and has been found to combine with organic matter (i.e., carboxyls, quinine hydroxls), making them more biodegradable (Burton et al 1998). Thus, in landfills, any ammonia that is produced within the landfill may re-dissolve and react with organic matter before exiting the landfill.

Little research has been conducted evaluating the rate of ammonification in landfills. Ammonia-nitrogen release from wastes has been evaluated in both solid waste digestion and composting studies (de Laclos et al 1997) Ammonification rates were not quantified, although the generation trends appear to follow first-order reaction kinetics. Additionally, ammonification occurs during the organic hydrolysis phase of landfill stabilization, which is also often represented by first-order kinetics. (cit Al-Yousofi 1992). In compost, ammonification has been found to be optimal between 40 and 50°C.

2.7.2 Ammonia Flushing/Loading

Usually the ammonia-nitrogen that can be leached from the waste is controlled by the volume of water passed through the landfill, the nitrogen content of the waste and the ammonia-nitrogen concentration in the bulk liquid. Reducing the ammonia-nitrogen concentration by washout and diluition to acceptable levels within a landfill requires the addition of large volumes of water.

Berge et al reported that at a solid waste moisture content of 30% (wet weight basis) and an initial liquid-phase ammonia-nitrogen concentration of 5833 mg/L as N, a flushing volume of approximately 2.4 m3/tonne of waste was necessary to reduce the nitrogen concentration to 2 mg/L as N. It was also noted that other studies had been conducted suggesting that flushing volumes between 5 and 7.5 m3/tonne of waste were needed to adequately reduce nitrogen concentrations in the landfill.

The assumptions on the water balance and on the landfill body lead, in consideration of the lysimeter to the water balance in the landfill, to a replacement of water between about 70 and 160 times greater per unit of time. The estimation of emissions over time lead to this hypothesis on the relation water / solids. This relation, as well as the index is not dependent on the time until reaching the limit concentration (C_E) as shown in the following Table

Table 1 Estimation emission time of leachate compounds

Parameter	**C_E Final Concentration [mg/l]**	**C_0 Initial Concentration [mg/l]**	**$T_{1/2}$ Initial half-life [years]**	**W/S In relation to C_E [m^3/Mg TS]**	**T_E Time to reach C_E [year]**
COD	200	500-12700	10-40	1.0 6,0	80 360
	Average value	3000	28	2,4	140
TKN	70	200-2100	15-57	2,6-7,7	120-450
	Average value	900	43	4,4	220
Cl	100	340-2950	15-43	1,4-4,1	90-250
	Average value	1200	33	2,4	140

Where W/S is the solid liquid ratio.

The prediction of the spaces of time until it reaches the limit concentration in the water infiltration can be explained not by the exact amount of time to set up, but through the horizon of time in which the limit value is considered realistic.

For the pattern of the COD water infiltration are evaluated hypotheses choices of the spaces of time between 80 and 360 years with an average of 140 years, and an average of report water / solids of 2.4, until the limit concentration eco is reached, About The chlorides, space of time is between 90 and 250 years in each case 140 years of media. The differences between the lysimeters must trace in principle between the different concentrations output (C_0). (Heyer and Stegmann 1997).

Collaterally to the composition of the waste in this case the different spaces of settling time are reflected especially in the landfill since before the beginning of the experiment on the lysimeter. The range of half-life depends on the beginning of the experiment and in the same way from the composition of the waste and proven by the degree of reduction (specific matters and others) as well as from the water balance (specific landfill and lysimeter respectively)

The effectiveness of flushing will be dependent on hydraulic conductivity of the waste, as it will be harder to introduce liquid in areas of lower permeability. As the hydraulic conductivity decreases, the time required for leaching to occur increases, as does the ammonification process. (Berge et al 2005)

2.7.3 Ammonium Sorption

Sorption of ammonia-nitrogen to waste may be significant in bioreactor landfills because of the high ammonium concentrations present. Ammonium is known to sorb onto various inorganic and organic compounds (Laima et al 1994). The amount of ammonium sorbed on some organics has been reported to exceed the mass found in the bulk liquid (Bazin et al 1991). Sorption of ammonium to the waste will allow for temporary storage of ammonium prior to it being used in other processes, such as nitrification and volatilization, and may also result in the slow dissolution of ammonium over time.

Sorption is dependent on pH, temperature, ammonium concentration, and ionic strength of the bulk liquid.

For ammonia to sorb to waste particles, it must be in the form of ammonium (NH_4). At pH levels expected in a landfill, the dominant form of the ammonia species is the ammonium ion. As ionic strength of the bulk liquid increases, ammonium sorption tends to decrease do to ion-exchange effects. The sorbed ammonium is released and exchanged with other ions present in the bulk liquid, especially those with higher selectivity or concentration. A common procedure used to extract sorbed ammonium from solid particles involves the addition of a sodium or potassium sulfate solution. The conductivity of a landfill leachate is usually high (approximately 7000µmho/cm) and thus may influence ammonium sorption. The effect of the ionic strength in leachate on the sorption of ammonium needs to be evaluated.

2.7.4 Volatilization

In conventional landfills, ammonia makes up approximately 0.1 to 1.0% (dry volume basis) of landfill gas exiting the landfill (cit Al- Yousofi 1992). Ammonia is not a greenhouse gas, so its impact on the environment is not as harmful as methane; however, there are some adverse health effects that may result from exposure to the gas. Volatilization only occurs when free ammonia is present. At pH levels above 10.5 to 11.5, the majority of the ammonia-nitrogen present in solution is in the form of free ammonia gas (NH_3).

$$[NH_3\text{-}N] = \frac{[NH_4^+\text{-}N] \times 10^{pH}}{\frac{K_a}{K_w} + 10^{pH}}$$

Figure 7 Evaluation of Ammonia concentration

The free ammonia concentration at a particular pH level may be computed via (insert quotation) where NH3-N is the free ammonia concentration, (mass/volume), NH_4-N the ammonium concentration (mass/volume), *Ka* the acid dissociation constant, and K, the water ionization fraction (10^{-14}). As temperature increases, more of the ammonia is converted to free ammonia gas because of the temperature dependence of the acid dissociation constant. However, in this work, as a matter of simplicity, will be utilized the following equation (Wiesmann. 1994):

$$c_{N-NH_3} = \frac{c_{N-NH_4^+} \times 10^{pH}}{e^{6344/(273+T)}}$$

Figure 8 Evaluation of ammonia concentration

At a pH level of 7, under standard conditions (i.e., temperature is 25°C and pressure is 1atm), 0.56% of ammonia present is in the form of free ammonia. When the temperature increases to 60°C, a temperature commonly found in aerobic landfills, the percentage of free ammonia present at pH 7 increases to 4.90%. Ammonia volatilization has been measured in numerous compost studies. Results have shown that as temperature increases, the dominant ammonia removal mechanism becomes volatilization. Tiquia and Tami also found that at temperatures above 40°C and at pH levels of 7 and above, the majority of nitrogen removed from compost is via volatilization. Air flow also plays an important role in ammonia-nitrogen volatilization.

As air is introduced, it begins to agitate the leachate, creating a removal pathway for dissolved free ammonia to volatilize and leave the landfill. Air flow also dilutes the concentration of gas-phase ammonia-nitrogen above the leachate, increasing the driving force for dissolved ammonia-nitrogen to partition to the gaseous phase

2.7.5 Nitrification in landfills

Nitrification has been successfully used in wastewater treatment processes as a means to convert ammonium-nitrogen to nitrite, and the mechanisms in which it is conducted and operated have been deeply studied.

The purpose of this section is to discuss how nitrification may occur in bioreactor landfills.

Nitrification is a two-step aerobic process in which ammonia-nitrogen/ ammonium is microbially oxidized to nitrite and nitrate via obligate aerobe, autotrophic, chemolithotrophic microorganisms.

Because nitrification is an aerobic process, it is almost nonexistent in conventional landfills and in bioreactor landfills in which air is not added. In those systems, nitrification is restricted to upper portions of the landfill or the cover where air may infiltrate. In landfills in which air is purposely added, nitrification can be a significant nitrogen removal pathway.

During the first step of nitrification, *Nitrosomonas* bacteria oxidize ammonia-nitrogen to nitrite, according to the equation

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

Equation 1 Nitrification reaction first step

The second step of the nitrification process is the oxidation of nitrite to nitrate by *Nitrobacter* bacteria (or the more recently implicated *Nitrospira).*

$$NO_2^- + 0.50O_2 \rightarrow NO_3^-$$

Equation 2 Nitrification reaction Second step

Nitrifiers must fix and reduce inorganic carbon to use as their carbon source, resulting in low cell yields and thus small maximum specific growth rates. Additionally, nitrification results in the consumption of alkalinity as nitrous acid is formed.

The first step of nitrification is often the limiting step, as the *Nitrosomonas* bacteria grow more slowly than *Nitrobacter* or *Nitrospira.*

Some heterotrophic microorganisms are able to nitrify; however, their specific nitrifying rates are considered generally very slow, three to four orders of magnitude lower than that of the autotrophs. Thus, heterotrophic nitrification is generally considered to be a minor pathway.

Some of the heterotrophic nitrifiers are able to denitrify (reduce nitrate) aerobically as well.

Nitrification may occur in bioreactor landfills in which air is added. Although the metabolic processes associated with nitrification may be essentially the same in landfills and wastewater treatment processes, the operation, control, and potential extent of such processes are not the same.

Nitrification in landfill environments is complicated by oxygen and temperature limitations, heterotrophic bacteria competition, and potentially pH inhibition.

Oxygen is a required element for nitrification. Adding air to a landfill would be dual-purpose: to nitrify, removing the ammonia-nitrogen, and to enhance the degradation of solid waste.

However, maintaining and controlling sufficient oxygen levels within the landfill, especially considering the heterogeneous nature of solid waste and the high temperatures characteristic of aerobic landfills, may be difficult and may result in oxygen limitations (dissolved oxygen concentration declines with temperature increases) and thus reduced nitrification rates. Additionally, oxygen may become limiting to nitrifiers in areas within the landfill containing large amounts of organic carbon (newly placed waste) due to competition with heterotrophs. Nitrification usually occur at a minimum oxygen level of 1,0 mg/l.

Under oxygen-limiting conditions, autotrophic ammonia-oxidizing bacteria may produce nitric and nitrous oxides, which would be a distinct disadvantage of this technique as they are potent greenhouse gases. Heterotrophic nitrifiers are also capable of producing nitrous oxide.

When air is added to landfills, in situ temperatures generally increase, often as high as 55 to 66'C, which is a temperature range potentially inhibitory to nitrification.

Nitrification reaches maximum rate at temperature between 30 to 35 °C.

Willers et al (1998) reported that pure *Nitrosomonas* cultures have a thermal death point between 54 and 58°C. In landfills, there may be pockets of lower temperatures, allowing for the nitrifiers to be protected. Additionally, nitrifiers that may be present within biofilms on waste particles may be temporarily protected from high temperatures. At these high temperature levels, volatilization may become the predominant ammonia-nitrogen removal mechanism. Sanchez-Monedero et al (2001) completed studies evaluating the dynamics of nitrogen transformations during organic waste composting.

They reported that nitrification did not occur when temperatures rose above 40°C. Several studies evaluating nitrification in thermophilic wastewater processes have been conducted. Juteau et al (2004) found that nitrification did not occur under thermophilic conditions.

However, Lubkowitz-Baily (1999) found that nitrification was achievable at temperatures as high as 44°C in wastewater and 50'C in veal-calf slurry, respectively, although the rate of nitrification was decreased significantly at both temperature levels Methanotrophs have been shown to oxidize ammonium to nitrite under thermophilic conditions (53°C); however, nitrification by the methanotrophs was highly dependent on oxygen and methane concentrations; at methane concentrations above 841 Nm^3 , nitrification was inhibited (Mevel et al 1998).

It is suspected that in situ nitrification may be optimized when operated in landfill cells containing older waste, because, as in composting, as the age of the waste increases, the temperature of the system decreases due to reduced biological activity (Berge 2005)

Additionally, since older waste contains fewer biodegradable organics, less competition with heterotrophs for oxygen will occur. Sanchez-Monedero et al (2001) also reported that nitrification did not occur in compost processes until the majority of the organic matter was degraded, something also seen in wastewater treatment processes.

Additionally, in older waste, more recalcitrant organics, such as humic acids, are present when humic acid was added at rates above that level, nitrification was inhibited. It is suspected that in landfills humic acids may affect nitrification.

pH may also be a complication during nitrification processes in landfills. The pH of leachate in aerobic landfills is generally near neutral, or slightly above (Read et al 2001). The alkalinity of leachate is generally in the range of 1000 to 10000 mg/L as calcium carbonate. Because nitrification consumes alkalinity, there may not be sufficient alkalinity present to buffer pH changes that would result from nitrification of high ammonia-nitrogen leachates.

Optimum pH level for Nitrosomonas and Nitrobacter is between 7.5 and 8.5. Some wastewater treatment plant are able to nitrify with pH between 6.5 to 7. It is possible that alkalinity may need to be added to the landfill to buffer the leachate. (Berge et al 2005)

2.7.6 Nitrification kinetics

Traditional nitrification kinetics in wastewater systems are derived from the net growth rates of both *Nitrosomonas* and *Nitrobacter,* with the growth rate of *Nitrosomonas* considered as the rate-limiting step and thus the most critical from a design perspective. Monod kinetics are often used, as they describe first-order substrate-limiting growth at low ammonia-nitrogen concentrations and zero-order at higher concentrations. Because ammonia oxidation is the rate-limiting step, it is often used as the overall rate of nitrification. Several environmental factors influence the rate and must be accounted for in the rate expression, including pH, dissolved oxygen (DO) concentrations, and temperature. These factors are included in the rate expression of ammonia oxidation in a multiplicative Monod manner. The Monod relationship can also be modified to account for substrate inhibition, which could be relevant at high ammonia-nitrogen concentrations. The nitrification process in solid waste environments may be better approximated by fixed-film theory rather than suspended, as the waste may act as an attachment surface for the microorganisms. In fact, a bioreactor landfill may contain both suspended and fixed-film populations, but it seems likely that in most cases the greater portion of the biomass will be associated with biofilms. This means that diffusion of electron acceptors and donors and other mass transfer limitations become significant. In landfills, mass transfer of ammonium and/or oxygen may be a bigger factor than in wastewater treatment because of the large particle sizes of the waste and because the liquid to solid ratio is much smaller than in typical wastewater treatment processes. Mass transfer limitations would likely become apparent in the value of the half-saturation constant in the Monod model. The half saturation constants in wastewater for nitrification are generally 1 to 2 mg/L as N; a much larger value may indicate mass transfer limitations.

Nitrification and denitrification are well-known processes and widely described in the literature (Wiesmann, 1994) together with kinetic approaches. Although, those processes are also investigated in landfill leachate treatment area , there are very few papers concerning kinetics of nitrogen removal in landfill leachate treatment. In the literature, two different attempts to the kinetics of nitrogen removal from leachate can be found. Yalmaz and Ozturk (2001) described both nitrification and denitrification as zero order chemical reactions:

$$\frac{\mathrm{d}c_{\mathrm{N-NH_4^+}}}{\mathrm{d}t} = -k_{\mathrm{N}},$$

$$\frac{\mathrm{d}c_{\mathrm{N-NO_x}}}{\mathrm{d}t} = -k_{\mathrm{D}}.$$

Equation 3 Zero order kinetics Nitrification/Denitrification

Dockhorn et al (1997) established that the best model for the two step nitrification process is substrate limitation with nitrite competitive inhibition in the ammonia oxidation and substrate limitation with noncompetitive ammonia inhibition for the nitrite oxidation

$$v_{\mathrm{NH_4}} = v_{\mathrm{max,NH_4}} \frac{c_{\mathrm{N-NH_4^+}}}{K_{\mathrm{S,NH_4}}\left(\frac{c_{\mathrm{N-NO_2^-}} + K_{\mathrm{I,NO_2}}}{K_{\mathrm{I,NO_2}}}\right) + c_{\mathrm{N-NH_4^+}}},$$

$$v_{\mathrm{NO_2}} = v_{\mathrm{max,NO_2}} \frac{c_{\mathrm{N-NO_2^-}}}{K_{\mathrm{S,NO_2}} + c_{\mathrm{N-NO_2^-}}} \frac{K_{\mathrm{I,NH_4}}}{K_{\mathrm{I,NH_4}} + c_{\mathrm{N-NH_4^+}}}.$$

Equation 4 Substrate inhibition of ammonia

2.7.7 Denitrification

Denitrification has been applied in many wastewater treatment processes. The intent of this section is to discuss how denitrification may occur in bioreactor landfills. Information regarding denitrification processes may be found in the previous chapters

In situ denitrification is also complicated in solid waste systems, although it may be easier to implement than nitrification. Denitrifiers are more robust than nitrifiers; however, they require a sufficient organic carbon source for high nitrate removal rates. Because of the carbon needs, denitrification may occur most efficiently in young waste, rather than in older, partially oxidized waste. Price et al. (2003) evaluated the potential need for an external carbon source in the laboratory and noted that a fresh layer of refuse contained sufficient carbon to stimulate significant nitrate consumption. If a sufficient organic carbon source is not readily available, partial denitrification may occur, which may lead to the production of harmful intermediates (N2O and NO), which are potent greenhouse gases.

Typically, in situ denitrification occurs in anoxic bioreactor landfills. However, because of the potential for anoxic pockets to be present in aerobic systems, denitrification may also occur in portions of aerobic bioreactor landfills that air does not reach.

2.7.8 Heterotrophic Denitrification

Denitrification is an anoxic process that reduces nitrate to nitrite, nitric oxide, nitrous oxide, and finally nitrogen gas, as shown in reactions

$$\begin{aligned} NO_3^- + 2e^- + 2H^+ &\rightarrow NO_2^- + H_2O \\ NO_2^- + e^- + 2H^+ &\rightarrow NO + H_2O \\ 2NO + 2e^- + 2H^+ &\rightarrow N_2O + H_2O \\ N_2O + 2e^- + 2H^+ &\rightarrow N_2(g) + H_2O \end{aligned}$$

Equation 5 Heterotrophic Denitrification reactions

Typically, denitrifying bacteria are heterotrophic, facultative aerobes, which use nitrate as an electron acceptor when oxygen is absent or limiting. A potential advantage of denitrification is the simultaneous carbon and nitrate destruction without requiring oxygen input. Denitrification also recovers half of the alkalinity consumed during nitrification. Approximately 3,6 g of alkalinity (as CaCO3) is produced per 1 g of nitrate, thus partially mitigating the lowering of pH caused by nitrification.

It is important to note that processes in which nitrate is used as a terminal electron acceptor are energetically favored over acetogenic, sulfate reduction, and methanogenic processes.

Thus in landfills in anaerobic/anoxic environments in which nitrate reduction occurs, inhibition of such processes may occur. The process needs a dissolved oxygen concentration less than 0.5 mg/l, ideally less than 0,2 mg/l.

Optimum pH values for denitrification are between 7.0 and 8.5.. Researchers have evaluated in situ, or partially in situ, denitrification at both laboratory and field scale. Burton and Watson-Craik operated a landfill test cell designed to denitrify externally nitrified leachate. Nitrate returned to the landfill cell was efficiently consumed under the anoxic/anaerobic landfill conditions, confirmed using labeled isotopic nitrate. Jokela et al (2002) conducted a laboratory study demonstrating that in situ denitrification is possible and can result in the elimination of nitrogen. Ammonia was detected in the effluent from the solid waste column, which was attributed to either release from the waste or high leachate COD to nitrate ratio, which may promote the reduction of nitrate to ammonia. It was also concluded that at an oxidized nitrogen loading rate below 3.8 g N/total solids day, methanogenesis was not inhibited. High leachate COD concentrations inhibited nitrification in the ex-situ process, presumably due to competition for available oxygen Price et al. also conducted studies evaluating the ability of older waste (with low organic carbon) to denitrify nitrified leachate. It was shown that the landfill does have the capacity to denitrify, as significant nitrate consumption was observed, and that fresh waste contained enough organic carbon to support denitrification, while older waste required the addition of an external carbon source. Additionally, it was observed that methanogenic activity was inhibited during denitrification, but quickly resumed following nitrate removal.

2.7.9 Autotrophic Denitrification

Nitrate removal in wastewaters containing high sulfur concentrations or reduced sulfur sources, such as hydrogen sulfide, may occur via autotrophic denitrification. Thiobacillus denitrificans use an inorganic sulfur source (i.e. H2S, S) rather than an organic carbon source when reducing nitrate to nitrogen gas (Onay and Poland 2001) according to reaction.

$$2NO_3^- + 1.25HS^- + 0.75H^+ \rightarrow N_2 + 1.25SO_4^{2-} + H_2O$$

Equation 6 Autotrophic Denitrification reaction

This nitrate removal mechanism produces sulfate. At low carbon to nitrogen ratios this removal mechanism is favored over heterotrophic denitrification. Autotrophic denitrification may occur in landfills, especially in older landfills or older portions of landfills where the carbon to nitrogen ratio may be low. The increased sulfate concentrations may have an adverse effect on methane production rates by limiting the amount of organic carbon available to the methanogens due to competition with sulfidogens.

While operating their reactors, Onay and Pohland (2001) observed the presence of autotrophic denitrification. To confirm their findings, a spike of nitrate was added and gas samples from the headspace of the reactor were measured for nitrogen and hydrogen sulfide. It was found that 13 days after the nitrate spike, the hydrogen sulfide present in the gas phase disappeared.

After the nitrate source was exhausted, the sulfate was converted back to hydrogen sulfide. Onay and Pohland (2001) concluded that autotrophic denitrification accounted for between 15% and 55% of the nitrate conversion to nitrogen gas, with the variation being attributed to the mass of organics present in the system. Additionally, it was stated that autotrophic denitrification is advantageous, as it converts nitrate to nitrogen gas in the absence of an organic carbon source and can utilize inorganic sulfur compounds. High sulfate concentrations (increased to approximately 350 mg/L sulfate) were produced; however, the impact of sulfate on methanogenesis was not quantified.

2.7.10 Denitrification kinetics

Traditionally, Monod kinetics are used to describe denitrification in wastewater systems. The nitrate removal rate is dependent on several factors that must be accounted for in the rate expression. Because an organic carbon source is desirable for rapid denitrification, the amount present in the system affects the rate, as does the biodegradability of the carbon source. Additionally, pH and dissolved oxygen (DO) levels affect the denitrification rate and can be accounted for in a Monod expression in a multiplicative manner. As in nitrification, the denitrification process in solid waste may be better approximated by fixed-film theory rather than suspended, as the waste may act as an attachment surface for the microorganisms. Mass transfer effects may also be severe in denitrification processes and may be reflected in higher half-saturation values when fitting the data to the Monod model.

It is unlikely the kinetics of in situ denitrification will fit well to either strict Monod or biofilm kinetic models; rather, an expression combining both types of consortia may be appropriate.

The denitrification process was described as a two substrate process—electron donors were nitrate and nitrite. The temporary accumulation of nitrite being a transient product of nitrate reduction was observed and taken into account. The best results were obtained with substrate limitation only (Dockorn et al 1997)

$$v_{\mathrm{NO_3}} = v_{\mathrm{max,NO_3}} \frac{c_{\mathrm{N-NO_3^-}}}{K_{\mathrm{S,NO_3}} + c_{\mathrm{N-NO_3^-}}},$$

$$v_{\mathrm{NO_2}} = v_{\mathrm{max,NO_2}} \frac{c_{\mathrm{N-NO_2^-}}}{K_{\mathrm{S,NO_2}} + c_{\mathrm{N-NO_2^-}}}.$$

Equation 7 Denitrification Kinetics

The above-mentioned models did not take into account the influence of the oxygen concentration on the process kinetics.

2.7.11 Annamox

Biological oxidation of ammonia-nitrogen may also occur under anaerobic conditions and is termed the ANAMMOX process (anaerobic ammonium oxidation).

Bacteria capable of ANAMMOX use ammonium as the electron donor and nitrite as the electron acceptor, as shown in reaction

$$\begin{gathered} NH_4^+ + 1.26NO_2^- + 0.085CO_2 + 0.02H^+ \rightarrow \\ N_2 + 0.017H^+ + 0.24NO_3^- + 1.95H_2O \end{gathered}$$

Equation 8 Anammox reaction

There has been little research concerning ANAMMOX in solid waste environments; however, studies conducted in wastewater have shown that ANAMMOX readily occur. (Jeten et al 1998)

This process is generally favorable in environments in which retention time is long, operation is stable, nitrite is present, and electron donors that would cause nitrite reduction via denitrification are absent.

Anammox bacteria did not consume ammonia and nitrite in a ratio 1:1 as it could be expected from their catabolism, but in a ratio of 1:1.3 instead. The excess 0.3 mol of nitrite is anaerobically oxidized to nitrate (Van der Graaf et al 1996).

These bacteria are very sensitive to oxygen and nitrite. Indeed, oxygen concentrations higher than 0.06 mg/L, nitrite concentrations between 230 mg/L and 920 mg/L, and phosphate concentrations higher than 180 mg/L inhibit the Anammox activity completely but reversibly (Jetten et al 2001). The Anammox bacteria can sustain partial oxygen pressure lower than 0,5% air sauration (Schmith et al 2003).

Anammox bacteria are also very sensitive to the presence of some organic carbon sources. For instance, Anammox bacteria are very susceptible to alcohols, especially methanol. Even as low a methanol concentration as 40 mg/L led to the immediate, complete and irreversible inhibition of the Anammox process (Paredes et al 2007)

Because of the potential for anaerobic regions located within an aerobic landfill, this biological ammonia-nitrogen removal mechanism may incidentally occur simultaneously with nitrification. However, the growth rates of the ANAMMOX bacteria are extremely slow; thus, ammonia-nitrogen removal is slow as well. It is questionable whether or not the ANAMMOX microorganisms will be able to compete with denitrifiers for nitrate and nitrite within landfills. Removal rates have been shown to be less than half that of aerobic nitrification (Burton et al 1998)

2.7.12 Dissimilatory Nitrate Reduction

Dissimilatory nitrate reduction to ammonium (DNRA) in anaerobic or anoxic environments may also occur in landfills according to reaction Picture

$$NO_3^- + 2H^+ + 4H_2 \rightarrow NH_4^+ + 3H_2O$$

Equation 9 Dissimilatory nitrate reduction

As shown, ammonium is produced as a result of nitrate reduction. This pathway is generally favored when the microbes are electron acceptor (nitrate) limited in high organic carbon environments (Price et al 2003) and has been shown to occur readily in anaerobic digestion and anoxic sediments where the redox potential is low.

DNRA is favored over denitrification in anaerobic and anoxic environments in environments with a high COD to nitrate ratio because in an electron acceptor limiting environment it is more advantageous for the microorganisms to metabolize nitrate to ammonium and gain 8 electrons per mole of nitrate than denitrify and only gain 5 electrons per mole of nitrate (Berge 2005)

In electron acceptor rich environments (higher COD to nitrate ratios), denitrification is usually the favored nitrate reduction process because the greatest need by the microorganisms is to gain energy. The microbes responsible for the DNRA process differ from denitrifiers in that they are generally fermentive (obligate anaerobes, facultative anaerobes, and aerobes), using nitrate as electron sink, rather than being respiratory and using nitrate as a terminal electron acceptor. DNRA depends highly on redox conditions and the amount of labile carbon available (Yin et al 2002)

Buresh and Patrick (1981) conducted an experiment on estuarine sediment and found that approximately 15% of the nitrate was converted to ammonium at a redox potential of 0 mV.

When decreasing the redox potential to -200 mV, approximately 35 to 42% of the nitrate was reduced to ammonium, while an increase in redox potential (300 mV) resulted in a significant decline of ammonium production, supporting the theory that DNRA is optimal in low redox environments.

When nitrate is added to systems, a general increase in the redox potential occurs.

If nitrate is added to environments with a sufficiently low redox potential, DNRA may be favored. However, if the nitrate addition results in an increase in redox above 0 mV, denitrification of the nitrate is more likely.

In anaerobic or anoxic areas within the bioreactor landfill in which low nitrate concentrations are present in areas containing young waste (high degradable organic carbon) and low redox potentials, DNRA may be favored over denitrification (Tiedje et al 1988) The dissimilatory nitrate reduction pathway is not desired because it results in an increase in ammonium concentration. However, this removal mechanism may be limited because of competition from the denitrifiers for nitrate. The nitrate-reducing bacteria require a tenfold greater population than denitrifiers to reduce 50% of the nitrate. Bonin (1995) reported that a ratio of 1.8:1.0 denitrifiers to DRNA microbes is generally present in an environment.

In landfills, there is generally adequate denitrifying populations naturally present to out-compete any DNRA capable microorganisms. Price et al. conducted laboratory studies in solid waste evaluating the denitrification capacity of the waste and found that there was no noticeable increase in ammonium due to DNRA. However, the redox potential of the laboratory reactors was not measured. Because there had been several additions of nitrate to each reactor, it is possible the redox potential was high enough to inhibit DNRA activity.

2.7.13 Simultaneous Nitrogen Removal Processes

Simultaneous nitrification and denitrification has been observed in wastewater processes, particularly in trickling filter and other biofilm processes.

Because the potential for anoxic pockets in aerobic landfills is high, simultaneous nitrification and denitrification may occur in aerobic bioreactor landfills.

Pochana and Keller (1999) conducted experiments evaluating the factors that may affect simultaneous processes in activated sludge flocs. They determined that the most influential parameters are DO, particle size, and carbon source.

Of particular interest is that as the floc size increases, the potential for anoxic zones inside the particles increases due to oxygen flux limitations. Solid waste particles are large compared to activated sludge flocs; thus the probability of oxygen flux limitations is high, supporting the likelihood of simultaneous processes.

Because landfills are heterogeneous and may support several different micro environments simultaneously (i.e., aerobic, anaerobic, and anoxic), several combinations of nitrogen transformation processes mentioned may be present.

In aerobic bioreactor landfills, it is possible that partial nitrification (only resulting in the production of nitrite) followed by either ANAMMOX or denitrification will occur naturally because of the heterogeneous nature of the in situ environment. There will be portions of the landfill that are aerated well, some only partially aerated, and others not aerated at all. As leachate flows from one section of the landfill to another, it is possible that it will come into contact with aerobic, anoxic and anaerobic regions, leading to multiple nitrogen transformation processes. For example, leachate ammonium may be converted only to nitrite before the leachate flows to an anaerobic pocket.

In that anaerobic pocket, the nitrite may then be converted to nitrogen gas.

The hydraulic conductivity of the landfill will be a factor, as the time during which the leachate remains in each type of environment will ultimately determine the extent of the reactions that may occur. The ability to predict which nitrogen transformations will occur allows for more strategic design and operation of bioreactor landfills. (Berge 2005)

2.8 In situ ex situ treatment

The above overview of the fate of nitrogen demonstrates all the complex chemicals, physical relation between several process involved. It is a system multi connected and hard to control, with several fluxes and feedbacks. During the years, discovering others pathways, several treatment has been theorized in order to find the most suitable to apply in different cases, trying to take advantage of the possible reactions that can happen. Here a short overview is shown.

2.8.1 *Ex situ treatments*

Ex situ treatment systems usually involve aerobic and anaerobic / anoxic reactors (Fu et al 2009). Studies by(Canziani et al 2006) had achieved biological nitrogen removal from old landfill leachate of 0.5 to 3 g/L NH_3-N concentration by partial nitrification to nitrite in a pure oxygen membrane bioreactor (PO – MBR) and by subsequent denitrification in a moving-bed biofilm reactor (MBBR) with SRT higher than 45 days. When DO concentration in the MBR was kept in the range 0.2–0.5 mg/ L, 90% oxidation of ammonia to nitrite was achieved by ex situ means, with stable inhibition of nitrite-oxidizing bacteria. Usually the sequence of operation is nitrification / partial nitrification – denitrification – discharge. In the nitrification stage, NH4+ is first oxidized to nitrite by *Nitrosomonas* bacteria, and the nitrite produced is oxidized to nitrate by *Nitrobacter* and finally to nitrogen.

There is a high demand for oxygen during the nitrification process. When the degradable organic carbon level is high in the environment, heterotrophic microorganisms would outcompete the nitrifiers for oxygen and nutrients. However, the most denitrifying bacteria exist in the environment in which organic compounds are present, and use organic matter as carbon resources and electron donors (He and Shen 2006). Denitrification is inhibited by the presence of oxygen, and limited to anoxic environments. Therefore ex situ treatment need spatial separation of nitrifying and denitrifying units or temporal separation of each step by alternating the supply of aeration and no aeration in the same unit (He and Shen 2006). Furthermore, for the high ammonia/low carbon leachate, this system usually needs air-stripping pretreatment and external carbon sources such as methanol to adjust C/N ratio (He and Shen 2006). This increases the costs and enhances the difficulty of management which are its obvious disadvantages (Valencia et al 2005,). The ex situ methods are good at nitrogen removal but not suited for landfill bioreactor concept, as leachate recirculation is pertinent for optimal performance.

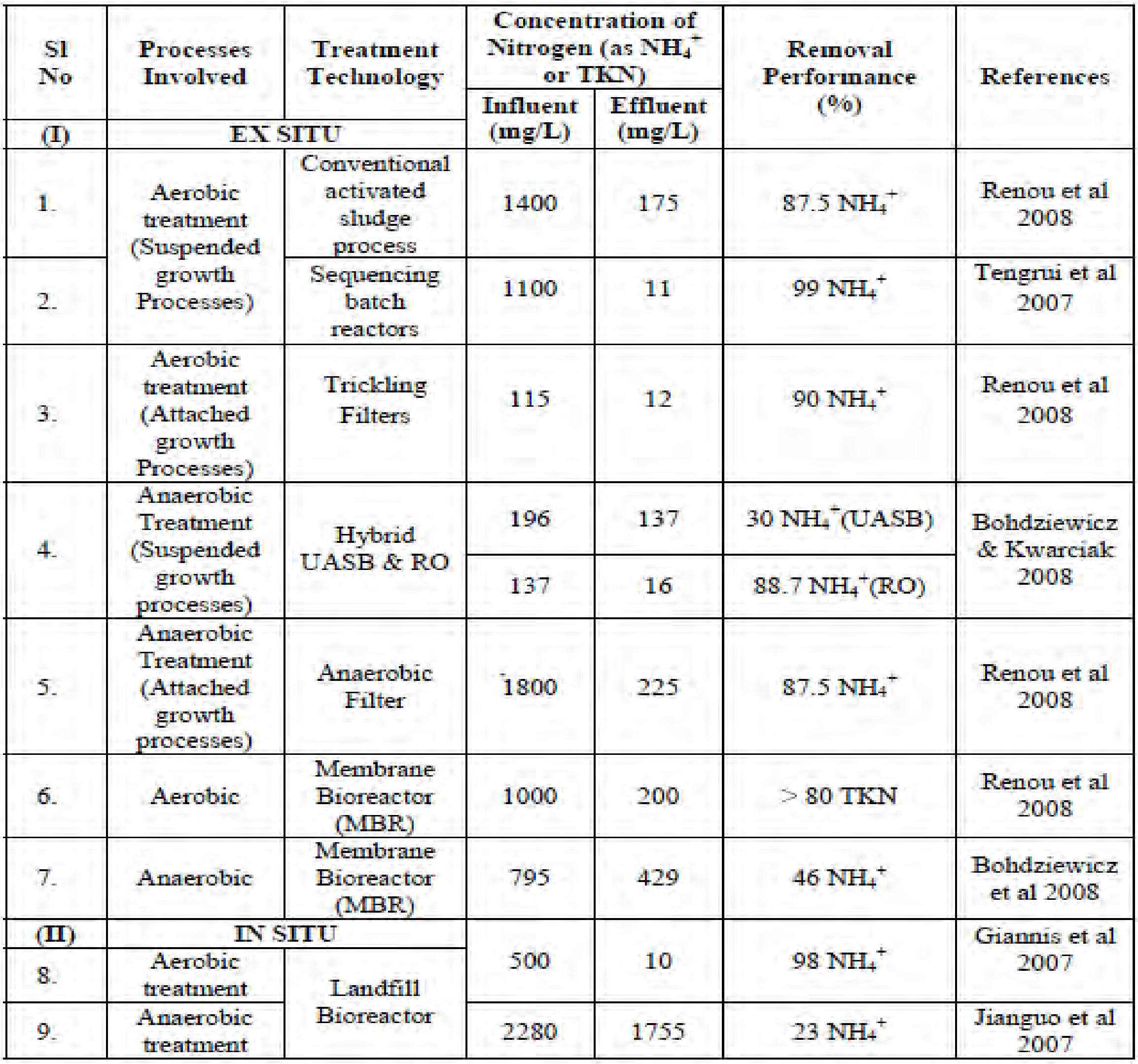
2.8.2 In situ treatments

Control of in situ conditions in a landfill bioreactor is carried out by moisture addition (such as leachate recirculation) and / or aeration as said in the previous chapters. Besides that, aeration and moisturization favors ammonification, results in accumulation of ammonia at a higher concentration (5000mg/L, Connolly et al 2004) than that of conventional landfills.

Onay and Pohland (1998) had expounded the potential of in situ attenuation of high residual leachate ammonia nitrogen concentrations by nitrification and denitrification. This was performed by utilizing compost as the waste matrix, and by adopting the air inlet at the bottom of the reactor to simulate 3 components of landfill bioreactor system, encompassing anoxic, anaerobic and aerobic zones. Since oxygen penetrates in the interstices of the landfilled waste, vertical aerobic/anoxic/anaerobic biological zones are formed naturally in landfill ecosystems. System performances of both combined and separate and with leachate recycling had resulted in 95% nitrogen conversion, whereas combined operation without recycling had conversion efficiency per cycle ranging from 30 – 52% by nitrification and from 16 – 25% by denitrification. Simultaneous nitrification and denitrification in aerobic landfill bioreactor cell has occurred. In another study, an efficacy of 99.5% by in situ ammonia removal in a biofilter comprising of old waste by making use of anaerobic and aerobic sections was attained (He et al 2007).

Thus in situ approach is feasible when waste stabilization (active phase) is completed, by applying forced aeration at the bottom and recirculation (Valencia et al 2005). Periodical aeration was carried out at the top of landfilled waste by He and Shen (2006). Besides, semi-aerobic landfill system bodes well with the simultaneously occurring nitrification and denitrification. Further studies (Giannis et al 2007) on this approach carried out by had achieved ammonia removal from 750 mg/L to 10 mg/ L in 250 days. The process of nitrification had contributed to ammonia conversion to nitrate, but the levels of nitrate (10 – 30 mg/L) was not removed by denitrification, and suggested that other processes like partial nitrification might be occurring. Even anaerobic landfill bioreactor studies focusing on in situ treatment performed by Jianguo et al 2007 had concluded that the ammoniacal nitrogen of 11, 000 mg/L had reduced to 5000 mg/L in 15 weeks of operation. In 28 30 weeks, mean of 23% removal rate was observed. Thus in situ practice disposes the leachate effectively, removes ammonia to a certain extent and accelerates the stabilization of the waste. The common limitations observed just like ex situ method are due to carbon requirement issues in denitrification and aeration needs (Karthikeyan and Joseph 2005).

Table 2 Summary of the treatment approaches for nitrogen removal in landfill leachate



Sl No	Processes Involved	Treatment Technology	Concentration of Nitrogen (as NH_4^+ or TKN)		Removal Performance (%)	References
			Influent (mg/L)	Effluent (mg/L)		
(I)	EX SITU					
1.	Aerobic treatment (Suspended growth Processes)	Conventional activated sludge process	1400	175	87.5 NH_4^+	Renou et al 2008
2.		Sequencing batch reactors	1100	11	99 NH_4^+	Tengrui et al 2007
3.	Aerobic treatment (Attached growth Processes)	Trickling Filters	115	12	90 NH_4^+	Renou et al 2008
4.	Anaerobic Treatment (Suspended growth processes)	Hybrid UASB & RO	196	137	30 NH_4^+(UASB)	Bohdziewicz & Kwarciak 2008
			137	16	88.7 NH_4^+(RO)	
5.	Anaerobic Treatment (Attached growth processes)	Anaerobic Filter	1800	225	87.5 NH_4^+	Renou et al 2008
6.	Aerobic	Membrane Bioreactor (MBR)	1000	200	> 80 TKN	Renou et al 2008
7.	Anaerobic	Membrane Bioreactor (MBR)	795	429	46 NH_4^+	Bohdziewicz et al 2008
(II)	IN SITU					
8.	Aerobic treatment	Landfill Bioreactor	500	10	98 NH_4^+	Giannis et al 2007
9.	Anaerobic treatment		2280	1755	23 NH_4^+	Jianguo et al 2007

3 MATERIAL AND METHODS

3.1 SITE DESCRIPTION

The old Kuhstedt landfill (Germany) has been constructed in the middle of the sixties in a former sand- resp. gravel pit. From 1973 on, the old disposal site was filled in a controlled way as combined pit-/landraising landfill. In 1987, when operation stopped, the total waste volume came to about 220.000 m³, deposited within an area of 3.2 ha. The landfill height is between 8 and 10 m, but the basis is about 2 – 3 m below the surface of the site. The old landfill can be regarded as typical for a large number of old landfills in Germany due to its volume, the deposited kinds of waste (mainly household waste, industrial waste similar to household waste, bulky- and construction waste) and due to geological and hydro-geological conditions. Most of these old disposal sites do not have the necessary installations for the collection of landfill gas and/or leachate or they do not meet the requirements. However, exactly these emissions represent a significant risk potential for the environment. As far as landfill gas production is concerned, assessments (basing on laboratory investigations) indicate periods of 20 to 30 years for the occurrence of significant gas quantities (partly usable) whereas assessments indicate a considerably longer period of time for contaminated leachate resulting from these old landfills (Krümpelbeck, 2000; Heyer, 1997). The occurring contamination (especially reduced nitrogen compounds) might necessitate a collection and purification of leachate for up to 100 or even more years, involving costs and technical requirement

Figure 9 Old Kuhstedt Landfil

3.2 Investigated samples

Since the beginning of preliminary tests at the old Kuhstedt landfill in autumn 1998, a large number of waste samples has been analysed at the Department of Waste Management, Technical University of Hamburg-Harburg. The samples were taken from different landfill depths in the course of the drilling of the aeration wells and analyzed in the laboratory.

Apart from the determination of different physical and chemical parameters, leaching tests for the assessment of the potential of leachate emissions as well as investigations of the biological activity of the waste samples were made. The obtained results were also used for the setup of LSR-tests.

Table 3 Waste sample characteristic

	Weight	**TS**	**Dry Mass**	**Volume**	**Wet Density**	**Dry Density**	**Carbon Content**	**TKN**
	Kg	%	Kg	m^3	ton/m^3	ton/m^3	g C/Kg TS	g TKN/Kg TS
LSR 1	44,20	74,46	32,91	0,0557	0,79	0,59	58	2,91
LSR 2	62,30	66,36	41,43	0,0549	1,13	0,75	92,80	3,02
LSR 3	50,70	72,49	36,75	0,0557	0,91	0,66	71	3,04
LSR 4	50,45	72,49	36,57	0,0546	0,92	0,67	67	3,04
LSR 5	48,20	68,27	32,91	0,0546	0,88	0,66	59,90	3,41
LSR 6	69,15	69,54	48,09	0,0561	1,23	0,86	62,40	n.e.
LSR 7	66,25	69,54	46,07	0,0581	1,14	0,79	64,50	2,91
LSR 8	62,30	73,59	45,84	0,0561	1,11	0,82	70,10	3,23

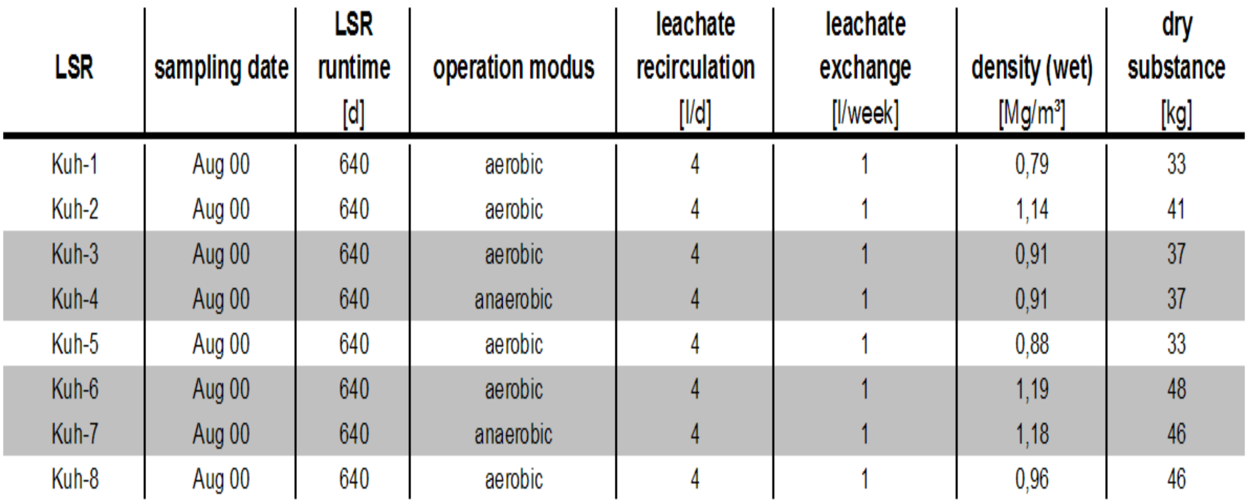
3.3 Aerobic and anaerobic treatment of waste samples in landfill simulation reactors

In two cases, the same waste material was placed in two landfill simulation reactors which, subsequently, were operated under aerobic resp. anaerobic conditions at a constant temperature of 35°C. Here, the anaerobic LSR serve as a control in order to simulate the emission behavior under the initial, anaerobic landfill milieu conditions. By means of an intensive process water circulation (twice a day), associated by a weekly leachate exchange (1 liter), it is possible to simulate both effects, the “flushing” as well as the aeration of the waste. Therefore the experiments simulate a base sealed landfill, applied with leachate re-circulation and aeration. By modifying the experimental set up to a LSR-operation with only limited process water circulation (according to the actual amount of precipitation, infiltrating into the landfill body) and minimized water exchange it is possible to simulate an aeration measure for an unsealed old landfill. For the described investigations, leachate and gas samples were taken at regular intervals and analyzed in the laboratory.

3.4 Operation of the landfill simulation reactors

The waste material, sampled in August 2000 (LSR-1, -2, -3, -5, -6, -8) resp. was adjusted to the maximum water holding capacity two weeks after the placement into the aerobically operated LSR. In addition, more water was added to obtain “free” process water for the operation of the leachate re-circulation.

Approximately 3 weeks after the begin of the circulation, the aeration with a low continuous volume flow was applied, adjusted to the oxygen demand of the waste samples as certained beforehand. As a control, the anaerobic LSR were operated under strictly anaerobic conditions. LSR 4 and 7 resp. contain the same test material as the aerated landfill simulation reactors LSR-3 and LSR-6 . Here, the exhaust gas was transported through two acid scrubbers in order to absorb the ammonia compounds from the gas phase. In Table moperation parameters of the LSR are shown. Figure 1 shows the principle operation set up for the LSR.



LSR	sampling date	LSR runtime [d]	operation modus	leachate recirculation [l/d]	leachate exchange [l/week]	density (wet) [Mg/m³]	dry substance [kg]
Kuh-1	Aug 00	640	aerobic	4	1	0,79	33
Kuh-2	Aug 00	640	aerobic	4	1	1,14	41
Kuh-3	Aug 00	640	aerobic	4	1	0,91	37
Kuh-4	Aug 00	640	anaerobic	4	1	0,91	37
Kuh-5	Aug 00	640	aerobic	4	1	0,88	33
Kuh-6	Aug 00	640	aerobic	4	1	1,19	48
Kuh-7	Aug 00	640	anaerobic	4	1	1,18	46
Kuh-8	Aug 00	640	aerobic	4	1	0,96	46

Figure 10 Lysimeters characteristic and set up

3.5 Landfill simulation reactors (LSR) setup

In order to study an aerobic in situ remediation strategy for the Kuhstedt Landfill, Germany, eight landfill simulation reactors (LSR) were prepared.

A scheme of the setup adopted for lysimeters is shown in Fig 11. :

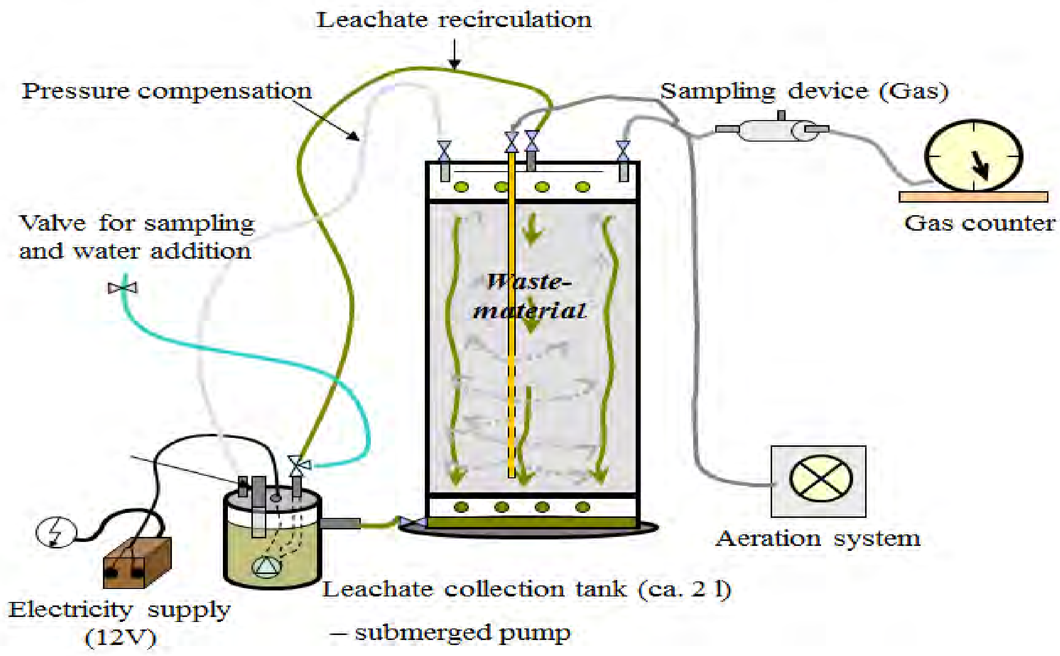


Figure 11 Schematic Diagram of the Lysimeters

The LSR´s are made of stainless steel and have a capacity of 80 l. each. Reactors have been first of all cleaned from previous waste used for other landfill simulation experiments.

Before starting the setup, every reactor is equipped with a lid where four threaded holes fitted with tap are present for the following purpose:

- Leachate recirculation;
- Aeration inlet;
- Flue gas exit;
- Pressure compensation.

Injection of air is realised by a perforated pipe inserted into the waste material and connected with the accordant inlet in the lid. The incoming air flow is adjusted by a manometer and a flow meter.

At the bottom of the LSR a grid for caption of material has been placed in order to avoid clogging in the leachate exit tap. The latter one allows for leachate outflow into a tank of 2l capacity. In this tank a submerged pump has been installed in order to recirculate leachate into the system passing through the central hole in the cover lid.

Using an electronic timer, 1l of leachate will be recirculated two times per day. Recirculated liquid is dropped into the LSR system through a percolation device. Along the pipe that connects the tank with the lid a valve with three exits has been placed. The function of this device is to have the possibility to sample leachate for analysis (weekly) and introduce fresh water into the system in order to simulate the rainfall contribute. Pump tank is connected through a tube with the lid to have pressure compensation between reactor and tank (Fig.12).

Figure 12 Leachate collection tank

The gases produced inside the system due to aeration processes go out through the dedicated exit on the lid and the quantity is measured with a volumetric gas counter (Fig.). Every week the gas composition (e.g. CO_2, CH_4) will be checked by means of GC-analysis (HP 6990 GC System). The gas will be taken from a sampling device positioned along the pipe that connects the exit gas tap with the gas counter. All connections were done with PVC pipes with an internal diameter of 5 mm. and fixed with hose clamps.

Figure 13 LSR´s lid and gas counter

Before the beginning of the simulation experiments all LSRs has been tested in order to check if some leakages are present in the system. The lid is fixed with 12 screws to the reactor and a rubber seal positioned between the lid and the reactor. Leakage test is conducted introducing air inside the reactor with a pressure of 0.2 bar and checking leakages with a specific spray. The system can be considered tight if in the next twenty-four hours the pressure losses are less than 10% of initial pressure.

Once all reactors can be considered tight the waste samples can be placed inside. The LSR will be place in a 36°C air-conditioned room (Fig.14). Here the aeration tap in the lid is connected with the aeration system.

Figure 14 LSR installed inside 36°C conditioned room

Landfill simulation experiments allow for the analysis of the behavior of physical/chemical degradation processes of waste samples under aerobic or anaerobic conditions at laboratory scale. The main advantage of this approach is to understand the evolution of main emissions during a relatively short time (months) compared with emissions for full scale landfills which may last for many decades. The construction of bioreactors setup allows sampling the most important products of aerobic digestion (leachate and gases) in an easy way. Through this the trend of the most important parameters such as TKN, TN, TOC, CH_4 and CO_2 can be determined.

Through the aeration device it is possible to inject different flows of air or mixture of other gases (for example oxygen plus inert gases as argon). The aeration system could be activated when is preferred giving the possibility to switch the reactor from strictly anaerobic condition to aerobic one. It´s also possible to compare the same sample´s behaviour under anaerobic and aerobic conditions: this possibility is important in order to compare the emission behaviour under strictly anaerobic conditions (landfill without remediation) to the emissions to occur under the influence of aeration. With the data collected from the experiments it´s possible to evaluate the efficiency of the aerobic treatment comparing the evolution of the same compound in each LSR.

The main problem is related to the uncontrolled infiltration of air into LSR. For the simulation period being quite long (up to two years) it´s possible that an unknown quantity of air is introduced inside the system due to the slackening in the connection or in the screws which seal the lid. To avoid this possibility, it´s very important to check at the beginning and also during the simulation the tightness of all connections using a specific spray detector.

3.6 Simulation setup

The solid waste will be placed in six LSRs heated to a constant temperature of 36°C, all located in an air-conditioned room. In two case the waste sample will be placed under anaerobic conditions in order to simulate the emission behaviour that normally prevails in landfills. Through the pump system leachate will be recirculated twice a day in conjunction with weekly leachate exchange to simulate the percolation of rainfall and subsequent elution of substances that occur in old landfills. Gas composition will be over measured using a drum gas-meter.

The waste material will be adjusted to maximum water storage capacity 2 weeks after the placement into the LSR. Additionally, water will be added to obtain conditions in excess of field capacity to use in the operation of the leachate recirculation system. After one month form recirculation began aeration will be applied with different flow rates for each LSR adapting it with the actual oxygen demand (determined by oxygen content in the off-gas).

The main parameter affecting the aeration can be resumed in the air injected, leachate recirculation (flushing) and temperature control.

For the quantity of inlet air, every experiment used different flows related to the different masses of waste to aerate. From this point of view it is difficult to determine an exact flow rate to enhance the aerobic degradation but the efficiency of this methodology is given. Flow parameters are dependent from the stabilization level of waste analyzed, occurred during anaerobic decomposition in the landfill before the simulation experiments.

The moisture recirculation and the use of higher amount of water provide some advantages, mainly affecting organic compounds in the leachate. In some cases (a suitable base sealing system is required at a full scale level), an active enhancement of leaching may be useful in shortening the aeration period and reaching relevant limit values more rapidly. Has to be considered that leaching and aeration in parallel might be difficult to achieve due to the void space filled with water.

It is important to underline that these kind of laboratory-scale experiments are set to understand the behavior of stabilization processes under aerobic and anaerobic conditions. When the aeration is applied at full scale problems related to the control of all parameters may occur.

For the air inlet and flushing it is possible to adapt the results of the lab scale to a landfill through a model that permits to supply the proportional air and moisture content to the landfill body. It is very difficult to control the temperature. In a lab scale simulation the temperature is always maintained at a certain value creating then a perfect situation for the microorganisms interested in the degradation processes. When we move the set-ups to full scale, the temperature is not more constant and can change considerably. Temperature rises as a result of aerobic degradation due to the metabolism of microorganism. Above certain values (around 40-45°C) the influence of temperature on nitrification paths is crucial. The nitrification doesn´t occur following the normal pathways and an increase on ammonia nitrogen values may be observed. In this way almost all TKN is break down through the gas phase and not via leachate. For this reason it is very important to consider a strategy for the mitigation of temperature into the landfill body, especially where lower waste biological stabilization was observed. From this point of view discontinuous aeration or leachate recirculation could be considered proper solutions. It is then important to understand the optimal flushing ratio and the less quantity of air that is possible to inlet into waste in order to avoid a significant increase of temperature for the abovementioned reasons.

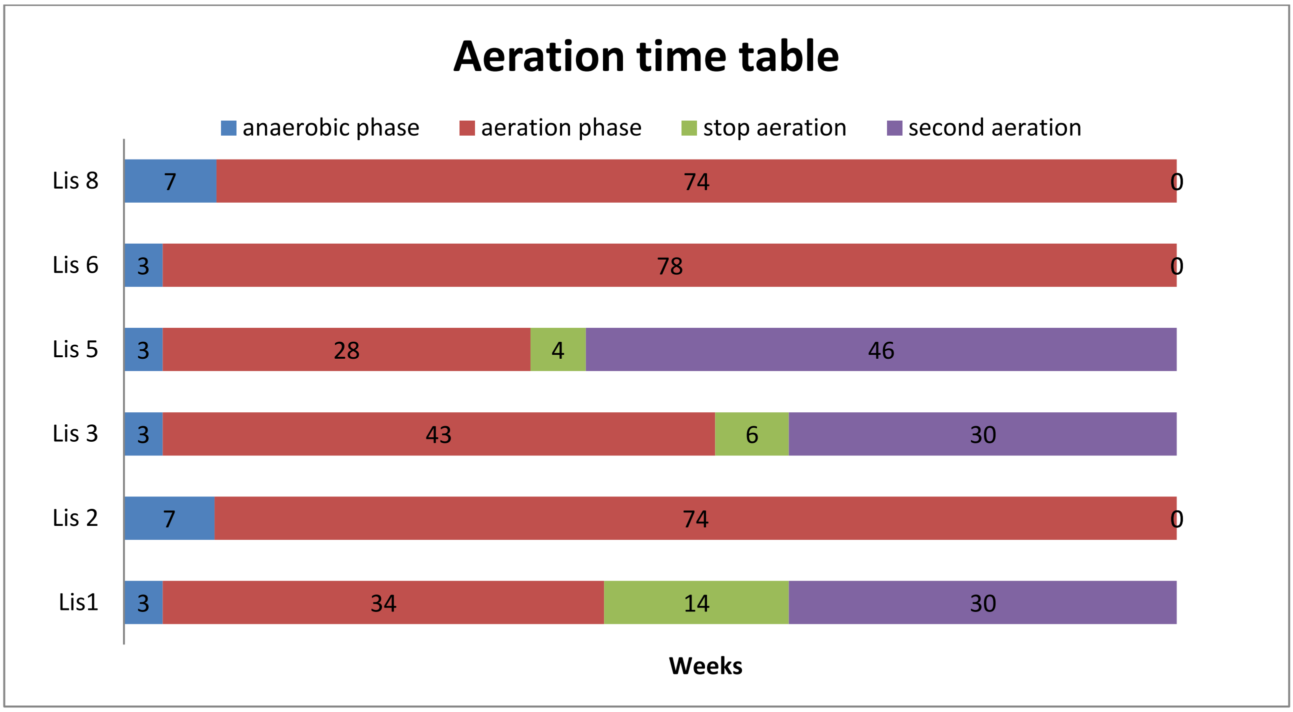
3.7 Test description

All the examined bioreactor have been studied for a time period of about 570 days. During this time the aerated lysimeters have been inflated with ambient air for several weeks as said in previous chapter.

After a time comprised between the 3 to the 7 week, where the bioreactors have been maintained in an anaerobic condition, the aeration started for long periods. Lysimeters 2,6 and 8 have been aerated for a time comprised between the 74 to the 78 week continuously

The other ones (lysimeters 1, 3, 5) after an aeration time comprised between 28 to 43 weeks had a short time (confronted to the aeration time) where the air insufflations has been stopped for 4 to 14 weeks.

Table 4 Aeration time table



About the aeration flow has to be said that the measurements have been taken trough the lectures of a flow meter, and a large range of values has been evaluated. The average values of air flow are comprised between 0,55 to 1,8 l/h with several peaks of aeration probably due to a not perfect calibration of the machine, a great data dispersion has been evaluated. In general the lysimeter are in low aeration flow in order to simulate a in situ landifil aeration and to satisfy the stoichiometry need for nitrification.

The original aim of this experiment was to treat the waste sample with a long aeration in order to study the final degradation obtained and to evaluate the possible stability achieved.

In the following table has been indicated the maximum, minimum and average values of air inlet. The aeration peaks measured can be considered as error of measurement than furthermore than a specific decision of the user.

Table 5 Aeration fluxes Maximum, minimum and average values

	Max aeration	**Minimum aeration**	**Average**
	l/h	l/h	l/h
Lis 1	1,85	0,2	0,88
Lis 2	4,3	0,1	1,15
Lis 3	1,95	0,25	1,1
Lis 5	1,95	0,15	0,55
Lis 6	1,31	0,1	0,9
Lis 8	5,05	0,31	1,8

4 VISUAL BASIC TOOL DEVELOPMENT

4.1 Data set structure

Before investigating the possible pathways of Nitrogen in the waste material, and trying to asses a mass balance, an analysis of the data set provided has been performed in order to evaluate the possible “lacks” of values and their magnitude, and elaborate possible solution to obtain a congruent series of them.

The final target of this part of the study is to generate a forecast model of the exiting concentrations of NH4 and TN from the column reactors in order to evaluate the missing values.

The data are, as previously said, both from the leachate characteristic and gas composition.

Regarding the leachate characteristic the weekly concentration of several compound has been evaluated from the sample extracted from the bottom of the lysimeters (both aerobic that anaerobic). These data are (table 5)

Table 6 Evaluated leachate parameters

Parameters	**Unit Measure**
pH (before filtration and after filtration)	---
Redox	[mV]
L/S ratio	[l/kgTS]
BOD	[mgO/l]
COD	[mgC/l]
TOC	[mgC/l]
TN	[mgN/l]
NH_4-N	[mgNH4-N/l]
NO_2-N	[mgNO2-N/l]
NO_3-N	[mgNO3-N/l]
Cl, PO_4-P, SO4, HCO_3	[mg/l]
Heavy metals concentration (Cr, Ni, Cu, Cd, Pb)	[μg/l]

Regarding the off-gas measurement the evaluated data have been usually collected with a various and not continuous range of time. For the first 3-4 months measurements has been taken about every three days (average), but after usually several months, because of the lower level of gas produced, the gas sample has been evaluated in weeks (or more). The data gas are the following:

- Air inlet [l/h]
- Gas outlet [l/h]
- Gas composition (CO_2 , CH_4 , O_2 , N_2) [%]

The different values have been analyzed to evaluate the missing factors in the measurements of the collected leachate. Focus has been put on the TN and NH4 compounds since it is objective of the study understanding the fate of Nitrogen in the samples.

In table has been indicated the percentage of missing values for TN. Regarding the NH4 almost all the values are measured so the few missing one have been interpolated.

Table 7 Percentage of missing TN values

Lysimeter	Missing Values TN (%)
LSR 1	70,9
LSR 2	44,44
LSR 3	67,27
LSR 4	69,1
LSR 5	72,73
LSR 6	77,78
LSR 7	61,3
LSR 8	76,28

After this analysis it resulted clear the need of finding a way to forecast the TN trend emitted from the bottom of the lysimeter, in order to asses a Nitrogen mass balance.

First step to obtain a model for the variation of quantity of TN and NH_4 is to evaluate the kinetics of the concentration in the samples analyzed. The tool development has the aim of understanding various results like, for example, if the effect of the interpolation of missing data gives back realistic trends of the system behavior and its changing during time.

4.2 Kinetics modelling

4.2.1 Theory and Assumption for the model development

Considering the high quantity of missing TN values for the aerobic lysimeters (in the anaerobic they are totally absent) the question posed was if just the interpolation of the missing data will give feasible data that could be utilized in the mass balance.

The second question that emerged from the data set analysis was that if we consider the kinetics of varicompounds variations with as a first order kinetics, is the half-life method feasible to model the Nitrogen decrease ?

Starting from the concept of a central difference method for the evaluation of Ammonia removal kinetics (Berge et al 2006) has been decided to apply the System Dynamic model approach.

The theory that underlies this study is that, starting from the evaluation of Ammonia removal kinetics, could be possible to connect the obtained results to TN removal kinetics, even if they belongs from a poor data set analysis. Applying a statistical approach it should be possible to relate the two obtained values of kinetics.

In the end, in order to understand if the obtained data are feasible, a model system will be applied to check the results.

Some assumption has been taken at the beginning of the work:

- Experimental data are highly not constant or continuos
- The observed variation are related to defined time shift (week)
- Every equation are at the finite difference
- In the aerobic reactor the decrease of Ammonia concentration in the samples, after the start aeration, has been considered due to the nitrification reaction
- In the aerobic reactors all the decrease of Organic nitrogen has been considered due to the ammonification reaction.

- In the anaerobic reactors NH4 decrease are considered due to a removal ammonia kinetics (not a nitrification rate) due to several factors probably connected to the eluition and slight pH variation
- In the anaerobic reactor the increase of NH4 variation are considered due to an increase of Ammonification removal kinetics
- TN concentration consider NO_3 and NO_2 inorganic nitrogen quantity, but their quantity is low, so the error has been considered as acceptable.
- Inside the lysimeter the quantity of water is the sum of the waste water content plus the added water at the beginning of the experiment.
- The reactor is considered as a CSTR system (complete stirred tank reactor)
- The same model will be applied at the anaerobic model with slight variation due to the different characteristic of the reactor.
- The kinetics rates calculated, for the aerobic lysimeter, are reported as ammonia removal kinetics, not nitrification kinetics. However is believed that the ammonia removal kinetics will be very close to the nitrification kinetics (Berge et al 2006)

This assumption will be considered as a starting point for the further tool development.

4.3 Kinetics Theory

As a first step it is important to define the studies based on differential equation that brings to the evaluation the half life time . Now will be shown an example to clarify the approach.

Here is descrived one example of calculation of the Nitrification velocity based on the half life time.

If we consider Nitrification as a first order kinetics, the related differential equation is in this form:

$$\frac{d[NH4]}{dt} = -kn \cdot [NH4];$$

Splitting the variables it will became:

$$\int_0^t \frac{d[NH4]}{[NH4]} = \int_0^t -kn \cdot dt\ ;$$

$$\ln[NH4]_t - \ln[NH4]_0 = \ln\frac{[NH4]_t}{[NH4]_0} = -kn \cdot t\ ;$$

If:

$$[NH4]_{t_{1/2}} = \frac{[NH4]_0}{2}$$

Then:

$$\ln\frac{[NH4]_{t_{1/2}}}{[NH4]_0} = \ln\frac{1}{2} = 0{,}693 = -kn \cdot t_{1/2}\ ;$$

And in the end:

$$\boxed{kn = -\frac{0{,}693}{t_{1/2}} \quad day^{-1}}$$

But analyzing the experimental data of NH_4 concentration (reported below) inside LSR 1, some considerations has to be done. From the aeration start the ammonification process can be considered feasible, meaning that the production of new NH_4 is lower than the consumption.

- Aeration starts at the 21 day and the NH4 concentration is of 328 mg/l
- One concentration of 328/2 = 164 mg/l is achieved about after 59 days
- The half- life time is: $t_{1/2}$ = 59-21=38 days

So Nitrification velocity should be about:

$$\boxed{kn = -\frac{0{,}693}{38} = -0{,}0182 \quad day^{-1}}\ ;$$

Adopting this values we achieve the constant concentration (5 mg/l) weeks later respect the experimental data

This evaluation bring to the research of a different approach the velocity kinetics.

4.4 System Dynamic

The basis of System Dynamic (SD) are now introduced (J.W. Forrester 1961).

As a knowledge domain, SD can be thought of as a logical extension of systems engineering (SE) and systems analysis (SA). SD put into account the dynamic behavior that results due to delays and feedbacks in the system and has been utilized to solve problems in the business and social science domains (Forrester, J.W., 1961). A basical use, based on the concepts of the mass balance, is explained below in equations:

$$\frac{\Delta L}{\Delta t} = \lambda - \mu \cdot L$$

$$\left(\frac{\Delta L}{\Delta t}\right)_t = \frac{\Delta L_t}{\Delta t} = \lambda_t - \mu_t \cdot L_t$$

$$\Delta L_t = \lambda_t \cdot \Delta t - \mu_t \cdot L_t \cdot \Delta t$$

$$L_{t+\Delta t} - L_t = \lambda_t \cdot \Delta t - \mu_t \cdot L_t \cdot \Delta t$$

$$L_{t+\Delta t} = L_t + \lambda_t \cdot \Delta t - \mu_t \cdot L_t \cdot \Delta t$$

Table 8 Mass balance concept

Where:

L = level
ΔL = Δlevel
Δt = Δtime
λ = input rate
$-\mu \cdot L$ = output rate $= \frac{L}{T}$
μ = unit rate $= \frac{1}{T}$
T = system time

Some starting assumption brought to the utilization of this approach.

- Experimental data are highly not constant or continuos
- The observed variation are related to defined time shift (week)
- Every equations are at the finite difference

Furthemore it’s important to define two others simple mathematical equation that will be utilized in the second part of the model end are:

- Evaluation of equilibrium level value L used in the calculation of the ratio between nitrification velocity and TN variation velocity

$$\boxed{\begin{array}{l} \frac{\Delta L_e}{\Delta t} = \lambda - \mu \cdot L_e = 0 \\ \lambda = \mu \cdot L_e \\ L_e = \frac{\lambda}{\mu} \end{array}}$$

- Evaluation of μ assuming λ feasible.

$$\boxed{\begin{array}{l} \frac{\Delta L}{\Delta t} = \lambda - \mu \quad \frac{\Delta L}{\Delta t} = -\mu L \\ \mu_i = \frac{1}{\Delta t} \frac{\Delta L_i}{L_i} \\ \overline{\mu} = \frac{1}{n} \sum_{1}^{n} \mu_i \end{array}}$$

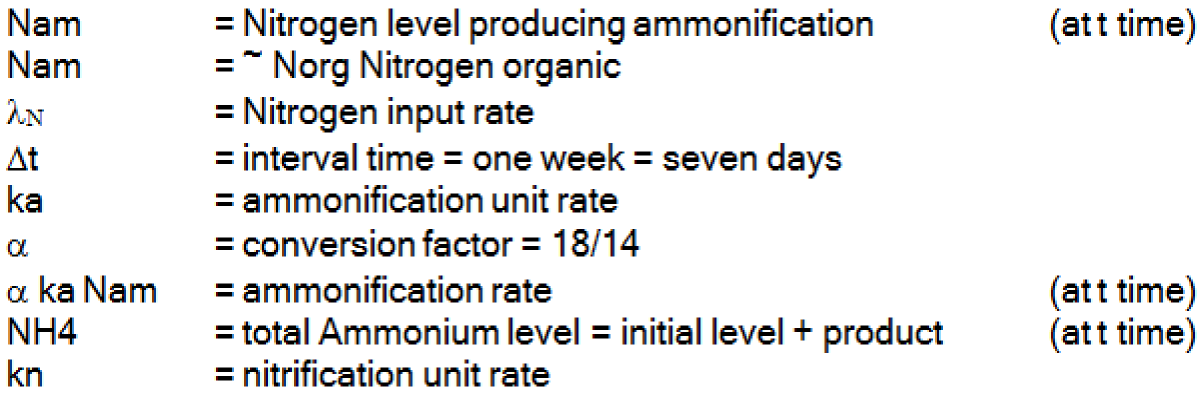
4.5 Simple Dynamic model

The evaluation of the aerobic model is based on the assumption that the Ammonification rate is slower than Ammonia variation rate. The quantity of generated NH4 is lower than the disappearance. These are the aerobic equation utilized to evaluate the kinetics:

Table 9 Aerobic model

1. $$\frac{\Delta Nam}{\Delta t} = \lambda_N - ka \cdot Nam$$
2. $$\Delta Nam = (\lambda_N - ka \cdot Nam) \cdot \Delta t$$
3. $$\frac{\Delta NH4}{\Delta t} = \alpha \cdot ka \cdot Nam - kn \cdot NH4$$
4. $$\Delta NH4 = \alpha \cdot ka \cdot Nam \cdot \Delta t - kn \cdot NH4 \cdot \Delta t$$
5. $$NH4_{t+\Delta t} = NH4_t + \alpha \cdot ka \cdot Nam \cdot \Delta t - kn \cdot NH4_t \cdot \Delta t$$

Where:



Nam = Nitrogen level producing ammonification (at t time)
Nam = ~ Norg Nitrogen organic
λ_N = Nitrogen input rate
Δt = interval time = one week = seven days
ka = ammonification unit rate
α = conversion factor = 18/14
α ka Nam = ammonification rate (at t time)
NH4 = total Ammonium level = initial level + product (at t time)
kn = nitrification unit rate

The ka and kn values are obtained from the data set, the missing values have been obtained through interpolation. It's important to say that many data present (especially TN values) are themselves interpolated data. The objective of this model is to understand if even in this poor data set is possible to obtain realistic trends of concentration.

4.6 Anaerobic model

In the anaerobic model the variation of Ammonia nitrogen and Ammonification doesn’t depend on the inflated air. The only variations depends on the quantity of leachate, collected from the bottom of the lysimeter. Nitrification is almost absent so kn represents the variation of NH_4 concentration due to the elution. From these assumptions has been utilized a different mathematical model.

Table 10 Anaerobic model

$$1.\quad \frac{\Delta NAm}{\Delta t} = \lambda - ka \cdot NAm$$

$$2.\quad \frac{\Delta NH4Am}{\Delta t} = \alpha \cdot ka \cdot NAm - kn \cdot NH4Am$$

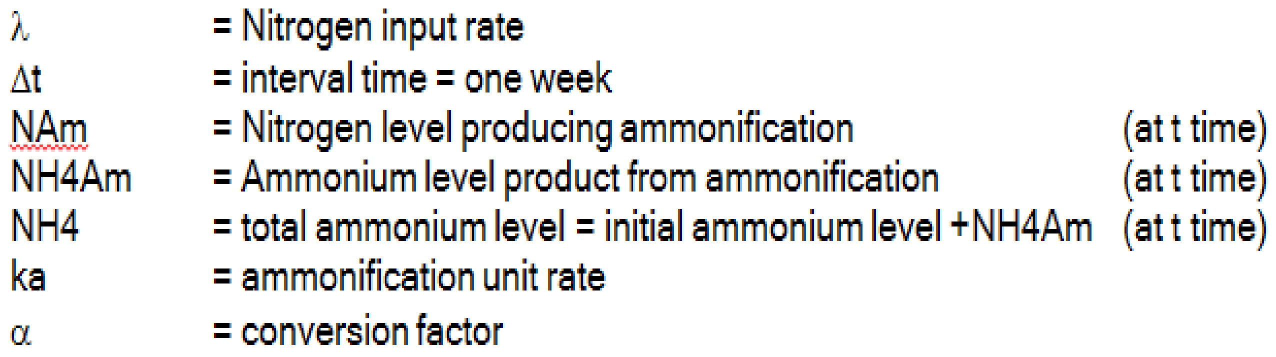
$$3.\quad \Delta NH4Am = (\alpha \cdot ka \cdot NAm - kn \cdot NH4Am) \cdot \Delta t$$

$$4.\quad \frac{\Delta NH4}{\Delta t} = \frac{\Delta NH4Am}{\Delta t} - kn \cdot NH4$$

$$5.\quad \Delta NH4 = \Delta NH4Am - kn \cdot NH4 \cdot \Delta t$$

$$6.\quad NH4_{t+\Delta t} = NH4_t + \Delta NH4Am_t - kn \cdot NH4_t \cdot \Delta t$$

Where:



λ = Nitrogen input rate

Δt = interval time = one week

NAm = Nitrogen level producing ammonification (at t time)

NH4Am = Ammonium level product from ammonification (at t time)

NH4 = total ammonium level = initial ammonium level +NH4Am (at t time)

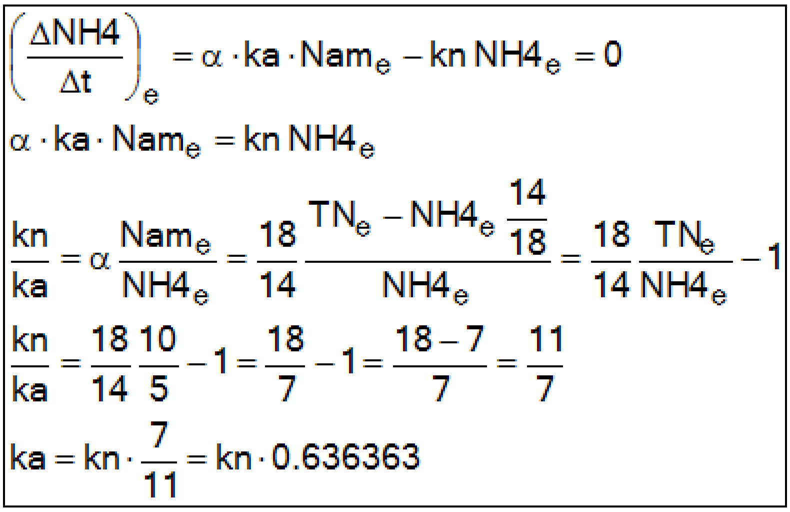
ka = ammonification unit rate

α = conversion factor

4.7 Evaluation of the velocity ratio between nitrification rate and ammonification rate

All the aerobic lysimeter achieved, after an aeration period comprised between 50 to 120 days, an almost equilibrium concentration of NH_4 (5 mg/l) and TN (10mg/l). This numbers bring to the theorization of a statistical equilibrium (J.W. Forrester 1961). As theorized it is possible to say that ammonia concentration variation is depending on two rate (ka and kn evaluated with the Visual Basic tool). Starting from this point, when the equilibrium is achieved the delta ammonia is equal to zero.From this point is possible find a correlation between the two k as shown intable 10. This equilibrium is not achieved in the anaerobic reactor, and so this methodology cannot be applied.

Table 11 Equilibrium equation



$$\left(\frac{\Delta NH4}{\Delta t}\right)_e = \alpha \cdot ka \cdot Nam_e - kn\, NH4_e = 0$$

$$\alpha \cdot ka \cdot Nam_e = kn\, NH4_e$$

$$\frac{kn}{ka} = \alpha \frac{Nam_e}{NH4_e} = \frac{18}{14} \frac{TN_e - NH4_e \frac{14}{18}}{NH4_e} = \frac{18}{14} \frac{TN_e}{NH4_e} - 1$$

$$\frac{kn}{ka} = \frac{18}{14} \frac{10}{5} - 1 = \frac{18}{7} - 1 = \frac{18-7}{7} = \frac{11}{7}$$

$$ka = kn \cdot \frac{7}{11} = kn \cdot 0.636363$$

This last mathematical equation will be analyzed afterwards, with the real data, in order to check the effect and the feasibility of the model.

4.8 Kinetics.xls

The model generation is, as previously said, the definition of the different kinetics of NH_4 and TN variation.

For this phase has been generated four excel files called “Kinetic Statistic”. Here are indicated:

- Kuh aerob (1,2) Kinetic Statistic.xls
- Kuh aerob (3,6) Kinetic Statistic.xls
- Kuh aerob (5,8) Kinetic statistic.xls
- Kuh anaerob (4,7) Kinetic statistic

These Excel sheets perform different actions and work through a series of generated Visual Basic Macro.

It is important to say that the “aerob” and “anaerob” files have some slight differences due to the nature of the reactions (anaerobic and aerobic) that develop inside the lysimeters as before explained

Firstly will be described the ”aerobic.xls”, how tit works and the results obtained.

Every file contain several sheet

- “Kn” sheet that evaluate the nitrification velocity
- “Ka” sheet that evaluate the TN concentration variation
- “Test” sheet that check the results of the velocity constant evaluated
- “Kuh” sheet that contain the original data fournished

“Kn” sheets automatically perform different operation through Visual Basic Macro. Every action is activated by the button “Kuh NH4 average kn”

- The tool copies the values of NH4 from the “Kuh sheet” into the “Kn” sheet
- All the differences between the weekly concentration are calculated

- The negative difference, the decreasing concentration of NH4, are the data that are utilized for the evaluation of the weekly velocity
- Average velocity kn is evaluated
- Standard Deviation of the values is evaluated
- The Standard deviation/average value is evaluated
- Organic nitrogen content is evaluated

The model results will examined in Chapter 5

5 RESULTS

5.1 Analytical leachate results

In the following table are shown the initial values of compounds evaluated in the leachate samples.

Table 12 Initial leachate composition

	pH	BOD	TOC	BOD/TOC	TN	NH_4-N	NO_2-N	NO_3-N	SO_4
	-	[mgO/l]	[mgC/l]	-	[mgN/l]	[mgN/l]	[mgN/l]	[mgN/l]	[mg/l]
LSR 1	7,1	1375	1061	1,28	347,5	280	n.v.	n.v.	2
LSR 2	6,21	15690	9931	1,61	470	361	n.v.	n.v.	98
LSR 3	7,02	942	939	1	457,7	359	n.v.	n.v.	3
LSR 4	6,95	947	909	1,04	317	253	n.v.	n.v.	1,1
LSR 5	7,05	2500	1805	1,39	459	392	n.v.	n.v.	2
LSR 6	7,05	2282	1633	1,4	384	316	n.v.	n.v.	1,3
LSR 7	7,08	2059	1825	1,13	468,9	348	n.v.	n.v.	1,9
LSR 8	6,02	15481	9447	1,64	865	634	n.v.	n.v.	8

As can be seen the chemical parameter examinated have heterogeneous starting values, except the LSR 3 and LSR 4 and the bioreactor LSR 6 and LSR 7 that contain the same waste material.

The highest level of TOC, TN and BOD are in the LSR 2 and 8 indicating that probably they are the "younger" one, located in the higher part of the landfill. The average nitrogen starting concentration of NH_4-N and TN are 367,85 and 471,13 mgN/l. The pH values are in a range between 6,02 to 7,08 indicating a slightly acidic conditions.

The leachate analysis concordantly indicate a notably accelerated biodegradation of organic waste compounds due to the aeration. This can be shown by a fast and significant decrease of the parameters TOC, COD and BOD_5. Additionally, the concentrations of the inorganic nitrogen compounds are noticeably reduced under the influence of aeration as well.

For this study the focus will be put on the Nitrogen compounds in order to understand their behavior.

As already said Ammonium/ammonia (NH_4 / NH_3) are the most relevant compounds in the leachate with respect to the aftercare phase, as the NH_4-leachate concentrations decrease only over very long periods of time (several decades up to centuries) (Heyer and Stegmann, 1997).

Significant removal rates can be achieved through the well know processes of Nitrification and Denitrification. Regarding the nitrification process analysis of leachate components from aerated and LSR show, that the NH_4^+-concentrations clearly decline after the start of aeration. A short increase of the nitrite concentrations can be observed with a slight delay. In some individual cases (e.g. LSR 3) the subsequent short-term occurrence of nitrate or nitrite as “end product” of nitrification can be noticed.

In general, the concentrations of the inorganic nitrogen compounds are within the measuring accuracy range (< 5 mg/l) after about 50 to 120 test days in the aerated LSR, whereas no significant reduction can be observed for the anaerobically operated reactors LSR 4 and LSR 7. Figures shows the average trend of nitrogen N leachate components for aerated (fig 15) and a comparison of nitrogen trend between LSR 3 and LSR 4 (fig16). The Nitrogen variation of the anaerobic reactor is mostly due to the elution effect. For all the aerated lysimeters is obtained a NH_4 removal performance higher than of the 90%.

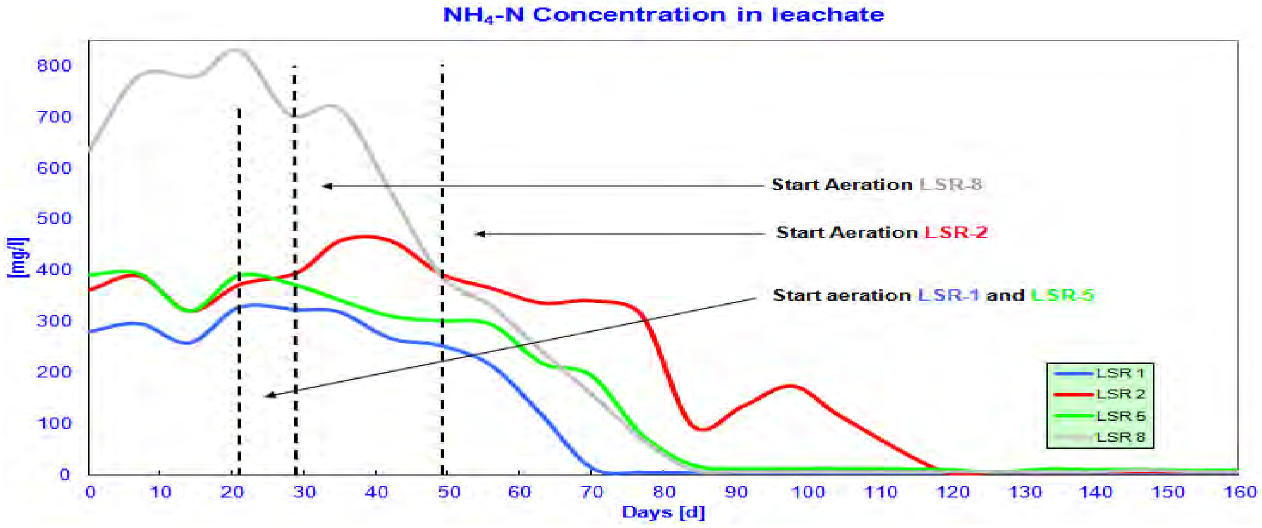


Figure 15 NH_4 concentration decrease in time for LSR 1, 2,5,8

The low presence of other inorganic nitrogen compound (NO_3 and NO_2) that are Nitrification products is probably due to denitrification reaction inside the anaerobic pockets of the reactor.

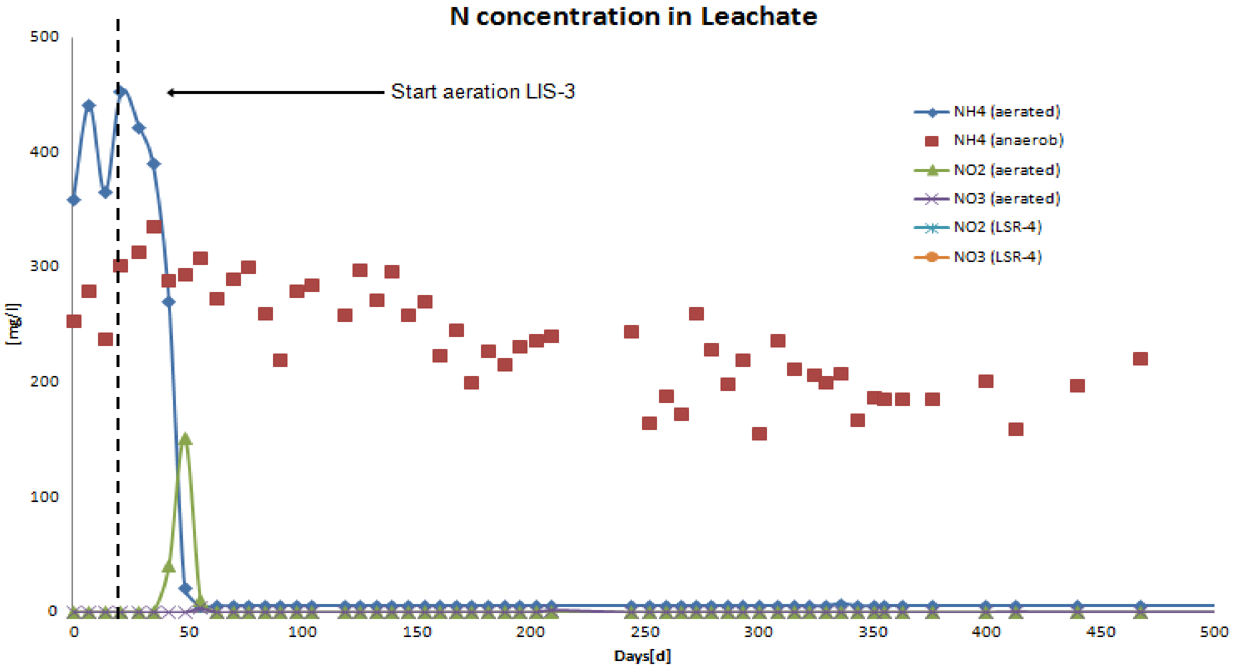
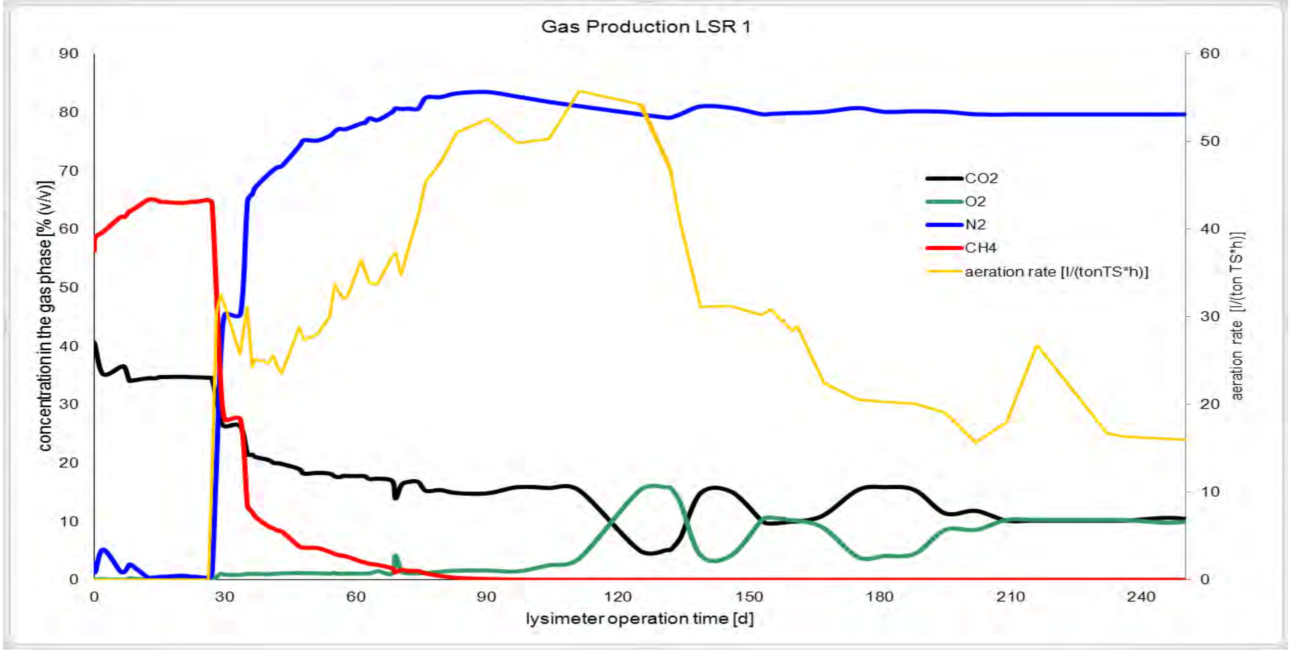


Figure 16 Comparison between Nitrogen concentration leachate in LSR 3and LSR 4

5.2 Gas production

The data regarding CO_2, CH_4, O_2 and N_2 gas percentage for LSR 1and LSR 6 aerobic reactors have been reported in the following pictures :



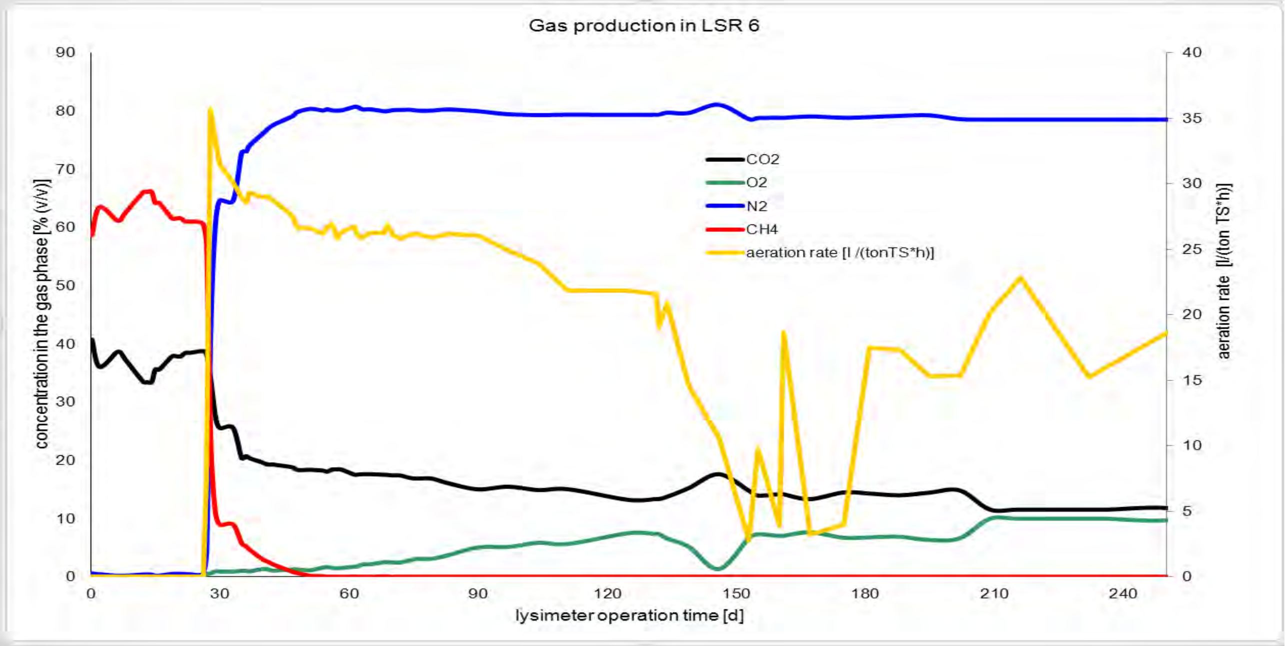


Figure 17 Gas trend composition LSR 1 and LSR 6

The results of the data gas analysis show an almost similar behavior between all the aerated simulator except for the LSR 8

At the beginning of the experiment the lysimeters has been set up in an anaerobic condition for a time range between 21 to 49 days in order to consume the possible entrapped oxygen in the waste. This type of treatment has been reprise after a long time of aeration (approx. after 250-300 days) in order to make a set up of interesting parameters and evaluate the effects of stopping the air flow on the exit gas.

As expected from previous studies in the anaerobic phase has been observed an increase in percentage by volume of CH_4 and CO_2 until reaching the typical stable methanogenical value (around 60% CH_4 and 35-40 CO_2) (Christensen et al 1989).

If the pH trend is examined is possible to see that during the first anaerobic phase the values are slightly acidic (6-6,5) but then they increase around 7 after the start aeration. Ph of about 6,5-7 is suitable for the enstablishment of a methanogenic phase (Christensen et al 1989). Confronting LSR4 (aerobic) and LSR 3 (anaerobic) is interesting to see that as expected the pH values are more close to acidic in the anaerobic one while in the aerobicthe pH tend to increase even if some oscillation are present.For the aerbic LSR, regarding nitrification, the values of pH are almost the optimum for both nitrification that denitrification

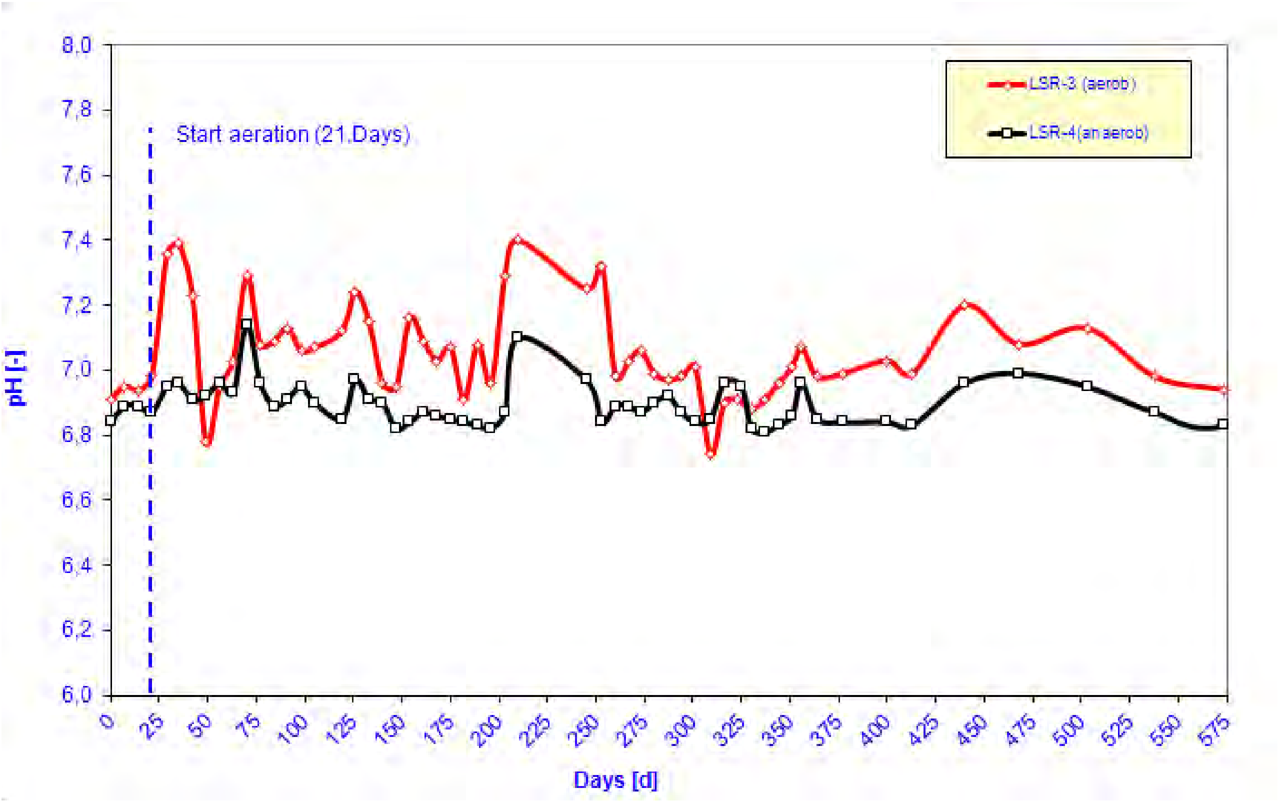


Figure 18 pH variation in LSR 3 and LSR 4

When aeration starts is possible to see a stipe decrease of methane production, due to the variation of condition for the methanogenic microorganism. At same time the percentage composition of nitrogen gas rapidly increase until reaching stable values of almost the 80% in a time range comprised between 15-30 days.

The quantity of oxygen present in initial air flow is utilized immediately by the Hetherotrophic microorganism, this fact can be related to the very low quantity of not utilized oxygen exiting the reactors in the first 60-90 days.

Regarding the CO_2 percentage after the starting aeration period is possible to see that during the change of condition from anaerobic to aerobic the the quantity of carbon dioxide tends to halve from the evaluated 30- 40% till 15-20% and remain close to this values along the entire duration of the aerated phase.

As said before the aeration, for some lysimeter, has been stopped after a variable time and during this phase can be seen an increase of the CO_2 concentration and hereafter some traces of CH_4 can be detected, but at the restart of the aeration this methane quantity immediately decreases. Regarding the N_2 gas can be seen that the stop aeration doesn't influence the achieved stable quantity of the 80%. Probably the reasons could be related to some factors like the release of trapped ambient air accumulated inside the reactor during the process or air infiltration from the outside system or maybe a measurement error.

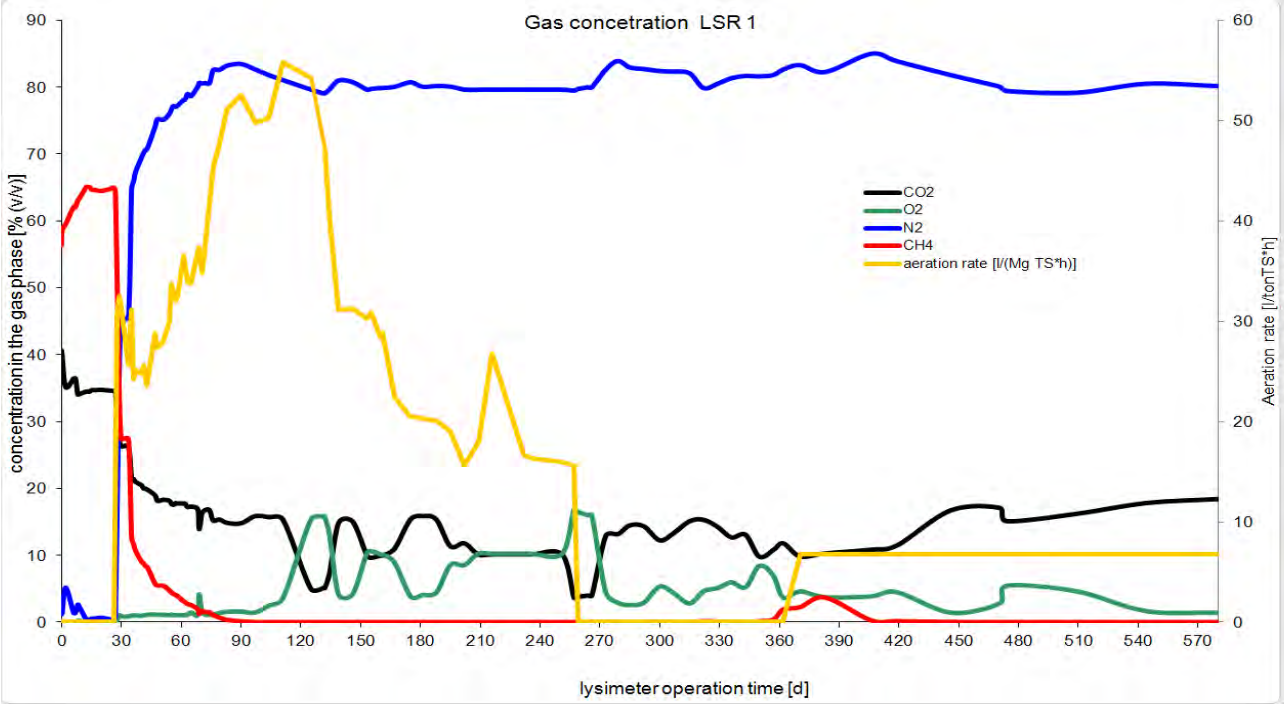


Figure 19 Gas composition in LSR 1along all the experiment

It is important to say that the N_2 measurement has been utilized especially to study the trend of gas realesed, it is very hard to evaluate the quantity of Nitrogen gas generated inside the reactor through the Nitrification/Denitrification processes (or other processes involved) because the values are inside the precision error of the machine. Nitrogen inflated inside the reactors is about the 78-79% of the total gas, the exiting quantity is often a little more (usually the 80-81%). Considering that little percentage as the real nitrogen generated is not feasible and will bring to an overestimation of the gas. It seems better trying to asses a mass balance trough some indirect measurement.

Regarding LSR 8 are evident some possible measurement error, due to not defined reasons. The trend of oxygen and nitrogen in the anaerobic phase achieve values almost identical to the composition of atmospheric air, without any inflated air. The reason could be related to a release of air inside the waste, or advective phenomena or a not controlled air inlet due to malfunction of the safe valves.

After a short time, however a substantial quantity of CH_4 and CO_2 is produced as expected and decreases after the consecutive aeration phase.

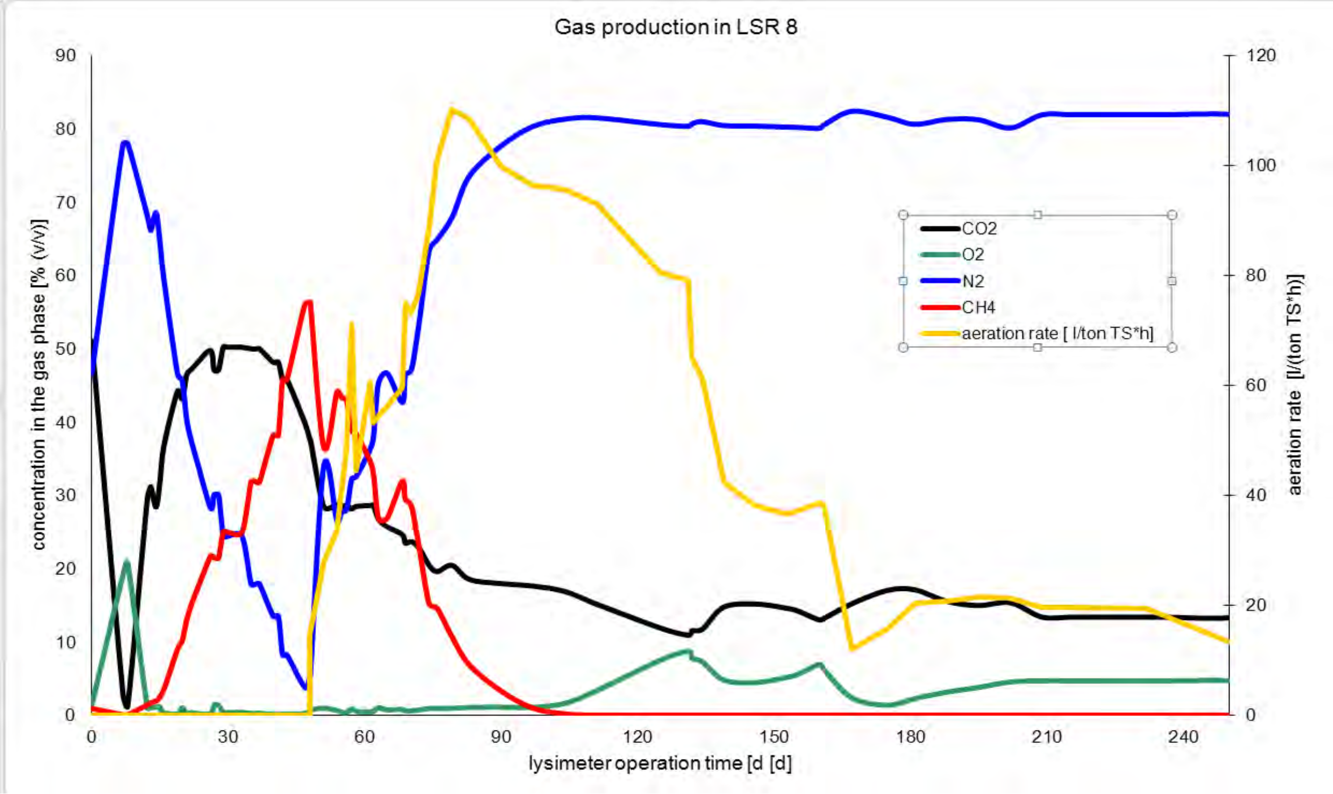


Figure 20 Gas composition LSR 8

5.3 Kinetics Evaluation results

5.3.1 Aerobic Kinetics

For the aerobic lysimeter, utilizing the previously defined equation in chapter 3, has been obtained trends of NH_4 variation with errors comprised in a range of 2-3 weeks in comparison with the real measured data. The evaluation of a average Kn from the different Lysimeters fits quiet good simulating a first order kinetics trends

It's important to remember that many of the real data belongs themselves from interpolation and, about the almost constant 5mg/l concentration of Nitrogen achieved, there are very sharp variation that depends on velocity variations.

As said the obtained trends are shaped as a first order kinetics and in general the results demonstrate an over-estimation of the NH_4 variation but the equilibrium level is achieved almost in the same time. This overestimation probably depends on the little quantity of data measured. Data taken more frequently (every three days for example) should give a more precise evaluation.

One interesting results is that, as theorized in the equilibrium equation before, seems that there is a correlation between the Kn and Ka removal kinetics**.** If we see the table below the average value of all the average Ka/Kn ration is equal to 0,64093, very close to the 0,6363 ratio obtained through the equilibrium eqution. This results, or better said the model, can be utilized for every aerated system that achieve a statistical equilibrium level of TN and NH_4 concentration. This ratio can be utilized if, for example, many data are missing. Of course when the aeration stops this assumption are not usable because there will be no equilibrium between TN and NH_4

Tabella 1 Removal kinetics results

LSR	Kn **Week^{-1}**	Ka **Week^{-1}**	Ka/Kn **--**
LSR 1	-0,048071	-0,039477	0,821223
LSR 2	-0,043470	-0,031880	0,733379
LSR 3	-0,053025	-0,033392	0,629741
LSR 5	-0,045583	-0,035244	0,773183
LSR 6	-0,068276	-0,029261	0,428569
LSR 8	-0,049290	-0,027970	0,567458
Average	-0,051286	-0,032871	0,640931

5.3.2 *Anaerobic Kinetics results*

For the anaerobic lysimeters the model processing has been principally focused on the NH_4 concentration because too many TN values were missing. An interpolation of them should have resulted to a very different trends that furthermore couldn't be compared with real data.

Utilizing the defined equations in chapter 3, the trends for the LSR 4 is shown in the picture below (fig 21)

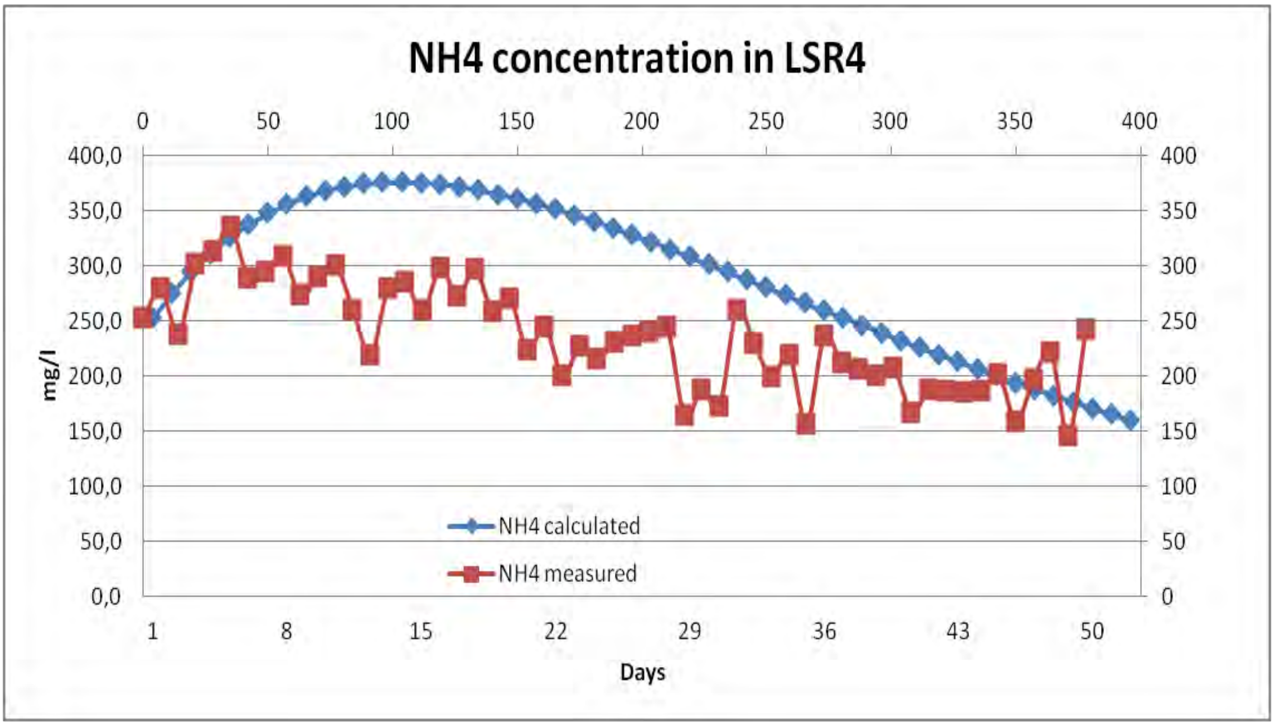


Figure 21 Comparison between NH4 calculated and NH4 measured

As can be seen the model shows an over-estimation of the NH_4 concentration in the initial phase, but in the final part the model almost tends to the same values of the measured NH_4 concentration. It behave like an exponential smoothing of the data. The difference between the two data set is due to some periodical "oscillations".

Trying to generate a model of that is quite hard, but a solution should be the introduction of another parameter in the anaerobic model.

After some examination has been found that one of these possible parameter, considering the data-set available, should be the pH or the strong elution effects. An investigation of the pH variation trend and the logarithm of the delta NH_4 concentration has been done with a Ki^2 test Excel function. This algorithm has the function of comparing two different data population in order to determine how “close“ their behavior is. The results gave back the maximum results (1) meaning their deep connection. Further studies in that direction could bring to interesting model results of NH_4 variation in anaerobic reactors and, for example, obtaining a prediction of the future quantity of this nitrogen compound

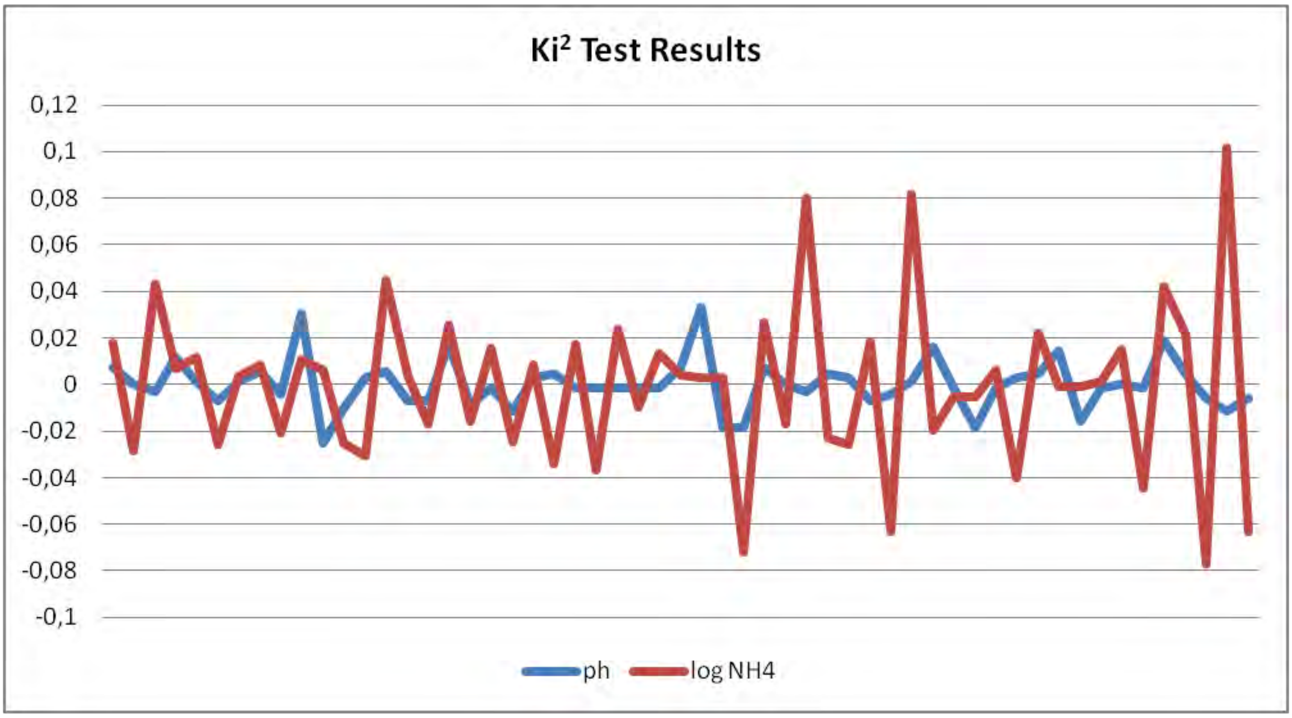


Figure 22 Comparison between pH variation and the log of NH4 variation

5.4 Mass Balance

The air insufflations inside the aerated column bring, as shown before, to a sharp and fast reduction of NH_4-N concentration. The theoretical quantity of ammonia that should have been released by volatilization, considering the pH range in the aerobic lysimeters, has been evaluated through equation () and it is in the order of few percentage unit.

This assumption brings to the theory that the decrease of ammonia in leachate should depends, mostly, on the nitrification reactions.

The quantification of nitrified ammonia is not easy because the time intervals between sampling are too long to have a sight of the exact trends of concentration inside the reactor and because the release of NH_4 from the solid to the liquid it is hardly quantifiable.

To evaluate the quantity of of NH_4 transferred from the solid to the liquid, has been decided to consider for every aerated lysimeter the initial anaerobic phase (comprised from 21 till 49 days, depending on the reactor) as a possible trend of future NH_4 release. An almost linear correlation has been evaluated between the quantity of the collected leachate from the lysimeters and the quantity of NH_4 concentration in every sample taken.(Fig 23).

The theory adopted is that the difference between the cumulative "theoretical" release and the evaluated values after the start of the aeration should be equivalent at the amount of missing ammonia(from now on will be defined as NH_4 nitrified).

To control if this procedure could be considered substantial the anaerobic lysimeter have been utilized to make a comparison between the supposed trend and the real one. The results show that there will be an over-estimation of the final nitrogen that should have been produced. The trend fits well for the first 245 days, but in the final results there is an error of about 25% fig()

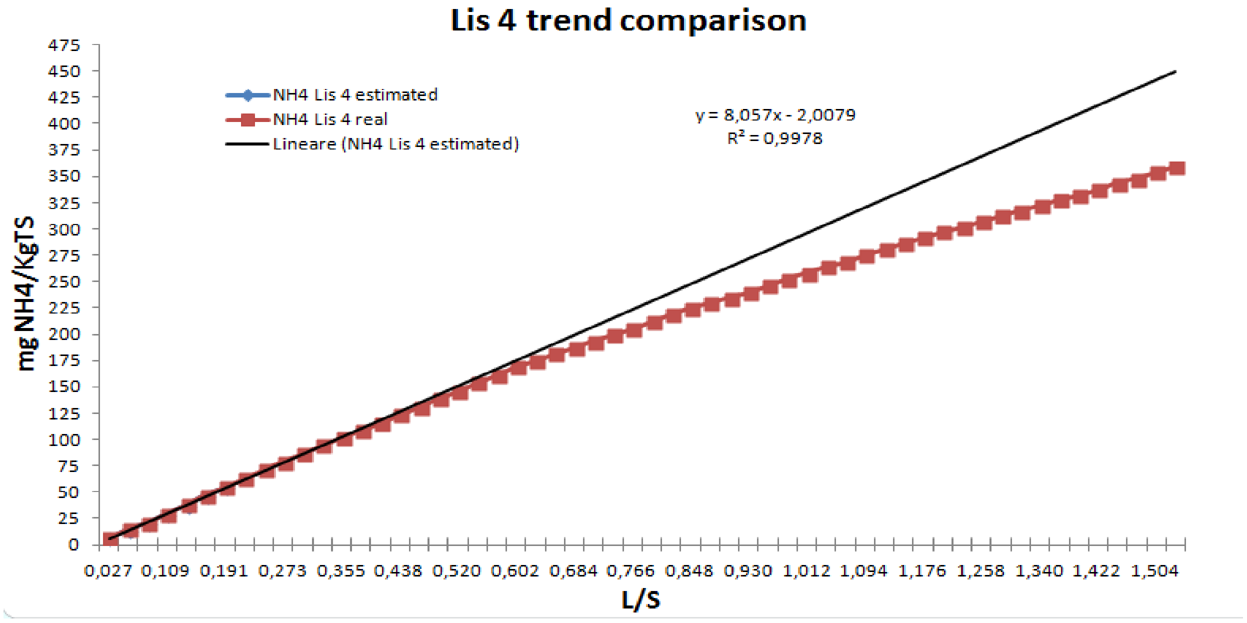


Figure 23 Comparison between the cumulative NH4 concentration in LSR 4and the estimated trend

After this considerations the Nitrogen mass balance has been assessed. It has to be said that the quantity of Nitrogen inside the solid are referred to TKN-N concentration while the leachate samples indicate the values of TN and NH_4, so a little percentage of NO_2 and NO_3 are evaluated inside the TN. This quantity of inorganic nitrogen compounds is under the precision of the machinery (< 5mg/l) and has never been measured, so it is relevant to underline that there will be a slight overestimation in the final mass balance due to this assumption; therefore TN will be considered as almost totally composed by NH_4 and Organic Nitrogen. The table below shows the results of the calculation.

Table 13 Mass balance results

	TKN initial	**TKN final**	**TN Cumulative**	**NH4 cumulative**	**NH4 nitrified**	**TKN calculated**	**Error**
	gTKN/kgTS	gTKN/kgTS	gTN/kgTS	gNH4/kgTS	gNH4/kgTS	gTKN/kgTS	%
LSR 1	2,65	3,11	0,113	0,087	0,477	2,06	n.v.
LSR 2	3,02	1,84	0,164	0,126	0,425	2,43	-20
LSR 3	3,04	2,30	0,121	0,08	0,55	2,97	-2
LSR 5	3,41	2,98	0,153	0,121	0,438	3,57	+4
LSR 6	2,91	n.v.	0,065	0,039	0,291	2,557	n.v.
LSR 8	3,23	n.v.	0,17	0,14	0,76	2,29	n.v.

TKN calculated is the sum of TN cumulative, NH_4 nitrified and the TKN final (evaluated in the solid at the end of the aerobic treatment). For all the aerated reactors the error, as difference between the initial TKN at the beginning of the experiment and the TKN calculated, has been quantified. The final quantity of TN inside the lysimeters has not been accounted because it is hard to evaluate the exact water content inside the reactors and, however, even considering the total water account, the results are always below the 10^{-3} gTN/KgTS.

One problem noticed during the balance procedure is that, for some lysimeter (LSR 6, LSR 8), the final TKN concentration in the solid has not been evaluated so the TKN calculated is obtained by the subtraction of the TN cumulative and NH_4 nitrified values from the initial TKN. Of course it couldn’t be possible to evaluate the possible magnitude of the error.

Regarding LSR 1 it can be observed that the final TKN values is greater than the initial TKN. Some hypothesis have been considered:

- A measurement error
- The quantity of Nitrogen present inside the solid due to the biomass growth (Fellner and Laner 2011)
- Sorption/Desorpiton of nitrogen in the solid.

All these assumption could be valid, but noticing that only this aerated lysimeter resulted affected by this variance, it could be possible to consider a measurement error as the most probable. The error could be correlated to the machinery or the sampling procedure utilized or maybe a wrong sample taken.

Returning to the mass balance, considering the lysimeter 2,3,5 can be seen that the greatest evaluable error is for LSR 2 (an overestimation of the 20%), while for the other two (3,5) the error is of about 2 and 4%.

After all the assumption above defined, it seems feasible to utilize this procedure to asses a Nitrogen mass balance. Obviously further studies in this direction are needed. The following fiure shws the abtained results (Fig 24)

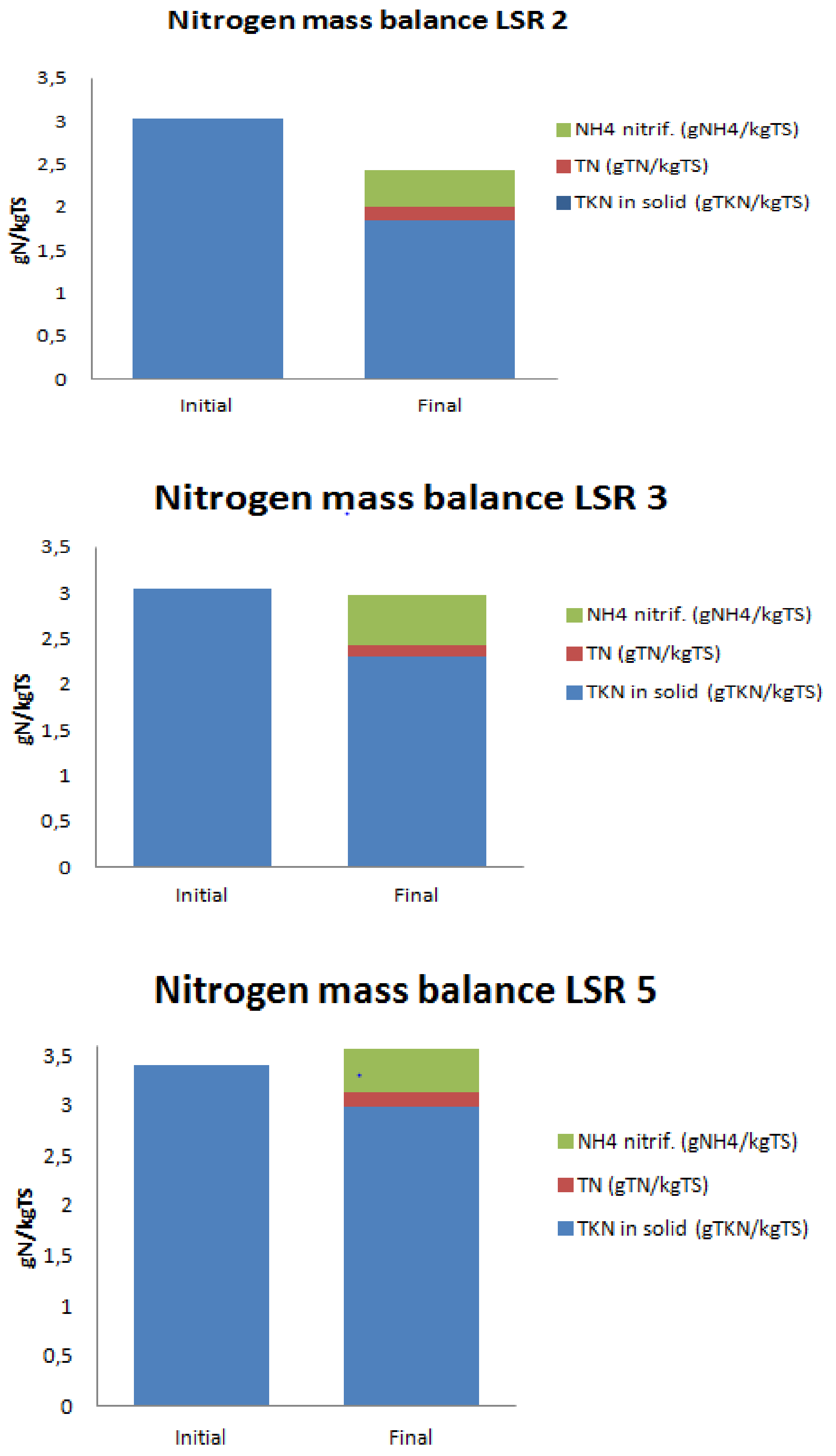


Figure 24 Nitrogen mass balance results LSR 2,3,5

A final step in the mass balance has been a gas mass balance in order to have a "control" for the data evaluated and the methodology applied.

To check the data obtained has been utilized the gas measurements shown in the previous chapter. Considering the quantity of air inlet and the chromatograph lectures with the gas composition percentage (N_2, CO_2,CH_4 and O_2) of the outlet gas, the following procedure has been applied.

- From the CO_2 percentage has been evaluated the liters of carbon dioxide generated by an aerobic degradation of carbon compounds inside the waste samples
- From the stoichiometry has been evaluated the quantity of oxygen needed to obtain the measured carbon dioxide liters
- Has been evaluated the measured oxygen exiting from the lysimeter as oxygen not utilized for reactions
- An oxygen mass balance has been assessed

The theory is that the difference between the oxygen inlet and the oxygen utilized for the aerobic degradation and the not utilized oxygen should be equivalent to the oxygen for nitrification eq()

$$Nitrification\ Ox = Inlet\ Ox - Oxy\ utilized\ for\ carbon\ degradation - Outlet\ Ox$$

The theoretical Nitrification oxygen has been utilized for the following chemicals consideration.

- From the Nitrification Oxygen the theoretical nitrate generated utilizing equation() has been evaluated
- The NO_3 (grams) has been totally denitrified by Hetherotrophic denitrification
- The quantity of N_2 generated (liters) has been compared with the theoretical N_2 generated by the complete Nitrification/Heterotrophic Denitrification of the NH_4 nitrified evaluated above for the TKN mass balance.

The results of this procedure are shown below tab()

Table 14 Comparison between N2 gas productions

	N2 from Oxygen	**N2 from Denitification**
	Liters	Liters
LIS 1	27,025	9,6
LIS 2	15,7	11
LIS 3	19,56	12,6
LIS 5	12,6	8,7
LIS 6	12,5	8,7
LIS 8	42,81	21,7

It is important to consider that obviously the quantity of N_2 obtained through the oxygen evaluation is an overestimation because a part of the oxygen has been utilized for others oxidative reactions and not all the N_2 evaluated from the NH_4 nitrified has been denitrified by Hetherotrophic denitrification considering that NH_4 nitrified itself is an overestimation of the possible ammonium that should have been nitrified. Other important aspect is that not only the Heterotrophic Denitrification is related to the utilization of the NO_3 nitrified. Processes like Autotrophic Denitrification or the Anammox bacteria are involved in the reaction inside the aerobic reactors.

Even though all these assumption is interesting to notice that except LSR 1 and LSR 2 the other reactors show level of N_2 production very close, giving confirmation that the followed procedure seems feasible for the assessment a nitrogen mass balance considering Hetherotrophic denitrification as the main reaction inside the aerated reactors. Under this aspect it has to be underlined that LSR 3 and LSR 5 have the closest N_2 production levels as they have the lowest error in the TKN evaluation.

6 CONCLUSIONS

The obtained results allowed to increase the knowledge available regarding the effects of a long aeration of municipal solid waste from an old landfill. This data could be used in future for the assessment of operations in real scale system. Focusing especially on the nitrogen compounds it is clear the positive effects of aeration and strong recirculation, with a stipe and fast reduction of Ammonia and Total nitrogen concentration in the leachate samples.

After a short time range, between 50 to 120 days, the abatement of NH_4 has been higher than the 90% in every aerated reactors. Regarding the anaerobic lysimeters the results are different with just a little variations due to the positive effects of elution.

Furthermore the survey results have allowed to verify the possibility of the simultaneous occurrence of nitrification and heterotrophic denitrification in the same reactor. In this sense the very low presence of inorganic nitrogen compounds (NO_2, NO_3), considering the stoichiometry of the theorized NH_4 consumption, seems to be a good indicator of both processes. Thanks to recirculation, leachate passes through the unsaturated zone of the landfill where aerobic conditions, induced by aeration, enable the development of nitrification processes. Due to the heterogeneity of the waste, oxygen distribution during aeration is not uniform and, as a result, the presence of anaerobic zones is expected, which may develop in the denitrification processes.

The tool development results shown that even in poor data-set values is possible to obtain a feasible variation trend of organic and inorganic nitrogen concentration compounds collected from the reactors. Treating data through statistical analysis and evaluating a model of nitrogen helps in the evaluation of missing values, in the calculation of the removal rate kinetics and to forecast future quantity of nitrogen especially for the anaerobic lysimeters. Obviously there are many possible further implementation that can be applied in the developed tool, like the introduction of other parameters and algorithm connected to pH and elution effect.

The results obtained through the model are quite feasible in order to asses a nitrogen mass balance and, considering the missing values in the final solid measurement of TKN values, for the aerobic lysimeters has been possible to evaluate interesting results. The methodology utilized for the mass balance seems to confirm the goodness of the followed procedure but it is important to say that more improvement can be applied in the system, like for example the evaluation of other possible nitrogen transformations (autotrophic denitrification, the effects of Anammox bacteria) that could bring, in future, to a deeper understanding of the several processes that can occur in a landfill.

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8 ANNEX 1 LEACHATE AND BIOGAS CHARACTERIZATION

Table 15: biogas characterization of bioreactor LSR1

LSR1							
Date	aeration rate	discharged gas (aeration)	delta gas volume outlet	CO2	O2	N2	CH4
	[l/h]	[l/kg TS]	[l]				
30-ago-00			2	40,592	0,1777	2,875	56,3547
30-ago-00			1,16	40,0027	0,06651	1,299	58,6315
1-set-00			0	35,194	0,11	5,177	59,517
5-set-00			0	36,433	0,00761	1,4089	62,082
6-set-00			0,02	36,433	0,00761	1,4089	62,082
7-set-00			0,01	34,0564	0,227	2,613	63,104
7-set-00			4,03	34,0564	0,227	2,613	63,104
11-set-00			0	34,493	0,05	0,394	65,063
12-set-00			8,4	34,493	0,05	0,394	65,063
13-set-00			5,1	34,493	0,05	0,394	65,063
14-set-00			6	34,705	0,09844	0,536	64,6607
15-set-00			3,1	34,705	0,09844	0,536	64,6607
18-set-00			15,68	34,74	0,09	0,66	64,51
19-set-00			11,82	34,74	0,09	0,66	64,51
20-set-00			9,83	34,74	0,09	0,66	64,51
21-set-00			10,95	34,665	0,13	0,54	64,66
22-set-00			8,76	34,665	0,13	0,54	64,66
25-set-00			37,75	34,57	0,08	0,36	64,98
26-set-00	0,7	0	6,36	34,45	0,16	0,91	64,48
27-set-00	0,7	4,446672744	24,24	31,06	0,43	18,98	49,83
28-set-00	0,7	5,249468247	26,42	27,09	1,03	38,61	33,27
29-set-00	0,7	5,988757217	24,33	26,25	0,87	45,5	27,38
2-ott-00	0,7	8,161956852	71,52	26,25	0,87	45,5	27,38
4-ott-00	0,7	9,363719234	39,55	21,5	1,03	64,87	12,6
5-ott-00	0,7	9,988453358	20,56	21,41	0,97	65,97	11,65
6-ott-00	0,7	10,45396536	15,32	21,01	1,04	67,2	10,76
9-ott-00	0,7	12,23761775	58,7	20,5	0,95	69,42	9,12
10-ott-00	0,7	12,90367669	21,92	20,01	1,03	70,14	8,82
11-ott-00	0,7	13,4840474	19,1	19,97	1,02	70,62	8,39
12-ott-00	0,7	14,01428137	17,45	19,83	1,12	70,81	8,25
16-ott-00	0,7	16,74141598	89,75	18,97	1,15	74,15	5,73
17-ott-00	0,7	17,44272258	23,08	18,17	1,13	75,21	5,5
20-ott-00	0,7	19,52233364	68,44	18,3	1,11	75,15	5,44
23-ott-00	0,7	21,59556366	68,23	18,17	1,06	75,98	4,79
24-ott-00	0,7	22,44272258	27,88	17,73	1,17	76,67	4,43
25-ott-00	1,06	23,26253418	26,98	17,56	1,02	77,17	4,25
26-ott-00	1,06	24,15982984	29,53	17,82	1,05	77,07	4,06
27-ott-00	1,06	24,90671528	24,58	17,76	1,09	77,24	3,91
30-ott-00	1,06	27,58037071	87,99	17,74	1,05	78,11	3,1
31-ott-00	1,06	28,23883318	21,67	17,73	1,09	78,17	3
1-nov-00	1,06	29,12032817	29,01	17,23	1,08	78,98	2,7
3-nov-00	1,06	30,66302036	50,77	17,29	1,47	78,69	2,55
6-nov-00	1,06	33,61409906	97,12	16,86	1,09	80,1	1,95
7-nov-00	1,06	34,21847463	19,89	13,92	4,18	80,65	1,25
8-nov-00	1,06	35,33394105	36,71	16,23	1,51	80,55	1,71
10-nov-00	1,41	36,8213309	48,95	16,75	1,11	80,63	1,51
12-nov-00	1,55	39,03767852	72,94	16,75	1,11	80,63	1,51
14-nov-00	1,65	40,99058037	64,27	15,23	1,17	82,52	1,08
17-nov-00	1,65	44,73837739	123,34	15,36	1,38	82,59	0,67
21-nov-00	1,65	49,35399575	151,9	14,85	1,57	83,23	0,35
28-nov-00	1,65	58,14524461	289,32	14,8	1,59	83,48	0,13
5-dic-00	1,65	66,50319052	275,06	15,86	1,44	82,67	0,03
12-dic-00	1,65	75,00121544	279,67	15,71	2,49	81,8	0
19-dic-00	1,65	84,34822242	307,61	15,34	3,6	81,06	0

2-gen-01	1,65	102,5907019	600,36	5	15,34	79,65	0
8-gen-01	1,41	110,4023093	257,08	5,11	15,8	79,08	0
9-gen-01	1,41	111,1996354	26,24	5,11	15,8	79,08	0
11-gen-01	1,06	113,482832	75,14	7,21	13,13	79,66	0
16-gen-01	0,89	116,9729565	114,86	14,87	4,12	81,01	0
23-gen-01	0,89	122,215436	172,53	15,06	4,18	80,76	0
30-gen-01	0,89	127,3257369	168,18	10,04	10,31	79,65	0
1-feb-01	0,79	128,8073534	48,76	9,62	10,64	79,74	0
6-feb-01	0,79	132,1929505	111,42	9,97	10,15	79,88	0
7-feb-01	0,73	132,9146156	23,75	9,97	10,15	79,88	0
13-feb-01	0,73	136,165907	107	11,03	8,9	80,06	0
21-feb-01	0,73	140,071103	128,52	15,38	3,88	80,74	0
27-feb-01	0,73	142,9930112	96,16	15,86	4,07	80,07	0
6-mar-01	0,73	146,3634154	110,92	15,36	4,46	80,18	0
13-mar-01	0,73	149,5703434	105,54	11,35	8,55	80,09	0
20-mar-01	0,73	152,206928	86,77	11,81	8,54	79,65	0
27-mar-01	0	154,7474932		10,13	10,25	79,62	0
3-apr-01	0,1	156,7128532	148,29	10,13	10,25	79,62	0
19-apr-01	0,1	163,1525372	211,93	10,13	10,25	79,62	0
23-apr-01	0,1	163,1689456	0,54	10,13	10,25	79,62	0
8-mag-01	0,1	171,9790337	289,94	10,13	10,25	79,62	0
14-mag-01	0,1	171,9902765	0,37	3,66	16,87	79,49	0
16-mag-01	0	171,9902765	0	3,77	16,5	79,73	0
21-mag-01	0	171,9902765	0	4	15,99	79,99	0
23-mag-01	0	171,9902765	0	4	15,99	79,99	0
30-mag-01	0	171,9902765	0	12,91	4,45	82,64	0
5-giu-01	0	172,1513218	5,3	13,15	2,92	83,93	0
11-giu-01	0	172,1504102	-0,03	14,47	2,57	82,96	0
18-giu-01	0	172,1504102	0	14,35	2,92	82,73	0
26-giu-01	0	172,1540565	0,12	12,25	5,33	82,42	0
3-lug-01	0	172,1349134	0	13,32	4,35	82,33	0
11-lug-01	0	172,1349134	0	15,1	2,81	82,09	0
18-lug-01	0	172,1452446	0,34	15,31	4,64	79,87	0,18
25-lug-01	0	172,1893042	1,45	14,26	5,11	80,52	0,1
1-ago-01	0	172,1890003	-0,01	12,69	5,97	81,35	0
8-ago-01	0	172,193862	0,16	13,08	5,23	81,69	0
15-ago-01	0	172,1130356	0	9,79	8,42	81,63	0,16
22-ago-01	0	172,09055	0	10,8	6,97	81,83	0,4
27-ago-01	0	172,0975387	0,23	11,8	3,65	82,66	1,89
4-set-01	0	172,0938924	0	9,84	4,6	83,31	2,25
17-set-01	0,15	172,0938924	0	10,29	3,74	82,27	3,7
10-ott-01	0,15	172,0978426	0,13	10,85	3,87	85	0,27
23-ott-01	0,15	172,1282285	1	11,48	4,48	83,89	0,15
19-nov-01	0,15	173,2078396	35,53	16,73	1,42	81,81	0,04
13-dic-01	0,15	177,2123974	131,79	17,11	2,8	80,09	0
17-dic-01	0,15	177,6858098	15,58	15,11	5,45	79,43	0
21-gen-02	0,15	182,3418414	153,23	16,2	4,63	79,17	0
25-feb-02	0,15	186,8799757	149,35	17,82	1,66	80,52	0
2-apr-02	0,15	191,9814646	167,89	18,41	1,42	80,17	0

Table 16 biogas characterization of bioreactor LSR3

LSR3							
Date	aeration rate	discharged gas (aeration)	delta gas v	CO2	O2	N2	CH4
	[l/h]	[l/kg TS]	[l]				
30-ago-00			0	36,397	2,796	12,689	48,117
30-ago-00			4,36	41,798	0,174	2,058	55,969
1-set-00			0,04	34,865	0,6537	5,509	58,9706
5-set-00			0,03	37,971	0,1306	1,487	60,411
6-set-00			19,22	37,971	0,1306	1,487	60,411
7-set-00			22,81	34,011	2,828	11,25	51,909
11-set-00			82,7	35,257	2,464	9,252	53,024
12-set-00			11,99	35,257	2,464	9,252	53,024
13-set-00			19,8	35,257	2,464	9,252	53,024
14-set-00			12,56	34,199	3,031	11,7058	51,063
15-set-00			12,49	34,199	3,031	11,7058	51,063
18-set-00			35,77	39,9	0,17	0,85	59,08
19-set-00			11,22	39,9	0,17	0,85	59,08
20-set-00			8,93	39,9	0,17	0,85	59,08
21-set-00			10	39,98	0,08	0,5	59,45
22-set-00			8,3	39,98	0,08	0,5	59,45
25-set-00			27,31	39,58	0,11	0,61	59,69
26-set-00	1,54	0,00	6,09	37,28	1,07	6,68	54,98
27-set-00	1,54	2,00	78,15	22,58	1,12	66,63	9,66
28-set-00	1,54	3,09	42,46	20,82	1,21	70,73	7,23
29-set-00	1,54	4,11	39,36	22,09	0,95	70,88	6,08
2-ott-00	1,54	7,35	124,53	22,09	0,95	70,88	6,08
4-ott-00	1,54	9,23	75,88	18,74	1,78	76,15	3,34
5-ott-00	1,54	10,32	42,48	19,59	1,26	76,01	3,13
6-ott-00	1,54	11,03	29,91	17,71	2,76	77,07	2,46
9-ott-00	1,54	14,27	128,37	18,13	1,51	77,99	2,37
10-ott-00	1,54	15,48	47,21	18,81	1,1	77,89	2,2
11-ott-00	1,54	16,56	42,06	19,05	1,13	77,74	2,08
12-ott-00	1,54	17,51	37,21	18,99	1,38	77,5	2,13
16-ott-00	1,54	21,31	148,23	19,16	1,18	77,68	1,99
17-ott-00	1,54	22,19	35,05	18,06	1,63	78,49	1,82
20-ott-00	1,54	24,95	112,15	17,1	2,02	79,62	1,26
23-ott-00	1,54	27,71	108,81	17,04	1,37	80,75	0,85
24-ott-00	1,54	28,77	41,32	16,86	1,23	81,25	0,66
25-ott-00	1,54	29,91	44,48	16,86	1,23	81,25	0,66
26-ott-00	1,54	30,99	41,74	17,33	1,11	80,84	0,72
27-ott-00	1,54	31,89	35,01	17,33	1,11	80,84	0,72
30-ott-00	1,54	35,63	145,07	17,42	1,1	81,02	0,46
31-ott-00	1,54	36,40	29,83	17,42	1,1	81,02	0,46
1-nov-00	1,54	37,41	39,48	17,42	1,1	81,02	0,46
3-nov-00	1,96	39,03	66,01	16,65	2,03	80,93	0,39
6-nov-00	1,96	42,41	133,9	16,97	1,53	81,34	0,16
7-nov-00	1,96	43,17	30,06	16,97	1,53	81,34	0,16
8-nov-00	1,96	44,57	55,49	16,97	1,53	81,34	0,16
10-nov-00	1,96	46,27	66,79	16,98	1,28	81,55	0,19
12-nov-00	1,96	48,60	91,36	16,98	1,28	81,55	0,19
14-nov-00	1,96	50,31	69,13	16,25	1,95	81,69	0,11
17-nov-00	1,96	53,34	119,19	17,21	1,36	81,34	0,09
21-nov-00	1,96	57,40	166,42	15,9	2,15	81,95	0
28-nov-00	1,41	64,43	308,57	15,4	3,4	81,2	0
5-dic-00	1,41	70,63	298,99	14,86	4,94	80,2	0
12-dic-00	1,41	76,50	268,88	15,6	4,12	80,21	0,07
19-dic-00	1,31	81,21	222,45	15,18	4,6	80,22	0
2-gen-01	1,31	89,56	505,21	12,01	8,16	79,83	0

8-gen-01	1,31	92,80	206,42	11,37	8,83	79,79	0
9-gen-01	1,31	93,09	18,85	11,37	8,83	79,79	0
11-gen-01	1,24	94,24	59,86	13,53	6,14	80,33	0
16-gen-01	1,24	96,83	187,64	10,41	10,24	79,35	0
23-gen-01	1,24	100,48	222,72	11,85	8,29	79,86	0
30-gen-01	1,24	103,58	199,44	11,47	8,89	79,64	0
1-feb-01	1,24	104,49	58,34	11,84	8,94	79,23	0
6-feb-01	1,24	106,62	142,68	11,62	9,37	79,01	0
7-feb-01	1,24	107,08	30,6	11,62	9,37	79,01	0
13-feb-01	1,24	109,48	158,55	11,57	9,23	79,19	0
21-feb-01	1,24	112,75	222,33	11,37	9,57	79,05	0
27-feb-01	1,24	115,15	152,32	12,29	8,73	78,98	0
6-mar-01	1,24	117,91	170,02	12,17	8,42	79,41	0
13-mar-01	1,24	120,78	172,99	12,75	8,11	79,15	0
20-mar-01	1,24	123,42	134,89	14,77	5,83	79,4	0
27-mar-01	0,76	126,91	232,61	11,99	9,34	78,67	0
3-apr-01	0,76	128,18	84,64	11,99	9,34	78,67	0
19-apr-01	0,76	132,41	282,51	11,99	9,34	78,67	0
23-apr-01	0,76	132,50	6,26	11,99	9,34	78,67	0
8-mag-01	0,76	138,55	403,17	11,99	9,34	78,67	0
14-mag-01	0,76	139,96	172,42	7,12	14,53	78,35	0
16-mag-01	0,51	140,42	71,4	5,38	15,87	78,75	0
21-mag-01	0,37	141,44	129,64	5,85	14,79	79,36	0
23-mag-01	0,37	141,72	35,21	5,85	14,79	79,36	0
30-mag-01	0,37	142,64	104,26	6,53	14,08	79,39	0
5-giu-01	0,26	143,77	121,9	6,89	13,69	79,42	0
12-giu-01	1,50	145,46	113,25	11,42	9,4	79,18	0
19-giu-01	1,50	146,70	80,63	11,63	9,04	79,32	0
26-giu-01	1,50	147,77	75,39	10,48	10	79,52	0
3-lug-01	1,10	148,74	82,24	8,78	11,7	79,52	0
5-lug-01	0,00	149,01	24,98	7,55	12,77	79,68	0
11-lug-01	0,00	149,78	43,72	11,93	7,31	80,76	0
18-lug-01	0,00	149,87	5,02	12,4	7,01	80,5	0,1
25-lug-01	0,00	149,94	3,88	11,9	7,69	80,42	0
1-ago-01	0,00	149,97	1,36	14,46	3,66	81,87	0
8-ago-01	0,00	149,98	0,54	14,04	4,31	81,65	0
15-ago-01	0,00	149,98	-0,03	12,77	6,38	80,7	0,15
22-ago-01	0,00	149,98	0	12,71	6,38	80,24	0,67
27-ago-01	0,00	149,98	0,28	10,25	8,73	79,63	1,39
4-set-01	0,25	150,12	5,83	12,31	3,02	80,26	4,42
17-set-01	0,35	152,08	95,87	13,74	5,14	80,89	0,23
10-ott-01	0,35	157,11	202,18	20,38	1,79	77,84	0
23-ott-01	0,35	159,98	113,34	19,67	1,47	78,86	0
19-nov-01	0,35	166,41	289,71	17,39	3,81	78,8	0
13-dic-01	0,35	172,42	291,56	16,09	5,05	78,86	0
17-dic-01	0,35	172,61	10,51	13,93	6,82	79,24	0
21-gen-02	0,35	180,82	414,94	15,56	5,69	78,75	0
22-gen-02	0,30	181,00	10,19	13,33	7,17	79,5	0
25-feb-02	0,30	186,25	225,87	18,52	3,04	78,43	0

Table 17 biogas characterization of bioreactor LSR5

LSR5							
Date	aeration rate	discharged gas (aeration)	delta gas v	CO2	O2	N2	CH4
	[l/h]	[l/kg TS]	[l]				
30-ago-00			0	41,34	0,14	1,24	57,28
30-ago-00			5,8	41,34	0,14	1,24	57,28
1-set-00			0,05	36,81	0,3	2,16	60,73
5-set-00			0	37,41	0,14	0,54	61,91
6-set-00			0	37,41	0,14	0,54	61,91
7-set-00			0,8	37,53	0,05	0,31	62,11
11-set-00			103,4	34,49	0,09	0,66	64,76
12-set-00			18,25	34,49	0,09	0,66	64,76
13-set-00			27,3	34,49	0,09	0,66	64,76
14-set-00			17,22	33,46	0,03	0,48	66,03
15-set-00			17,89	33,46	0,03	0,48	66,03
18-set-00			48,56	34,96	0,04	0,29	64,71
19-set-00			14,4	34,96	0,04	0,29	64,71
20-set-00			11,68	34,96	0,04	0,29	64,71
21-set-00			13,01	35,56	0,1	0,63	63,71
22-set-00			10,61	35,56	0,1	0,63	63,71
25-set-00			34,27	36,03	0,1	0,55	63,31
26-set-00	0,35	0	7,57	34,43	0,72	4,87	59,97
27-set-00	0,35	10,60376785	18,16	34,67	0,31	10,41	54,61
28-set-00	0,35	11,1890003	19,26	32,61	0,37	22,58	44,44
29-set-00	0,35	11,7234883	17,59	31,69	0,53	27,99	39,78
2-ott-00	0,35	13,26769979	50,82	31,69	0,53	27,99	39,78
4-ott-00	0,35	14,13339411	28,49	27,11	0,81	44,92	27,15
5-ott-00	0,35	14,60012154	15,36	26,75	0,74	46,39	26,12
6-ott-00	0,35	14,93011243	10,86	26,65	0,65	47,24	25,46
9-ott-00	0,62	16,17532665	40,98	24,37	0,99	53,71	20,93
10-ott-00	0,62	16,64843513	15,57	25,06	0,71	51,52	22,71
11-ott-00	0,62	17,05074445	13,24	25,18	0,68	51,82	22,32
12-ott-00	0,62	17,41415983	11,96	24,89	0,71	52,93	21,48
16-ott-00	0,62	18,89334549	48,68	24,62	0,98	54,01	20,39
17-ott-00	0,62	19,27013066	12,4	23,8	0,99	55,67	19,54
20-ott-00	0,62	20,89182619	53,37	21,51	1,49	66,59	10,42
23-ott-00	0,62	22,39228198	49,38	21,41	1,05	68,95	8,59
24-ott-00	0,62	22,94226679	18,1	21,23	0,98	69,16	8,63
25-ott-00	0,62	23,49893649	18,32	20,73	1,06	70,67	7,63
26-ott-00	0,62	24,09541173	19,63	21,39	0,98	69,16	8,46
27-ott-00	0,77	24,59191735	16,34	21,53	0,91	69,33	8,23
30-ott-00	0,77	26,40808265	59,77	21,02	0,91	71,01	7,06
31-ott-00	0,96	26,85809784	14,81	20,87	1,01	71,4	6,72
1-nov-00	0,96	27,51990277	21,78	19,52	1,49	73,35	5,63
3-nov-00	0,96	28,72105743	39,53	19,59	1,39	73,69	5,33
6-nov-00	0,96	30,8228502	69,17	19,71	1,31	74,13	4,86
7-nov-00	0,96	31,34123367	17,06	11,59	7,73	80,45	0,23
8-nov-00	0,96	32,23366758	29,37	11,74	7,64	80,52	0,11
10-nov-00	1,33	33,55515041	43,49	19,35	1,2	75,36	4,1
12-nov-00	1,56	35,68672136	70,15	17,1	2,75	77,51	2,65
14-nov-00	1,56	37,56001215	61,65	17,89	1,62	77,79	2,71
17-nov-00	1,8	40,68854452	102,96	18,87	1,13	77,78	2,22
21-nov-00	1,8	45,30507445	151,93	6,46	13,59	79,95	0
28-nov-00	0,62	52,68155576	242,76	6,74	13,68	79,58	0
5-dic-00	0,62	57,92190823	172,46	18,43	1,26	77,84	2,46
12-dic-00	0,62	60,8161653	95,25	19,37	1,67	74,85	4,11
19-dic-00	0,7	63,78972957	97,86	19,63	1,43	73,98	4,96

2-gen-01	0,62	70,70343361	227,53	12,75	7,4	79,85	0
8-gen-01	0,62	73,53570343	93,21	13,08	7,03	79,84	0,05
9-gen-01	0,62	73,86265573	10,76	12,71	7,5	79,79	0
11-gen-01	0,62	74,84260103	32,25	13,14	6,87	79,88	0,12
16-gen-01	0,35	76,66575509	60	13,1	6,82	80,09	0
23-gen-01	0,35	78,78213309	69,65	15,09	4,57	79,61	0,73
30-gen-01	0,35	80,68459435	62,61	20,01	1,32	74,94	3,72
1-feb-01	0,62	81,24491036	18,44	19,89	1,17	75,43	3,51
6-feb-01	0,62	83,13187481	62,1	13,96	6,1	79,68	0,26
7-feb-01	0,62	83,50714069	12,35	13,71	6,48	79,63	0,17
13-feb-01	0,35	85,49620176	65,46	16,05	3,91	79,23	0,81
21-feb-01	0,5	87,80674567	76,04	13,8	5,98	80,23	0
27-feb-01	0,5	90,01276208	72,6	19,19	1,16	79,44	1,21
6-mar-01	0,35	92,50470981	82,01	18,09	1,81	79,42	0,69
13-mar-01	0,35	94,58644789	68,51	14,5	5,19	80,32	0
20-mar-01	0,5	96,46277727	61,75	18,53	1,51	78,48	1,47
27-mar-01	0,5	97,48495898	33,64	16,65	2,37	79,62	1,36
3-apr-01	0,5	97,50379824	0,62	16,65	2,37	79,62	1,36
19-apr-01	0,5	97,53752659	1,11	16,65	2,37	79,62	1,36
23-apr-01	0,5	97,54421149	0,22	16,65	2,37	79,62	1,36
8-mag-01	0,5	97,55059253	0,21	16,65	2,37	79,62	1,36
14-mag-01	0,5	97,61440292	2,1	15,6	3,7	72,1	8,6
16-mag-01	0,5	97,73230021	3,88	16,31	1,94	76,06	5,69
23-mag-01	0,5	107,7511395	329,72	5,2	15,94	78,87	0
30-mag-01	0,5	107,771498	0,67	17,31	1,31	77,67	3,71
5-giu-01	2,4	107,7754482	0,13	18,35	1,13	70,05	10,46
12-giu-01	2,4	107,7790945	0,12	19,41	0,98	66,75	12,86
19-giu-01	2,4	111,3822546	118,58	18,3	1,75	79,95	0
26-giu-01	2,4	114,2601033	94,71	16,71	2	81,29	0
3-lug-01	2,4	117,1592221	95,41	16,01	2,17	81,82	0
11-lug-01	2,4	120,4357338	107,83	15,09	3	81,93	0
18-lug-01	2,4	123,0683683	86,64	14,08	4,34	81,53	0,05
25-lug-01	2,4	124,7459739	55,21	15,58	2,67	81,76	0
1-ago-01	2,4	125,5642662	26,93	16,32	1,58	82,11	0
8-ago-01	2,4	126,5432999	32,22	13,48	4,61	81,9	0
15-ago-01	2,4	127,3287754	25,85	14,87	4,02	81,1	0
16-ago-01	0,5	127,3342449	0,18	8,51	11,77	79,72	0
22-ago-01	0,5	127,605591	8,93	14,25	1,95	83,8	0
27-ago-01	0,5	129,5123063	62,75	4,63	15,8	79,56	0
4-set-01	0,2	131,2673959	57,76	14,28	5,02	80,69	0
17-set-01	0,3	131,2713461	0,13	6,98	13,27	79,75	0
10-ott-01	0,2	131,2728654	0,05	16,6	1,25	82,14	0
23-ott-01	0,2	131,3913704	3,9	16,49	1,39	82,12	0
19-nov-01	0,2	132,7906411	46,05	15,7	2,24	82,07	0
13-dic-01	0,1	137,8422972	166,25	6,36	14,38	79,25	0
17-dic-01	0,1	139,0246126	38,91	12,76	5,87	81,37	0
21-gen-02	0,2	150,0741416	363,64	15,06	2,53	82,41	0
25-feb-02	0,2	159,2196901	300,98	17,19	1,73	81,09	0
2-apr-02	0,2	167,3658462	268,09	14,32	4,99	80,69	0

Table 18: biogas characterization of bioreactor LSR6

LSR6							
Date	aeration rate	discharged gas (aeration)	delta gas v	CO2	O2	N2	CH4
	[l/h]	[l/kg TS]	[l]				
30-ago-00			0	40,72	0,03	0,56	58,69
30-ago-00			13,88	40,72	0,03	0,56	58,69
1-set-00			55,45	36,04	0,04	0,44	63,48
5-set-00			118,56	38,54	0,05	0,18	61,23
6-set-00			24,37	38,54	0,05	0,18	61,23
7-set-00			29,33	37,41	0,03	0,18	62,38
11-set-00			132,9	33,43	0,09	0,4	66,08
12-set-00			19,99	33,43	0,09	0,4	66,08
13-set-00			27,38	33,43	0,09	0,4	66,08
14-set-00			16,28	35,59	0,04	0,19	64,18
15-set-00			16,29	35,59	0,04	0,19	64,18
18-set-00			44,8	37,85	0,1	0,5	61,55
19-set-00			13,5	37,85	0,1	0,5	61,55
20-set-00			11,22	37,85	0,1	0,5	61,55
21-set-00			12,13	38,45	0,1	0,44	61
22-set-00			9,72	38,45	0,1	0,44	61
25-set-00			30,81	38,75	0,14	0,59	60,52
26-set-00	1,21	0	6,64	38,21	0,46	4,34	56,98
27-set-00	1,21	12,98793928	41,34	33,57	0,59	43,36	22,48
28-set-00	1,21	13,80619671	39,35	27,64	0,96	60,36	11,04
29-set-00	1,21	14,54813891	35,68	25,56	0,89	64,57	8,97
2-ott-00	1,21	16,81430651	108,98	25,56	0,89	64,57	8,97
4-ott-00	1,21	18,20565606	66,91	20,38	1,04	72,85	5,73
5-ott-00	1,21	18,94135995	35,38	20,72	1,03	73,04	5,21
6-ott-00	1,21	19,4834685	26,07	20,35	0,93	74,08	4,64
9-ott-00	1,21	21,5658141	100,14	19,61	1,33	76,05	3,01
10-ott-00	1,21	22,34040341	37,25	19,24	1,31	76,83	2,62
11-ott-00	1,21	23,011021	32,25	19,3	1,06	77,39	2,26
12-ott-00	1,21	23,65377417	30,91	19,21	1,06	77,79	1,95
16-ott-00	1,21	26,26803909	125,72	18,8	1,26	79,1	0,84
17-ott-00	1,21	26,95612393	33,09	18,34	1,24	79,8	0,63
20-ott-00	1,21	28,92701185	94,78	18,37	1,12	80,34	0,17
23-ott-00	1,21	30,73591183	86,99	18,23	1,6	80,07	0,0987
24-ott-00	1,21	31,40652942	32,25	18,05	1,65	80,3	0
25-ott-00	1,21	32,07943439	32,36	18,43	1,5	80,07	0
26-ott-00	1,21	32,80307756	34,8	18,43	1,5	80,07	0
27-ott-00	1,21	33,40819297	29,1	18,43	1,5	80,07	0
30-ott-00	1,21	35,3661884	94,16	17,55	1,72	80,69	0,03
31-ott-00	1,21	35,85443959	23,48	17,55	1,72	80,69	0,03
1-nov-00	1,21	36,52661676	32,325	17,61	2,13	80,26	0
3-nov-00	1,21	37,72593055	57,675	17,61	2,13	80,26	0
6-nov-00	1,21	39,81825743	100,62	17,5	2,51	79,94	0,05
7-nov-00	1,21	40,25202745	20,86	17,5	2,51	79,94	0,05
8-nov-00	1,21	41,08858391	40,23	17,39	2,45	80,15	0
10-nov-00	1,21	42,10854648	49,05	17,39	2,45	80,15	0
12-nov-00	1,21	43,49989603	66,91	16,98	2,82	80,2	0
14-nov-00	1,21	44,62466209	54,09	16,86	3,09	80,05	0
17-nov-00	1,21	46,65793304	97,78	16,86	3,09	80,05	0
21-nov-00	1,21	49,02578499	113,87	16,07	3,69	80,24	0
28-nov-00	1,1	53,38698274	209,73	15,01	5,04	79,95	0
5-dic-00	1,1	57,56602204	200,97	15,47	5,11	79,43	0
12-dic-00	1,1	61,60511541	194,24	14,88	5,84	79,28	0
19-dic-00	1,06	65,26013724	175,77	15,02	5,64	79,34	0

2-gen-01	1,06	72,60012477	352,98	13,2	7,49	79,31	0
8-gen-01	0,99	75,83385319	155,51	13,33	7,35	79,33	0
9-gen-01	0,99	76,16739447	16,04	13,33	7,35	79,33	0
11-gen-01	0,96	77,18007902	48,7	13,75	6,55	79,7	0
16-gen-01	0,96	78,91474319	83,42	15,22	5,15	79,64	0
23-gen-01	0,96	80,69349137	85,54	17,62	1,32	81,06	0
30-gen-01	0,96	81,16240383	22,55	14,74	6,7	78,56	0
1-feb-01	0,96	81,63027656	22,5	13,95	7,29	78,77	0
6-feb-01	0,96	82,0981493	22,5	14,17	7,02	78,81	0
7-feb-01	0,96	82,56602204	22,5	14,17	7,02	78,81	0
13-feb-01	0,96	83,03431067	22,52	13,32	7,64	79,04	0
21-feb-01	0,96	83,78311499	36,01	14,48	6,7	78,83	0
27-feb-01	0,96	86,29798295	120,94	14,29	6,77	78,94	0
6-mar-01	0,96	89,20274485	139,69	13,98	6,87	79,15	0
13-mar-01	0,96	91,77292576	123,6	14,45	6,31	79,24	0
20-mar-01	0,96	94,35537534	124,19	14,82	6,61	78,57	0
27-mar-01	0,96	97,73279268	162,42	11,53	9,97	78,5	0
3-apr-01	0,96	101,5643585	184,26	11,53	9,97	78,5	0
19-apr-01	0,96	107,4163028	281,42	11,53	9,97	78,5	0
23-apr-01	0,96	107,4215014	0,25	11,53	9,97	78,5	0
9-mag-01	0,96	114,7465169	352,26	11,53	9,97	78,5	0
14-mag-01	0,96	117,6281971	138,58	6,96	14,71	78,33	0
16-mag-01	0,96	118,6080266	47,12	8,69	11,44	79,87	0
21-mag-01	0	120,9282595	111,58	9,96	9,58	80,47	0
23-mag-01	0	120,9415679	0,64	9,96	9,58	80,47	0
30-mag-01	0	120,9623622	1	11,19	1,58	86,3	0,93
5-giu-01	0	121,0850489	5,9	13,47	1,41	78,1	7,02
12-giu-01	0	121,2098149	6	14,2	1,19	73,65	10,95
18-giu-01	1	121,275733	3,17	13,39	2,29	67,12	17,2
19-giu-01	1	121,7402786	22,34	4,22	18,16	77,39	0,23
26-giu-01	1	124,3849033	127,18	17,4	2,78	79,81	0
3-lug-01	1	126,4784779	100,68	15,22	3,58	81,2	0
11-lug-01	1	128,9224371	117,53	10,57	8,77	80,53	0,13
18-lug-01	1	129,0091495	4,17	14,35	1,68	80,26	3,71
25-lug-01	1	129,0472032	1,83	13,82	1,64	77,67	6,87
1-ago-01	1	129,0702849	1,11	13,2	1,69	70,79	14,32
8-ago-01	1	129,095654	1,22	13,21	1,97	68,33	16,49
15-ago-01	1	129,320025	10,79	13,53	3,84	64,35	18,28
16-ago-01	0,3	129,4138074	4,51	14,14	3,18	72,71	9,97
22-ago-01	0,3	129,6026201	9,08	14,65	2,13	75,63	7,59
27-ago-01	0,3	130,5491786	45,52	10,71	8,3	74,9	6,1
4-set-01	0,15	132,1555417	77,25	10,43	9,49	78,25	1,84
17-set-01	0,1	133,7311291	75,77	11,17	7,97	79,05	1,81
10-ott-01	0,1	137,8658765	198,84	19,36	1,19	79,18	0,27
23-ott-01	0,1	139,9070493	98,16	18,85	1,28	79,59	0,27
19-nov-01	0,1	143,3424828	165,21	18,55	1,63	79,82	0
13-dic-01	0,1	145,7889374	117,65	15,91	3,93	80,16	0
17-dic-01	0,1	146,2697026	23,12	15,17	5,27	79,56	0
21-gen-02	0,1	150,3191932	194,74	17,1	1,74	81,17	0
25-feb-02	0,1	154,499896	201,05	18,93	1,37	79,71	0
2-apr-02	0,1	159,1332917	222,82	15,63	2,46	81,91	0

Table 19: biogas characterization of bioreactor LSR8

LSR8							
Date	aeration rate	discharged gas (aeration)	delta gas	CO2	O2	N2	CH4
	[l/h]	[l/kg TS]	[l]				
30-ago-00			0	51,06	1,41	46,62	0,92
6-set-00			94,92	2,91	19,11	77,92	0,06
7-set-00			12,63	1,2	20,7	78,01	0,08
11-set-00			10,35	29,52	0,96	68,13	1,39
12-set-00			1,37	31,16	1,02	66,16	1,67
13-set-00			4,01	28,41	1,1	68,54	1,94
14-set-00			1,92	31,52	1,14	64,88	2,46
15-set-00			2,27	36,73	0,33	59,44	3,51
18-set-00			8,83	44,21	0,2	46,55	9,03
19-set-00			3,08	43,11	1,04	45,69	10,16
20-set-00			2,12	46,45	0,21	40,33	13,02
21-set-00			3,01	47,2	0,36	37,3	15,15
22-set-00			2,26	47,86	0,26	35,22	16,67
25-set-00			8,55	49,77	0,21	28,32	21,69
26-set-00			1,94	47,12	1,34	30,06	21,49
27-set-00			1,67	47,12	1,34	30,06	21,49
28-set-00			2,78	50,2	0,37	24,43	24,99
29-set-00			2,39	50,2	0,37	24,43	24,99
2-ott-00			6,91	50,2	0,37	24,43	24,99
4-ott-00			3,25	49,99	0,27	17,91	31,83
5-ott-00			1,76	49,99	0,27	17,91	31,83
6-ott-00			1,88	49,99	0,27	17,91	31,83
9-ott-00			10,32	48,16	0,12	13,52	38,19
10-ott-00			6,44	48,16	0,12	13,52	38,19
11-ott-00			5,61	45,81	0,15	8,23	45,81
12-ott-00			6,25	45,81	0,15	8,23	45,81
16-ott-00			39,43	39,88	0,26	3,81	56,05
17-ott-00			14,7	37,63	0,72	5,3	56,35
17-ott-00	0,57	0	1,9	37,63	0,72	5,3	56,35
20-ott-00	0,57	7,364840918	91,39	28,46	0,96	34	36,58
23-ott-00	0,57	9,605235602	105,96	28,76	0,64	26,51	44,09
24-ott-00	0,57	10,63063247	48,02	28,42	0,44	27,81	43,33
25-ott-00	1,13	11,81848109	55,41	28,64	0,36	27,99	43,01
26-ott-00	1,13	13,72225456	91,17	28,13	0,89	32,21	38,77
27-ott-00	1,13	14,72079663	46,97	28,48	0,53	32,54	38,46
30-ott-00	1,13	19,05877299	203,35	28,62	0,46	36,23	34,68
31-ott-00	1,53	20,03201667	45,78	28,6	0,53	38,07	32,81
1-nov-00	1,53	21,37873844	64,95	26,77	1,03	45,31	26,89
3-nov-00	1,53	23,85709313	117,74	25,71	0,73	46,68	26,88
6-nov-00	2	28,43824496	218,4	24,64	0,8	42,66	31,89
7-nov-00	2	29,61341738	55,47	23,5	0,6	46,44	29,47
8-nov-00	2	31,89617975	107,75	23,69	0,6	47,13	28,58
10-nov-00	2,77	34,81823724	138,75	22,85	0,72	53,35	23,08
12-nov-00	3,79	39,34269323	216,89	20,49	0,91	63,33	15,27
14-nov-00	3,82	43,48623641	198,73	19,6	0,92	64,88	14,6
17-nov-00	3,82	51,74208031	396,56	20,45	0,95	67,92	10,69
21-nov-00	3,82	61,04199473	449,2	18,54	1,06	73,52	6,89
28-nov-00	3,82	76,85469547	764,94	17,96	1,09	77,64	3,32
5-dic-00	3,82	92,2020009	742,05	17,63	1,08	80,32	0,97
12-dic-00	3,82	107,1271673	741,57	16,88	1,61	81,32	0,19
19-dic-00	3,8	120,1984888	714,22	15,16	3,35	81,5	0
2-gen-01	3,79	137,4815716	1239,95	11,9	7,51	80,59	0

8-gen-01	2,77	144,3519895	542,73	10,91	8,73	80,36	0
9-gen-01	2,77	145,0656203	52,14	11,54	7,75	80,71	0
11-gen-01	2	147,2802145	156,18	11,74	7,28	80,98	0
16-gen-01	2	150,9375846	217,95	14,75	4,8	80,45	0
23-gen-01	1,76	155,9665362	293,27	15,18	4,45	80,38	0
30-gen-01	1,76	160,5944812	282,86	14,57	5,2	80,23	0
1-feb-01	1,76	161,9073591	81,87	14,28	5,51	80,21	0
6-feb-01	1,76	164,9701952	210,55	12,99	6,93	80,08	0
7-feb-01	1,53	165,6352268	43,58	13,21	6,25	80,53	0
13-feb-01	1,13	167,1860759	80,32	15,2	2,39	82,4	0
21-feb-01	0,78	169,9681016	136,52	17,04	1,37	81,58	0
27-feb-01	0,95	172,5724836	134,01	17,11	2,27	80,62	0
6-mar-01	0,95	175,5170718	159,16	15,55	3,16	81,29	0
13-mar-01	0,95	178,4569357	164,79	14,96	3,79	81,24	0
20-mar-01	0,95	181,2463707	163,57	15,35	4,54	80,12	0
27-mar-01	0,95	183,8022504	151,27	13,38	4,69	81,93	0
3-apr-01	0,95	186,3574542	151,23	13,38	4,69	81,93	0
19-apr-01	0,95	192,1094085	340,43	13,38	4,69	81,93	0
23-apr-01	0,95	192,102819	-0,39	13,38	4,69	81,93	0
8-mag-01	0,95	195,7194385	214,05	13,38	4,69	81,93	0
14-mag-01	0,95	196,8092285	61,74	15,61	3,97	80,52	0
16-mag-01	0,95	197,5210245	46,87	13,68	6,32	79,99	0
21-mag-01	0,57	198,3634955	42,75	15,31	2,01	82,68	0
23-mag-01	0,57	198,7031351	17,08	16,57	1,84	81,59	0
30-mag-01	0,57	200,002649	64,77	17,91	1,67	80,42	0
5-giu-01	0,57	201,159266	57,14	17,02	1,5	81,48	0
12-giu-01	3,5	202,4732495	64,48	19,23	1,37	79,4	0
19-giu-01	3,5	203,859855	67,73	19,12	1,28	79,36	0,24
26-giu-01	3,5	205,1363099	62,8	18,91	1,42	79,67	0
3-lug-01	3,8	206,8203374	82,3	18,37	1,29	79,98	0,36
11-lug-01	3,8	209,0357285	108,77	18,56	1,38	79,9	0,17
18-lug-01	3,8	210,2066283	57,37	18,34	1,34	79,78	0,53
25-lug-01	3,8	212,2556989	100,14	19,13	1,29	79,38	0,2
1-ago-01	3,8	214,2536067	97,79	18,25	1,32	80,43	0
8-ago-01	3,8	216,2937085	101,47	18,21	1,63	80,16	0
15-ago-01	3,8	218,292757	99,48	18,84	1,64	79,52	0
16-ago-01	0,6	218,5998074	15,74	17,65	2,2	80,15	0
22-ago-01	0,6	218,6484704	2,92	13,91	4,91	80,42	0,75
27-ago-01	0,6	220,5323297	91,69	21,18	1,21	77,43	0,18
4-set-01	0,5	223,953563	169,81	19,56	1,59	78,86	0
17-set-01	0,4	228,044569	204,33	18,08	1,71	80,22	0
10-ott-01	0,4	233,6564422	280,88	16,49	1,75	81,75	0
23-ott-01	0,4	235,7032877	104,42	16,47	2,11	81,04	0,38
19-nov-01	0,4	239,7840814	200,77	14,98	1,42	82,29	1,31
13-dic-01	0,35	246,0683698	310,3	18,79	1,49	79,44	0,27
17-dic-01	0,35	247,0967207	52,21	16,4	2,02	81,59	0
21-gen-02	0,25	256,0123029	457,03	16,1	2,2	81,7	0
25-feb-02	0,25	262,9998898	378,98	18,12	3,22	78,66	0
2-apr-02	0,25	270,865706	429,79	16,95	3,35	79,7	0

Table 20: biogas characterization of bioreactor LSR2

LSR2							
Date	aeration rate	discharged gas (aeration)	delta gas volume o	CO2	O2	N2	CH4
	[l/h]	[l/kg TS]	[l]				
30-ago-00			1,8	0,376597	20,80894	78,81447	0
30-ago-00			0,98	84,57471	0,130424	2,995078	12,29978
1-set-00			4,78	78,42335	0,219619	7,117926	14,23911
5-set-00			11,79	76,642	0,283251	7,68524	15,38952
6-set-00			2,46	76,642	0,283251	7,68524	15,38952
7-set-00			4,37	75,306	0,186	7,754	16,754
11-set-00			14,01	72,638	0,217	7,795	19,3502
12-set-00			2,26	72,638	0,217	7,795	19,3502
13-set-00			3,35	72,638	0,217	7,795	19,3502
14-set-00			1,72	70,0618	0,2548	8,9161	20,7671
15-set-00			1,9	70,0618	0,2548	8,9161	20,7671
18-set-00			6,87	68,44	0,2	8,82	22,54
19-set-00			2,1	68,44	0,2	8,82	22,54
20-set-00			0,77	68,44	0,2	8,82	22,54
21-set-00			1,58	67,05	0,3	8,81	23,84
22-set-00			1,06	67,05	0,3	8,81	23,84
25-set-00			5,08	65,94	0,26	7,89	25,92
26-set-00			1,12	48,76	5,68	25,95	19,61
27-set-00			0,45	48,76	5,68	25,95	19,61
28-set-00			1,91	65,39	0,24	7,63	26,74
29-set-00			1,36	65,39	0,24	7,63	26,74
2-ott-00			3,86	65,39	0,24	7,63	26,74
4-ott-00			0,88	60	1,49	11,41	27,1
5-ott-00			0,22	60	1,49	11,41	27,1
6-ott-00			0,66	60	1,49	11,41	27,1
9-ott-00			2,73	62,74	0,19	6,74	30,34
10-ott-00			1,88	62,74	0,19	6,74	30,34
11-ott-00			0,57	62,74	0,19	6,74	30,34
12-ott-00			0,31	58,86	0,89	9,28	30,97
16-ott-00			1,99	59	0,49	7,62	32,89
17-ott-00			0,01	59	0,49	7,62	32,89
20-ott-00			1,38	58,04	0,54	8,15	33,27
23-ott-00			1,7	58,17	0,28	7,14	34,41
24-ott-00	0,048476821	0	1,22	58,17	0,28	7,14	34,41
25-ott-00	0,7636	2,582563916	19,09	47,12	0,44	29,47	22,98
26-ott-00	0,888928571	3,171907912	24,89	39,29	0,7	45,38	14,62
27-ott-00	0,877391304	3,643626958	20,18	32,86	1,1	57,13	8,92
30-ott-00	0,879180887	5,119055859	64,4	24,06	0,99	71,96	2,99
31-ott-00	0,8256	5,47568894	15,48	22,51	1,05	73,85	2,58
1-nov-00	0,818461538	5,964459361	21,28	20,83	1,09	75,68	2,41
3-nov-00	0,837153285	6,840768045	38,23	19,76	1,11	76,56	2,57
6-nov-00	0,832734864	8,363077412	66,48	19,05	1,16	76,82	2,97
7-nov-00	0,994020619	8,730125995	16,07	18,81	1,05	77,12	3,02
8-nov-00	0,966233766	9,442150576	31	18,5	1,24	77,28	2,98
10-nov-00	1,040253165	10,3768483	41,09	18,65	1,11	77,03	3,21
12-nov-00	1,249014085	11,89984463	66,51	18,65	1,11	77,03	3,21
14-nov-00	1,488372093	13,36536508	64	18,19	1,18	76,17	4,46
17-nov-00	2,093319194	17,11881908	164,5	18,75	1,01	74,79	5,45
21-nov-00	2,54875576	22,42263814	230,45	19,04	1,02	70,13	9,8
28-nov-00	2,919561753	33,66073078	488,54	19,25	0,91	69,15	10,69
5-dic-00	4,315176179	50,42147552	724,59	17,9	1,15	71,86	9,09
12-dic-00	4,182544379	66,57458029	706,85	17,05	1,17	79,25	2,53
19-dic-00	3,831701493	81,22644742	641,81	15,74	2,33	81,76	0,17
2-gen-01	3,818720238	108,7871452	1283,09	11,57	7,28	81,15	0
8-gen-01	3,744707846	117,6042835	560,77	9,92	9,1	80,99	0
9-gen-01	3,101764706	118,3217636	52,73	10,48	8,33	81,2	0

11-gen-01	2,912678571	120,6872107	163,11	10,61	8,24	81,16	0
16-gen-01	2,294464286	124,4408726	256,98	11,24	7,85	80,85	0,06
23-gen-01	1,999761905	129,5005582	335,96	11,77	7,05	81,18	0
30-gen-01	1,857278107	134,5197355	313,88	10,57	8,66	80,76	0
1-feb-01	1,903333333	135,8095907	91,36	10,19	9,07	80,74	0
6-feb-01	1,358907563	138,0155682	161,71	12,3	5,23	82,47	0
7-feb-01	1,4024	138,6504118	35,06	12,3	5,23	82,47	0
13-feb-01	1,324068966	142,1268412	191,99	11,14	7,57	81,28	0
21-feb-01	1,134368421	145,4429881	215,53	11,62	7,24	81,14	0
27-feb-01	1,031527778	147,7854326	148,54	12,28	6,67	81,05	0
6-mar-01	0,980416667	150,4920591	164,71	12,8	4,72	82,48	0
13-mar-01	0,924940476	153,3979232	155,39	12,21	7,05	80,73	0
20-mar-01		153,4908294	5,81	13,64	5,59	80,76	0
27-mar-01	0,666011905	155,4700158	111,89	13,62	4,78	81,6	0
3-apr-01	1,177380952	159,1551643	197,8	13,62	4,78	81,6	0
19-apr-01	0,59046875	163,3794846	226,74	13,62	4,78	81,6	0
23-apr-01		163,3908493	0,61	13,62	4,78	81,6	0
8-mag-01	0,579027778	167,2744146	208,45	13,62	4,78	81,6	0
14-mag-01	0,486111111	168,5785622	70	12,61	6,32	81,07	0
16-mag-01	0,545833333	169,0197627	26,2	13,22	5,08	81,71	0
21-mag-01	0,4575	170,023433	54,9	13,4	4,56	82,04	0
23-mag-01	0,37625	170,3645238	18,06	13,4	4,56	82,04	0
30-mag-01	0,405416667	171,6508855	68,11	12,77	5,95	81,28	0
5-giu-01	0,390625	172,6223237	56,25	13,15	8,2	81,65	0
12-giu-01	0,371904762	173,5378646	62,48	15,76	2,26	81,98	0
19-giu-01	0,358928571	174,8380139	60,3	15,69	8,42	81,89	0
26-giu-01		174,8480922	0,7	13,81	4,82	81,37	0
3-lug-01	0,71952381	177,0945456	120,88	14,7	2,81	82,49	0
11-lug-01	0,37038961	178,5862641	71,3	14,14	3,54	82,32	0
18-lug-01	0,514268657	180,3153312	86,14	12,58	6	81,31	0,12
25-lug-01	0,360237389	181,3600914	60,7	15,26	3,11	81,63	0
1-ago-01	0,384597015	182,6853931	64,42	11,44	6,73	81,83	0
8-ago-01	0,417100592	183,8388139	70,49	14,66	3,67	81,67	0
15-ago-01	0,405449102	185,1877034	67,71	14,04	5,15	80,8	0
16-ago-01	0,402962963	185,3857236	10,88	15,22	3,99	80,79	0
21-ago-01	0,638803419	186,8468473	74,74	14,71	4,44	80,85	0
27-ago-01	0,373032929	187,8706411	53,81	14,9	4,58	80,52	0
4-set-01	0,457135741	189,6017236	91,77	14,64	4,73	80,63	0
17-set-01	0,46683087	192,2583405	142,15	14,27	5,34	80,39	0
10-ott-01	0,466110607	196,8801303	257,06	13,87	5,85	80,28	0
23-ott-01	0,465705128	199,4063609	145,3	13,53	6,28	80,2	0
19-nov-01	0,467660232	204,5196815	302,81	12,82	6,97	80,22	0
13-dic-01	0,467299145	208,916507	273,37	11,79	8,18	80,02	0
17-dic-01	0,347851003	209,3619419	30,35	10,67	8,87	80,46	0
21-gen-02	0,348238095	213,4204106	292,52	11,27	8,28	80,45	0
22-gen-02	0,346236559	213,5376211	8,05	11,9	7,74	80,36	0
25-feb-02	0,344571078	217,8081174	281,17	12,54	6,11	81,35	0
2-apr-02	0,290089569	222,0961858	251	8,97	10,86	80,17	0

Table 21: Leachate characterization of bioreactor LSR1, LSR2

LSR1						LSR2					
Date	pH	L/S ratio	TN	NH4-N	SO4	Date	pH	L/S ratio	TN	NH4-N	SO4
	(ohne F)	[l/kgTS]	[mg/l]	[mg/l]	[mg/l]		(ohne F)	[l/kgTS]	[mg/l]	[mg/l]	[mg/l]
5-set-00	6,97	0,03030303	347,5	280	1,98	5-set-00	6,14	0,030386	470,6	361	98,2
12-set-00	7,02	0,060606061	371,5	296	1,3	12-set-00	6,02	0,060772	484,6	389	131
19-set-00	7,06	0,090909091	331	258	3,44	19-set-00	6	0,091158	451	320	9,31
26-set-00	7,03	0,121212121	378	328	1,66	26-set-00	5,98	0,121544	498	372	6,63
4-ott-00	7,28	0,151515152	369	323	94,1	4-ott-00	6,04	0,15193	515	395	11,08
10-ott-00	7,32	0,181818182		318	23,1	10-ott-00	5,98	0,182315	506	458	6,48
17-ott-00	7,31	0,212121212		267	71,8	17-ott-00	6	0,212701	500	458	7,47
24-ott-00	7,33	0,242424242	280	253	75,5	24-ott-00	6,05	0,243087	467	393	10,22
31-ott-00	7,43	0,272727273		214	163	31-ott-00	6,33	0,273473	444,25	365	12,58
7-nov-00	7,16	0,303030303	179	118	237	7-nov-00	6,27	0,303859	421,5	336	9,26
14-nov-00	7,15	0,333333333		14	614	14-nov-00	6,53	0,334245	398,75	340	6,46
21-nov-00	7,07	0,363636364	38	5	1284	21-nov-00	6,8	0,364631	376	312	8,3
28-nov-00	7,13	0,393939394		5	1847	28-nov-00	6,96	0,395017	293	96	7,59
5-dic-00	7,2	0,424242424	19	5	2246	5-dic-00	7,2	0,425403	213	133	53,7
12-dic-00	7,2	0,454545455	10	5	2483	12-dic-00	7,48	0,455789	193	173	66,4
19-dic-00	7,18	0,484848485		5	2243	19-dic-00	7,37	0,486174	131	111	105
2-gen-01	7,18	0,515151515		5	2502	2-gen-01	7,11	0,51656	60	5	342
9-gen-01	7,18	0,545454545		5	2096	9-gen-01	7,16	0,546946	10	5	364
16-gen-01	7	0,575757576		5	1073	16-gen-01	7,15	0,577332	10	5	363
23-gen-01	7,04	0,606060606		5	631	23-gen-01	7,14	0,607718	10	5	31,2
30-gen-01	6,93	0,636363636		5	1658	30-gen-01	7,08	0,638104	10	5	297
6-feb-01	6,97	0,666666667		5	1655	6-feb-01	7,13	0,66849	10	5	316
13-feb-01	6,99	0,696969697		5	1616	13-feb-01	7,14	0,698876	10	5	347
21-feb-01	6,98	0,727272727		5	1597	21-feb-01	7,08	0,729262	10	5	281
27-feb-01	7,11	0,757575758		5	1557	27-feb-01	7,14	0,759648	10	5	221
6-mar-01	7,03	0,787878788	10	5	1430	6-mar-01	7,02	0,790033	10	5	213
13-mar-01	6,94	0,818181818	10	5	1575	13-mar-01	7,29	0,820419	10	5	142
20-mar-01	6,91	0,848484848		5	1401	20-mar-01	7,09	0,850805		5	108
27-mar-01	6,98	0,878787879		5	1298	3-apr-01	7,1	0,881191	10	10	68
3-apr-01	7,5	0,909090909	10	5	1270	8-mag-01	7,43	0,911577		5	99
8-mag-01	7,24	0,939393939		5	1518	16-mag-01	7,18	0,941963		5	111
16-mag-01	7,25	0,96969697		5	1499	23-mag-01	7,18	0,972349		5	112
23-mag-01	6,84	1		5	1420	30-mag-01	7,3	1,002735		5	95,7
30-mag-01	6,87	1,03030303		5	1318	5-giu-01	7,23	1,033121		5	57
5-giu-01	6,81	1,060606061		5	1206	12-giu-01	7,25	1,063507		5	31
12-giu-01	6,85	1,090909091		5	1134	19-giu-01	7,25	1,093892		5	31
19-giu-01	6,89	1,121212121		5	781	26-giu-01	7,21	1,124278		5	16,04
26-giu-01	6,87	1,151515152		5	931	3-lug-01	7,19	1,154664		5	18,04
3-lug-01	6,91	1,181818182		5	813	11-lug-01	7,21	1,18505		5	19,65
11-lug-01	6,87	1,212121212		5	680	18-lug-01	7,25	1,215436		5	29,5
18-lug-01	6,94	1,242424242		5	598	25-lug-01	7,28	1,245822		5	38
25-lug-01	7	1,272727273		5	503	1-ago-01	7,15	1,276208		0	22
1-ago-01	6,9	1,303030303		0	364	8-ago-01	7,19	1,306594		6	23
8-ago-01	6,93	1,333333333		5	269	15-ago-01		1,33698		5	24,8
15-ago-01		1,363636364		5	85	22-ago-01	7,25	1,367366		5	30
22-ago-01	7	1,393939394		5	26	27-ago-01	7,37	1,397751		5	32
27-ago-01	6,99	1,424242424		5	16	4-set-01	7,2	1,428137		5	31
4-set-01	6,98	1,454545455		6,08	13	17-set-01	7,23	1,458523		5	34
17-set-01	6,85	1,484848485		7	8,83	10-ott-01	7,27	1,488909	10	5	41
10-ott-01	7	1,515151515	10	8	25,9	23-ott-01	7,25	1,519295		5	47
23-ott-01	6,92	1,545454545		5	51	19-nov-01	7,33	1,549681	10	5	61
19-nov-01	7,06	1,575757576	10	5	65	17-dic-01	7,34	1,580067	10	5	88
17-dic-01	6,94	1,606060606	10	5	406	21-gen-02	7,38	1,610453		5	78
21-gen-02	6,98	1,636363636	10	5	503	25-feb-02	7,28	1,640839		5	91
25-feb-02		1,666666667		5	762,6667	2-apr-02	7,2	1,671225		5	78,76
2-apr-02	6,93	1,696969697		5	892,43						

Table 22: Leachate characterization of bioreactor LSR3, LSR8

LSR3						LSR8					
Date	pH	L/S ratio	TN	NH4-N	SO4	Date	pH	L/S ratio	TN	NH4-N	SO4
	(ohne F)	[l/kgTS]	[mg/l]	[mg/l]	[mg/l]		(ohne F)	[l/kgTS]	[mg/l]	[mg/l]	[mg/l]
5-set-00	6,93	0,030303	458,7	392	1,5	19-set-00	5,97	0,021739	865	634	7,6
12-set-00	7,05	0,060606	480,6	394	0,7	26-set-00	5,91	0,043478	877	780	4,97
19-set-00	7,09	0,090909	426	321	2,3	4-ott-00	5,94	0,065217		780	6,16
26-set-00	7,07	0,121212	581	391	2,67	10-ott-00	6,26	0,086957		830	6,86
4-ott-00	7,29	0,151515	452	371	80,7	17-ott-00	6,51	0,108696		704	8,9
10-ott-00	7,27	0,181818		342	26,5	24-ott-00	6,82	0,130435	794	716	7,43
17-ott-00	7,25	0,212121		311	14,5	31-ott-00	7,05	0,152174		554	8,06
24-ott-00	7,31	0,242424	342	302	18,4	7-nov-00	7,33	0,173913		390	14,03
31-ott-00	7,39	0,272727		295	55,4	14-nov-00	7,58	0,195652		330	379
7-nov-00	7,38	0,30303		219	75,85	21-nov-00	7,62	0,217391	320	242	228
14-nov-00	7,53	0,333333		194	263	28-nov-00	7,3	0,23913		157	454
21-nov-00	7,3	0,363636	138	78	390	5-dic-00	7,15	0,26087	128	69	802
28-nov-00	7,15	0,393939		19	487	12-dic-00	6,87	0,282609	26	9	1177
5-dic-00	7,07	0,424242	32	12	379	19-dic-00	6,9	0,304348		5	1254
12-dic-00	7,21	0,454545	26	12	84,6	2-gen-01	6,9	0,326087		5	1694
19-dic-00	7,15	0,484848		12	38,5	9-gen-01	7,15	0,347826		5	1612
2-gen-01	7,07	0,515152		10	24,45	16-gen-01	7,1	0,369565		5	727
9-gen-01	7,22	0,545455		5	18,3	23-gen-01	7,07	0,391304		5	1383
16-gen-01	7,15	0,575758		11	11,9	30-gen-01	6,95	0,413043		5	1173
23-gen-01	7,13	0,606061		10	13,5	6-feb-01	7,01	0,434783		5	1157
30-gen-01	7,03	0,636364		10	10,6	13-feb-01	6,96	0,456522		8	741
6-feb-01	7,04	0,666667		8	15,6	20-feb-01	6,89	0,478261		5	1082
13-feb-01	7,08	0,69697		9	14,8	27-feb-01	6,96	0,5		5	934
20-feb-01	7,02	0,727273		8	12,9	6-mar-01	6,96	0,521739	14	5	785
27-feb-01	7,02	0,757576		5	24,7	13-mar-01	7,01	0,543478	16	5	843
6-mar-01	6,98	0,787879	12	5	22,6	20-mar-01	7,03	0,565217		5	758
13-mar-01	7,04	0,818182	14	6	14,8	3-apr-01	7,5	0,586957	10	10	730
20-mar-01	7,05	0,848485		5	12,5	8-mag-01	7,07	0,608696		5	730
27-mar-01	6,96	0,878788		5	7,7	16-mag-01	7	0,630435		5	714
3-apr-01	7	0,909091	10	10	3,9	23-mag-01	6,97	0,652174		5	687
8-mag-01	6,99	0,939394		16	2,99	30-mag-01	7,03	0,673913		5	633
16-mag-01	6,95	0,969697		8	4,71	5-giu-01	6,98	0,695652		5	514
23-mag-01	7,03	1		5	201	12-giu-01	7,03	0,717391		5	413
30-mag-01	6,95	1,030303		17	19,3	19-giu-01	7,08	0,73913		5	230
5-giu-01	7,04	1,060606		17	5	26-giu-01	7,07	0,76087		5	297,8
12-giu-01	6,98	1,090909		13	5	3-lug-01	7,06	0,782609		5	266
19-giu-01	7,16	1,121212		5	140	11-lug-01	7,02	0,804348		5	186
26-giu-01	7,12	1,151515		5	277,9	18-lug-01	7,04	0,826087		5	155
3-lug-01	7,32	1,181818		5	405	25-lug-01	7,1	0,847826		5	97
11-lug-01	7,18	1,212121		11	485	1-ago-01	6,99	0,869565		5	121
18-lug-01	7,31	1,242424		5	578	8-ago-01	7,02	0,891304		5	21
25-lug-01	7,35	1,272727		5	553	15-ago-01	7	0,913043		5	125
1-ago-01	7,17	1,30303		0	606	22-ago-01	7,01	0,934783		5	120
8-ago-01	7,23	1,333333		5	647	27-ago-01	7,22	0,956522		5	107
15-ago-01		1,363636		25	675	4-set-01	7,05	0,978261		5	85
22-ago-01	6,95	1,393939		5	499	17-set-01	6,92	1		5	110
27-ago-01	7,45	1,424242		5	543	10-ott-01	7,1	1,021739	10	5	143
4-set-01	7,75	1,454545		5	489	23-ott-01	7,04	1,043478		5	72
17-set-01	7,17	1,484848		5	651	19-nov-01	7,26	1,065217	10	5	24
10-ott-01	7	1,515152	10	8	25,9	17-dic-01	7,24	1,086957	10	5	45
23-ott-01	7,12	1,545455		5	552	21-gen-02	7,1	1,108696	10	5	439
19-nov-01	7,13	1,575758	10	5	902	25-feb-02	7,01	1,130435		5	625
17-dic-01	7,26	1,606061	10	5	1046	2-apr-02	7,05	1,152174		5	571,52
21-gen-02	7,2	1,636364	10	5	963						
25-feb-02	6,99	1,666667		5	1152						
2-apr-02	6,95	1,69697		5	834,61						

Table 23: Leachate characterization of bioreactor LSR3, LSR4

LSR3					LSR4				
Date	pH	TN	NH4-N	SO4	Date	pH	TN	NH4-N	SO4
		[mg/l]	[mg/l]	[mg/l]			[mg/l]	[mg/l]	[mg/l]
5-set-00	6,91	454,7	359	3,44	5-set-00	6,84	317,4	253	1,07
12-set-00	6,95	500,6	441	1,13	12-set-00	6,89	367,8	279	1,03
19-set-00	6,94	485	365	2,97	19-set-00	6,89	347	238	2,2
26-set-00	6,98	511	453	1,43	26-set-00	6,87	373	301	1,1
4-ott-00	7,36	491	422	524	4-ott-00	6,95	405	313	1,31
10-ott-00	7,39	416	390	361	10-ott-00	6,96	380	335	0,9
17-ott-00	7,23		270	253	17-ott-00	6,91		288	4,29
24-ott-00	6,78	137	21	299	24-ott-00	6,92	378	294	4,76
31-ott-00	6,95		5	943	31-ott-00	6,96		308	5,55
7-nov-00	7,03		5	1110	7-nov-00	6,93		273	6,41
14-nov-00	7,29		5	1231	14-nov-00	7,14		290	6,95
21-nov-00	7,08	40	5	1499	21-nov-00	6,96	355	300	8,46
28-nov-00	7,09		5	1999	28-nov-00	6,89		260	8,41
5-dic-00	7,13	19	5	2194	5-dic-00	6,91	337	219	7,69
12-dic-00	7,06	7	5	2212	12-dic-00	6,95	318	279	7,25
19-dic-00	7,07		5	2146	19-dic-00	6,9		285	6,66
2-gen-01	7,12		5	2336	2-gen-01	6,85		259	7,89
9-gen-01	7,24	17	5	1943	9-gen-01	6,97	323	298	8,79
16-gen-01	7,15		5	1933	16-gen-01	6,91		272	7,43
23-gen-01	6,96		5	1925	23-gen-01	6,9		297	7,95
30-gen-01	6,95		5	1917	30-gen-01	6,82		258	4,3
6-feb-01	7,16		5	1909	6-feb-01	6,84		270	9,4
13-feb-01	7,09	75	5	1907	13-feb-01	6,87		223	4,2
20-feb-01	7,03	74	5	1706	20-feb-01	6,86		245	9,9
27-feb-01	7,07	79	5	1749	27-feb-01	6,85		200	6,8
6-mar-01	6,91	10	5	1531	6-mar-01	6,84	265	227	9,2
13-mar-01	7,08		5	1750	13-mar-01	6,83	261	215	9,38
20-mar-01	6,96		5	1629	20-mar-01	6,82		231	4,07
27-mar-01	7,29		5	1245	27-mar-01	6,87		236	4,29
3-apr-01	7,4	10	5	1560	3-apr-01	7,1	240	240	4,2
8-mag-01	7,25		5	1590	8-mag-01	6,97		244	3,61
16-mag-01	7,32		5	1483	16-mag-01	6,84		164	13,2
23-mag-01	6,98		5	1383	23-mag-01	6,89		188	5,66
30-mag-01	7,03		5	1297	30-mag-01	6,89		172	5,54
5-giu-01	7,06		5	1281	5-giu-01	6,87		260	5
12-giu-01	6,99		5	1173	12-giu-01	6,9		229	5
19-giu-01	6,97		5	572	19-giu-01	6,92		199	5
26-giu-01	6,98		5	1104	26-giu-01	6,87		219	4,9
3-lug-01	7,01		5	982	3-lug-01	6,84		156	16,46
11-lug-01	6,74		5	1078	11-lug-01	6,85	234	236	5,76
18-lug-01	6,9		5	891	18-lug-01	6,96		212	36,6
25-lug-01	6,91		5	771	27-lug-01	6,95		206	8,6
1-ago-01	6,88		5	578	1-ago-01	6,82		200	3
8-ago-01	6,91		7	397	8-ago-01	6,81		207	5
15-ago-01	6,96		5	198	15-ago-01	6,83		167	3,97
22-ago-01	7,01		5	20	22-ago-01	6,86		187	4
27-ago-01	7,07		5	3	27-ago-01	6,96		186	4
4-set-01	6,98		5	4	4-set-01	6,85		185	4
17-set-01	6,99		5	75	17-set-01	6,84		186	4,5
10-ott-01	7,03	10	5	229	10-ott-01	6,84	187	201	4,3
23-ott-01	6,99		5	112	23-ott-01	6,83		159	9,53
19-nov-01	7,2	10	5	519	19-nov-01	6,96	122	197	5,48
17-dic-01	7,08	10	5	675	17-dic-01	6,99	84	221	5
21-gen-02	7,13		5	733	21-gen-02	6,95		146	5,98
25-feb-02	6,98		5	662	25-feb-02	6,87		242	4
2-apr-02	6,94		5	534,79	2-apr-02	6,83		171	2,65

Table 24: Leachate characterization of bioreactor LSR6, LSR7

LSR6						LSR7					
Date	pH	L/S	TN	NH4-N	SO4	Date	pH	L/S	TN	NH4-N	SO4
			[mg/l]	[mg/l]	[mg/l]				[mg/l]	[mg/l]	[mg/l]
5-set-00	6,93	0,020833	383,6	316	1,3	5-set-00	6,97	0,021739	468,9	348	1,92
12-set-00	7,14	0,041667	398,6	302	0,9	12-set-00	7,12	0,043478		368	0,92
19-set-00	7,08	0,0625	395	288	0,94	19-set-00	7,1	0,065217	595	327	0,83
26-set-00	7,04	0,083333	605	340	1,24	26-set-00	7,3	0,086957	306	371	0,83
4-ott-00	7,62	0,104167		288	320	4-ott-00	7,15	0,108696		376	2,09
10-ott-00	7,33	0,125	154	100	402	10-ott-00	7,1	0,130435		397	1,27
17-ott-00	7,25	0,145833		24	326	17-ott-00	7,1	0,152174	257	346	3,55
24-ott-00	7,18	0,166667	16	5	300	24-ott-00	7,08	0,173913	368	360	4,97
31-ott-00	7,25	0,1875		5	297	31-ott-00	7,11	0,195652		355	5,81
7-nov-00	7,23	0,208333		5	321	7-nov-00	7,08	0,217391		317	4,79
14-nov-00	7,48	0,229167		5	346	14-nov-00	7,31	0,23913		346	5,55
21-nov-00	7,45	0,25	51	5	359	21-nov-00	7,07	0,26087	428	354	6,08
28-nov-00	7,41	0,270833		5	371	28-nov-00	7,04	0,282609		314	4,76
5-dic-00	7,44	0,291667	15	5	369	5-dic-00	7,02	0,304348	369	274	4,62
12-dic-00	7,52	0,3125	15	5	320	12-dic-00	7,09	0,326087	368	328	5,11
19-dic-00	7,49	0,333333		5	235	19-dic-00	7,01	0,347826		339	4,59
2-gen-01	7,52	0,354167		5	134	2-gen-01	7,05	0,369565		326	6,24
9-gen-01	7,62	0,375		5	81,6	9-gen-01	7,11	0,391304		339	3,71
16-gen-01	7,61	0,395833		5	35,8	16-gen-01	7,05	0,413043		335	6,3
23-gen-01	7,56	0,416667		5	47,6	23-gen-01	7,07	0,434783		347	2,89
30-gen-01	7,54	0,4375		5	167	30-gen-01	7,04	0,456522		348	3
6-feb-01	7,49	0,458333		5	103	6-feb-01	7,01	0,478261		332	3,6
13-feb-01	7,51	0,479167		5	56,4	13-feb-01	7,03	0,5		264	3,7
20-feb-01	7,4	0,5		5	29,5	20-feb-01	7,03	0,521739		320	5,2
27-feb-01	7,51	0,520833		5	21,5	27-feb-01	7,03	0,543478		283	4,1
6-mar-01	7,41	0,541667	10	5	15,4	6-mar-01	7,03	0,565217	383	326	3,6
13-mar-01	7,41	0,5625		5	15,3	13-mar-01	7,03	0,586957		337	5,6
20-mar-01	7,38	0,583333		5	15,3	20-mar-01	7,1	0,608696		338	4,5
27-mar-01	7,59	0,604167		5	15,4	27-mar-01	7,01	0,630435		363	3,65
8-mag-01	7,73	0,625		5	34,7	8-mag-01	7,18	0,652174		365	2,44
16-mag-01	7,73	0,645833		5	36,6	16-mag-01	7,08	0,673913		342	2,87
23-mag-01	7,3	0,666667		5	21,4	23-mag-01	7,14	0,695652		245	8,72
30-mag-01	7,13	0,6875		5	4,44	30-mag-01	7,12	0,717391		312	3,94
5-giu-01	7,16	0,708333		5	3	5-giu-01	7,17	0,73913		363	3
12-giu-01	7,14	0,729167		5	3	12-giu-01	7,18	0,76087		317	3
19-giu-01	7,36	0,75		5	3	19-giu-01	7,15	0,782609		299	2
26-giu-01	7,54	0,770833		5	4,5	26-giu-01	7,21	0,804348		306	2,51
3-lug-01	7,53	0,791667		5	3,52	3-lug-01	7,19	0,826087		276	2,82
11-lug-01	7,5	0,8125		5	4,9	11-lug-01	7,2	0,847826	315	320	2,2
18-lug-01	7,06	0,833333		5	2,8	18-lug-01	7,17	0,869565		308	2,34
25-lug-01	7,07	0,854167		5	2,8	25-lug-01	7,23	0,891304		312	1,2
1-ago-01	7,01	0,875		0	3	1-ago-01	7,1	0,913043		200	1,5
8-ago-01	7,05	0,895833		7	3	8-ago-01	7,11	0,934783		301	2
15-ago-01	7,09	0,916667		5	3,09	15-ago-01	7,11	0,956522		263	1,51
22-ago-01	7,07	0,9375		5	3	22-ago-01	7,22	0,978261		275	7
27-ago-01	7,42	0,958333		5	4	27-ago-01	7,21	1		275	2
4-set-01	7,36	0,979167		5	2	4-set-01	7,08	1,021739		175	8
17-set-01	7,18	1		5	3,8	17-set-01	7,05	1,043478		271	1,65
10-ott-01	7,41	1,020833	20	5	10,3	10-ott-01	7,07	1,065217	276	282	1,7
23-ott-01	7,58	1,041667		5	61	23-ott-01	7,07	1,086957		270	1,37
19-nov-01	7,33	1,0625	10	5	149	19-nov-01	7,15	1,108696	192	275	1,79
17-dic-01	7,34	1,083333	10	5	24	17-dic-01	7,14	1,130435	109	267	1
21-gen-02	7,33	1,104167		5	19,8	21-gen-02	7,11	1,152174		162	1,65
25-feb-02	7,29	1,125		5	102	25-feb-02	6,94	1,173913		323	1,7
2-apr-02	7,4	1,145833		5	80,53	2-apr-02	6,92	1,195652		211	1,75

9 ANNEX 2 VISUAL BASIC MACRO

Evaluation of Kn and Ka

```
Sub kn1()
Rem velocità media di nitrificazione da Kuh1

Dim she, kuh As String
Dim w, y, x, n As Integer
Dim xnh4 As Integer
Dim dt As Integer
Dim avg, sdev As Double

Rem inizializza costanti
she = "kn1"
kuh = "Kuh1"
xnh4 = 16
w = 61

For y = 1 To w: For x = 1 To 26
Sheets(she).Cells(y, x) = ""
Next x: Next y

Rem estrae dati da kuh1
For y = 4 To w
Sheets(she).Cells(y, 1) = Sheets(kuh).Cells(y, 1)
Sheets(she).Cells(y, 2) = Sheets(kuh).Cells(y, 2)
Sheets(she).Cells(y, 3) = Sheets(kuh).Cells(y, 3)
Sheets(she).Cells(y, 4) = Sheets(kuh).Cells(y, xnh4)
Next y
```

```
Rem col.5 = delta(nh4)

Sheets(she).Cells(4, 5) = "delt.NH4"

Sheets(she).Cells(5, 5) = "[mg/l]"

For y = 6 To w - 1

Sheets(she).Cells(y, 5) = _

Sheets(she).Cells(y + 1, 4) - Sheets(she).Cells(y, 4)

Next y


Rem col.6 = kn NH4

Sheets(she).Cells(4, 6) = "kn"

Sheets(she).Cells(5, 6) = "1/day"

For y = 6 To w - 1

If Sheets(she).Cells(y, 5) < 0 Then

dt = Sheets(she).Cells(y + 1, 2) - Sheets(she).Cells(y, 2)

Sheets(she).Cells(y, 6) = _

Sheets(she).Cells(y, 5) / (Sheets(she).Cells(y, 4) * dt)

End If

Next y


Rem col.6 = average kn

Sheets(she).Cells(1, 6) = "Average kn"

n = 0

avg = 0

For y = 6 To w - 1

If Sheets(she).Cells(y, 6) < 0 Then

n = n + 1

avg = avg + Sheets(she).Cells(y, 6)

End If

Next y
```

```
avg = avg / n
Sheets(she).Cells(2, 6) = avg

Rem col.7 = quadrati delle velocità
Rem per la standard deviation
Sheets(she).Cells(4, 7) = "kn x kn"
For y = 6 To w - 1
If Sheets(she).Cells(y, 6) < 0 Then
Sheets(she).Cells(y, 7) = _
Sheets(she).Cells(y, 6) * Sheets(she).Cells(y, 6)
End If
Next y

Rem col.7 = media dei quadrati
Sheets(she).Cells(1, 7) = "Avg. kn x kn"
n = 0
avg = 0
For y = 6 To w - 1
If Sheets(she).Cells(y, 6) < 0 Then
n = n + 1
avg = avg + Sheets(she).Cells(y, 7)
End If
Next y
avg = avg / n
Sheets(she).Cells(2, 7) = avg

Rem col.8 = standard deviation di kn
Sheets(she).Cells(1, 8) = "St.Dev.kn"
sdev = Sqr(Sheets(she).Cells(2, 7) - _
        Sheets(she).Cells(2, 6) * Sheets(she).Cells(2, 6))
Sheets(she).Cells(2, 8) = sdev
```

```
Sheets(she).Cells(3, 8) = "St.Dev./Avg."
Sheets(she).Cells(4, 8) = _
Sheets(she).Cells(2, 8) / Abs(Sheets(she).Cells(2, 6))

Rem col.9 = ka = kn * 0.63
Sheets(she).Cells(1, 9) = "ka=kn*0.636363"
Sheets(she).Cells(2, 9) = Sheets(she).Cells(2, 6) * 0.636363
Sheets(she).Cells(3, 9) = "1/day"

fine: Rem kn1
End Sub

Sub ka1()
Rem velocità media di ammonificazione da Kuh1

Dim she, kuh, emp As String
Dim w, y, x, n As Integer
Dim a, b, c, d As Integer
Dim e, f, g, h, i As Integer
Dim j, k As Integer
Dim xnh4, xtn As Integer
Dim dt As Integer
Dim avg, sdev As Double

Rem inizializza costanti
she = "ka1"
kuh = "Kuh1"
xnh4 = 16
xtn = 15
w = 61
```

```
a = 1: b = 2: c = 3: d = 4:
e = 5: f = 6: g = 7: h = 8: i = 9:
j = 10: k = 11

For y = 1 To w: For x = 1 To 26
Sheets(she).Cells(y, x) = ""
Next x: Next y

Rem estrae dati da kuh1
For y = 4 To w
Sheets(she).Cells(y, a) = Sheets(kuh).Cells(y, a)
Sheets(she).Cells(y, b) = Sheets(kuh).Cells(y, b)
Sheets(she).Cells(y, c) = Sheets(kuh).Cells(y, c)
Sheets(she).Cells(y, d) = Sheets(kuh).Cells(y, xnh4)
Sheets(she).Cells(y, e) = Sheets(kuh).Cells(y, xtn)
Next y

Rem dati TN assenti
n = 0
avg = 0
For y = 6 To w
If Sheets(she).Cells(y, e) = "" Then
n = n + 1
End If
Next y
If n > 0 Then
emp = n
MsgBox ("TN " + emp + " empty cells")
End If
```

```
Sheets(she).Cells(1, e) = "Interpolate"
Sheets(she).Cells(2, e) = n / (w - 6)
Rem interpolazione dei dati TN assenti
For y = 6 To w
If Sheets(she).Cells(y, e) = "" Then
  For z = y To w
    If Sheets(she).Cells(z, e) > 0 Then Exit For
    If z = w Then Exit For
  Next z
  delta = (Sheets(she).Cells(y - 1, e) - Sheets(she).Cells(z, e)) / (z - y + 1)
  n = 1
  For z = y To w
    If Sheets(she).Cells(z, e) > 0 Then Exit For
    Sheets(she).Cells(z, e) = Sheets(she).Cells(y - 1, e) - n * delta
    n = n + 1
    If z = w Then Exit For
  Next z
  If z = w Then Exit For
  y = z
End If
Next y


Sheets(she).Cells(4, f) = "NOrg=TN-NH4*14/18"
Sheets(she).Cells(5, f) = "[mg/l]"
Rem su colonna f calcola l'azoto organico
Rem se TN valorizzato su colonna e
For y = 6 To w
Sheets(she).Cells(y, f) = ""
If Sheets(she).Cells(y, e) > 0 Then
Sheets(she).Cells(y, f) = _
```

```
Sheets(she).Cells(y, e) - Sheets(she).Cells(y, d) * 14 / 18
End If
Next y

Sheets(she).Cells(4, g) = "delta NOrg"
Sheets(she).Cells(5, g) = "[mg/l]"
Rem su colonna g variazioni di azoto organico
For y = 6 To w - 1
Sheets(she).Cells(y, g) = ""
If Sheets(she).Cells(y, f) = "" _
Or Sheets(she).Cells(y + 1, f) = "" Then
y = y
Else
Sheets(she).Cells(y, g) = _
Sheets(she).Cells(y + 1, f) - Sheets(she).Cells(y, f)
End If
Next y

Sheets(she).Cells(4, h) = "ka"
Sheets(she).Cells(5, h) = "1/day"
Rem su colonna h le velocità considerando
Rem solo i decrementi di azoto organico
For y = 6 To w - 1
Sheets(she).Cells(y, h) = ""
If Sheets(she).Cells(y, g) = "" _
Or Sheets(she).Cells(y + 1, f) = "" Then
y = y
ElseIf Sheets(she).Cells(y, g) < 0 Then
dt = Sheets(she).Cells(y + 1, b) - Sheets(she).Cells(y, b)
Sheets(she).Cells(y, h) = _
Sheets(she).Cells(y, g) / (Sheets(she).Cells(y, f) * dt)
```

```
End If
Next y

Rem calcola la velocità media di ammonificazione
n = 0
avg = 0
For y = 6 To w - 1
If Sheets(she).Cells(y, h) < 0 Then
n = n + 1
avg = avg + Sheets(she).Cells(y, h)
End If
If Sheets(she).Cells(y, d) = 5 _
And Sheets(she).Cells(y, e) = 10 Then Exit For
Next y
avg = avg / n
Sheets(she).Cells(2, h) = avg
Sheets(she).Cells(1, h) = "Average ka"

Sheets(she).Cells(4, i) = "ka x ka"
Rem su colonna i calcola i quadrati delle velocità
Rem per la standard deviation
For y = 6 To w - 1
Sheets(she).Cells(y, i) = ""
If Sheets(she).Cells(y, h) < 0 Then
Sheets(she).Cells(y, i) = _
Sheets(she).Cells(y, h) * Sheets(she).Cells(y, h)
End If
Next y

Rem calcola la media dei quadrati
n = 0
```

```
avg = 0

For y = 6 To w - 1

If Sheets(she).Cells(y, i) > 0 Then

n = n + 1

avg = avg + Sheets(she).Cells(y, i)

End If

Next y

avg = avg / n

Sheets(she).Cells(2, i) = avg

Sheets(she).Cells(1, i) = "Avg.ka x ka"


Rem su colonna j=10 calcola la standard deviation

sdev = Sqr(Sheets(she).Cells(2, i) - _

        Sheets(she).Cells(2, h) * Sheets(she).Cells(2, h))

Sheets(she).Cells(2, j) = sdev

Sheets(she).Cells(1, j) = "Standard Dev."


Sheets(she).Cells(3, j) = "St.Dev./Avg.k"

Sheets(she).Cells(4, j) = _

Sheets(she).Cells(2, j) / Abs(Sheets(she).Cells(2, h))


fine: Rem ka1

End Sub
```