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*MASTER THESIS*

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NITROGEN MASS BALANCE AND BIOGAS  
PRODUCTION IN INNOVATIVE SEMIAEROBIC –  
ANAEROBIC – AEROBIC (S.An.A.) LANDFILL

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# Chapter 1.

## INTRODUCTION

Landfill represents nowadays the most chosen solution for municipal solid waste disposal, even though during the last years several types have been adopted. The concept of sustainable landfill represents today a fundamental arrival point, developed for satisfying the requirements of protection, environmental maintenance and prevention from every pollution source.

As known, uncontrolled biogas and leachate production constitutes the most critical aspect in a landfill management, consequently it is necessary to guarantee the collection, avoiding the leakage and spreading within the surrounding environmental matrices.

The input of biodegradable organic substance into a landfill is still rather high, despite increasingly widespread implementation of separate collection systems, thereby causing the biogas production due to the anaerobic conditions naturally found in the waste body characterizing by high organic loads.

In the past years the tendency to complete isolate the waste body from surrounding environment, by preventing both water and air entry (dry tomb landfill), led today to high polluting old landfill, having damaged containment systems, without their original features.

So, starting from this configuration, passing through a landfill simply characterized by biogas and leachate collection system (contained landfill), it came to realize systems in which the air intake in the waste body and the leachate production are encouraged, in order to speed up the degradation of biodegradable organic substance. This configuration corresponds to the model of a sustainable landfill, which main goal is to ensure, during a specified period (usually 30 years, the generation time), a final storage quality of waste that will not cause adverse effects to the surrounding environmental matrices.

This thesis work aims to analyze the S.An.A. landfill system, focusing more on the second anaerobic phase. The main goal consists into demonstrate a greater efficiency in methane production compared to a traditional landfill system, stimulating the methanogenic process by means of a semi-aerobic phase, thus increasing the opportunities of biogas utilization for energy production and, at the same time, reducing the post-operative management phase.



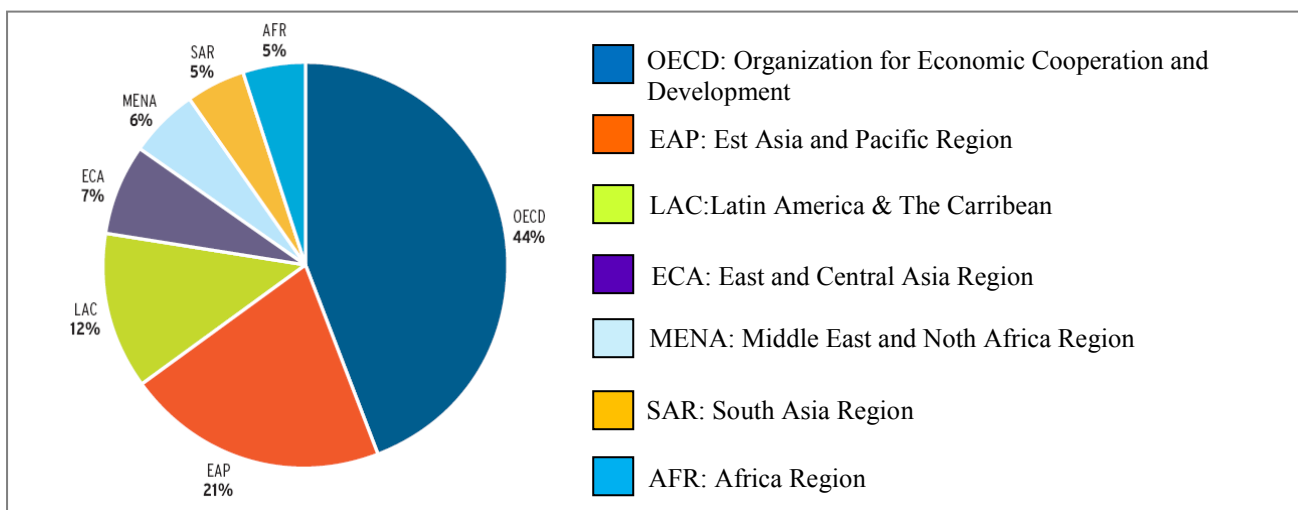
## Chapter 2.

# OVERVIEW ON WASTE PROBLEMS

### 2.1 Waste production in the world

Current global MSW generation levels are approximately 1.3 billion t/y, and are expected to increase to approximately 2,2 billion t/y by 2025. This represents a significant increase per capita waste generation rates, from 1,2 to 1,42 kg/person/d in the next fifteen years. However, global averages are broad estimates only, because rates vary considerably by region, country, city, and even within cities. (Hoorweg & Bhada-Tata, 2012).

MSW generation rates are influenced by economic development, the degree of industrialization, public habits, and local climate. Generally, the higher the economic development and rate of urbanization, the greater the amount of solid waste produced, as is shown in **Figure 2.1**.



**Figure 2.1 – Waste generation by Region**

Income level and urbanization are highly correlated and as disposable incomes and living standards increase, consumption of goods and services correspondingly increases, as does the amount of waste generated. Urban residents produce about twice as much waste as their rural counterparts.

As expected, high-income countries produce the most waste per capita, while low income countries produce the least solid waste per capita. Although the total waste generation for lower middle income countries is higher than that of upper middle income countries the average per capita waste generation amounts for the various income groups reflect the income level of the countries (see **Figure 2.2** and **Table 2.1**).

Countries are classified into four income levels according to World Bank estimates of 2005 GNI per capita. High: \$10.726 or above; Upper middle:\$3.466-10.725; Lower middle: \$876-3.465; and Lower: \$875 or less.

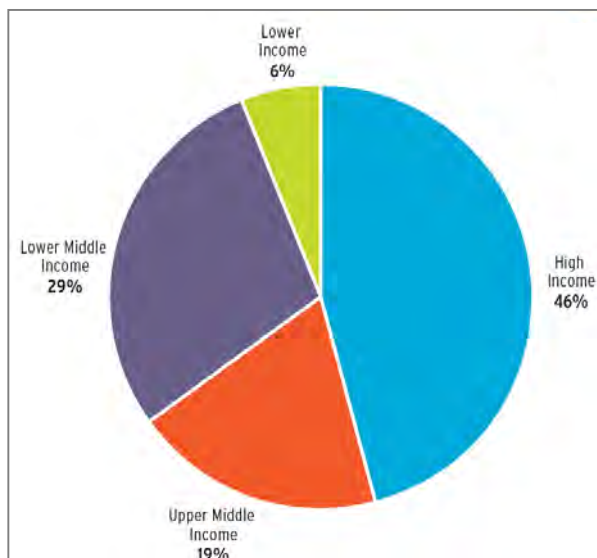


Figure 2.2 – Waste production by Income Capita Level

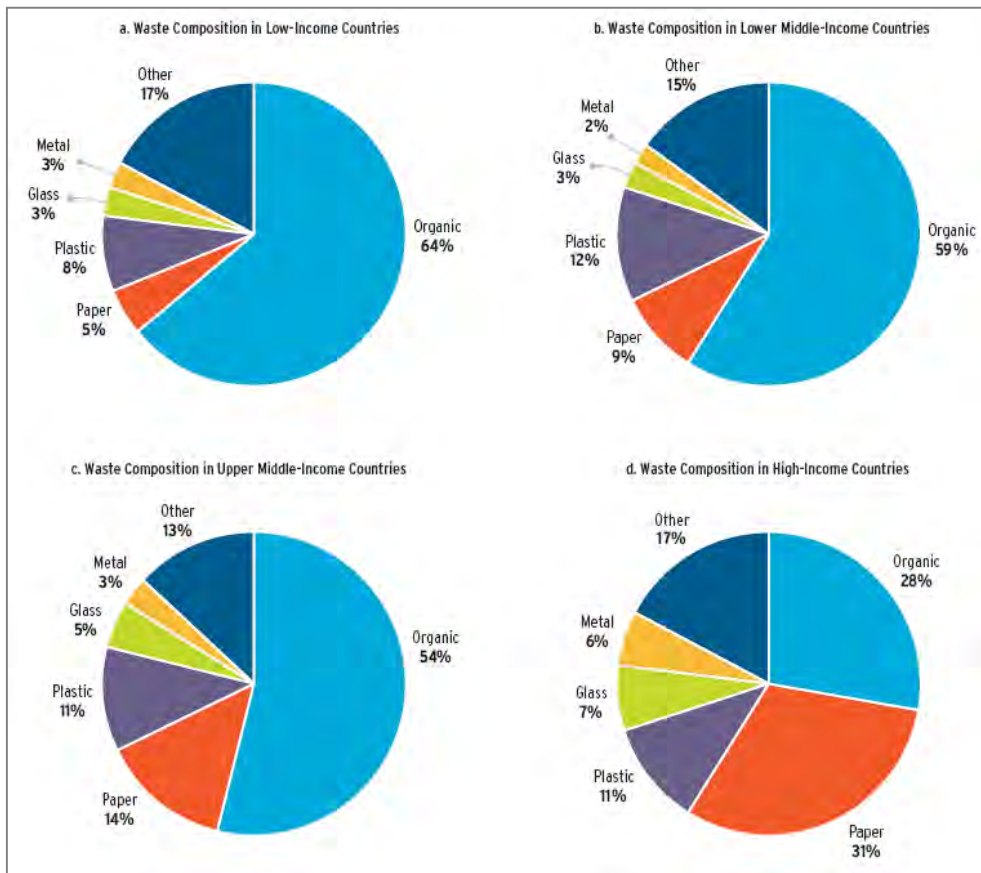
Table 2.1 – Actual and projected waste production according to Income Capita Level

Region	Current available data (2012)			Projection for 2025			
	Total Urban Population [millions]	Urban Waste Generation		Projected Population		Projected Urban Waste	
		Per Capita [Kg/capita/d]	Total [t/d]	Total Population [millions]	Urban Population [millions]	Per Capita [kg/capita/d]	Total [t/d]
Lower Income	343	0,6	204.802	1.637	676	0,86	584.272
Lower Middle Income	1.293	0,78	1.012.321	4.010	2.080	1,3	2.618.804
Upper Middle Income	572	1,16	665.586	888	619	1,6	987.039
High Income Total	774	2,13	1.649.547	1.112	912	2,1	1.879.590
<b>Total</b>	<b>2.982</b>	<b>1,19</b>	<b>3.532.256</b>	<b>7.647</b>	<b>4.287</b>	<b>1,4</b>	<b>6.069.705</b>

Waste composition is influenced by many factors, such as level of economic development, cultural norms, geographical location, energy sources, and climate.

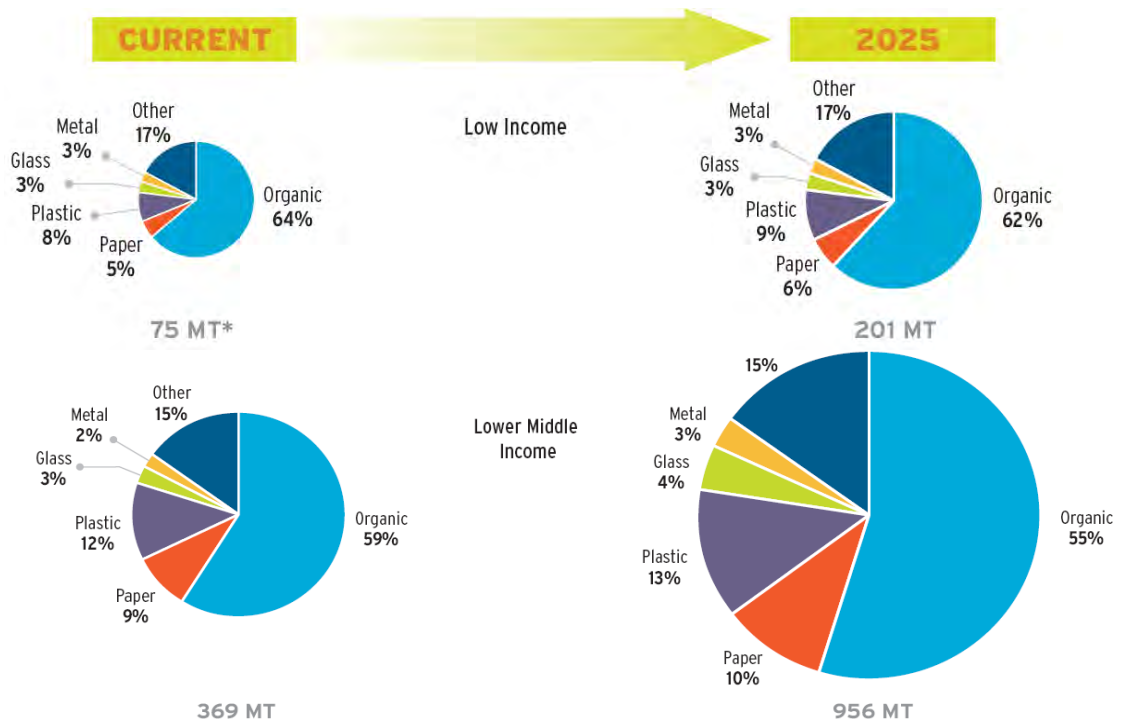
As a country urbanizes and populations become wealthier, consumption of inorganic materials (such as plastics, paper, and aluminum) increases, while the relative organic fraction decreases. Generally, low and middle-income countries have a high percentage of organic matter in the urban waste stream, ranging from 40 to 85% of the total. Paper, plastic, glass, and metal fractions increase in the waste stream of middle- and high-income countries.(See **Figure 2.3**)

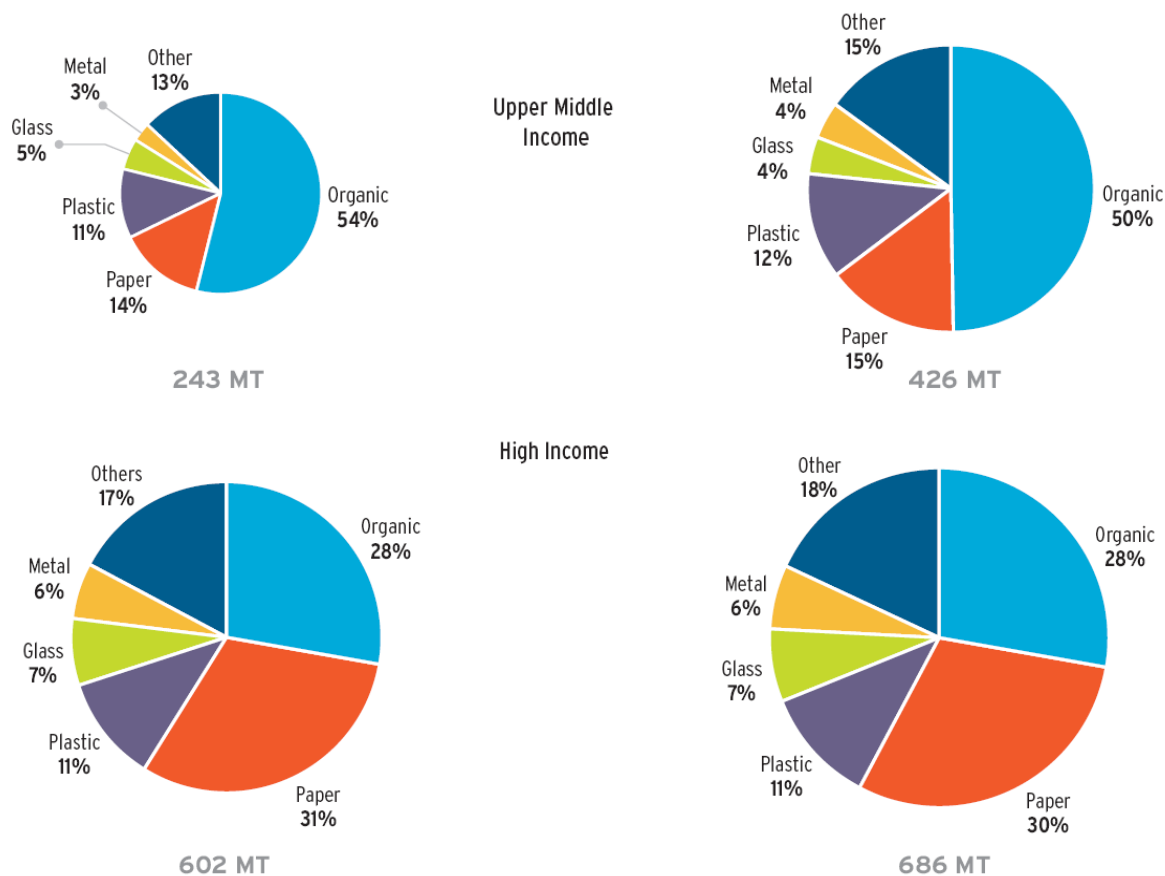




**Figure 2.3 – Waste production by Income Capita Level**

The waste production is designated to grow globally in the future, especially in Low Income Countries, as shown in **Figure 2.4**:





**Figure 2.4 – Solid Waste Composition by Income and Year**

The growth of waste production occurs also in the High Income Countries, although in a less substantial.

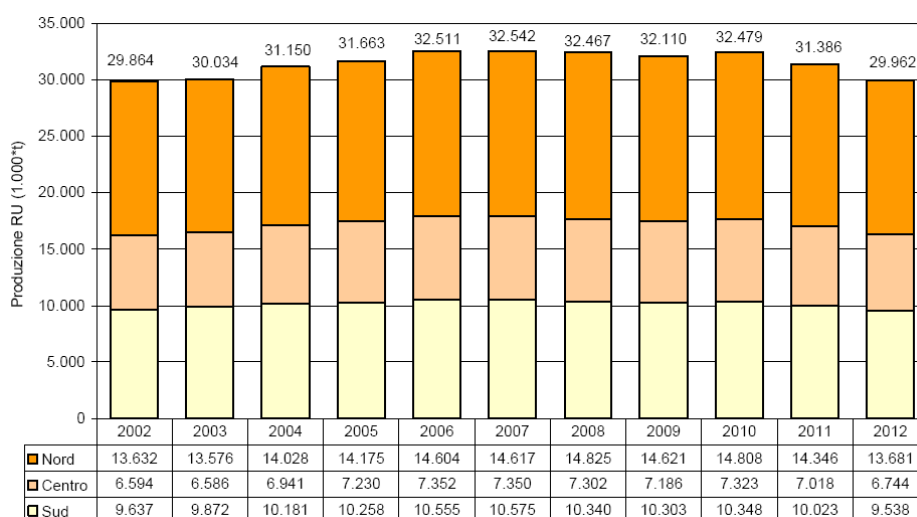
Due to these scenarios, proper waste management systems must be developed and improved.

The waste production in Italy during 2012 was about 30.000 t (Source: ISPRA), with a small reduction from 2011 to 2012, as shown in **Table 2.2**

**Table 2.2 – Solid Waste production in Italy, from 2007 up to 2012**

Region	2007	2008	2009	2010	2011	2012
	[t/y]					
Piemonte	2.269.881	2.253.552	2.245.191	2.251.370	2.159.922	2.027.359
Valle d'Aosta	75.755	77.197	79.365	79.910	78.418	76.595
Lombardia	4.932.260	5.021.804	4.925.126	4.957.884	4.824.172	4.625.032
Trentino Alto Adige	490.022	505.741	515.134	508.787	521.503	505.325

Veneto	2.372.072	2.415.077	2.371.588	2.408.598	2.305.401	2.213.653
Friuli Venezia Giulia	618.592	611.915	591.685	610.287	575.467	550.749
Liguria	981.314	988.128	978.296	991.453	961.690	918.744
Emilia Romagna	2.876.778	2.951.475	2.914.819	2.999.959	2.918.957	2.763.260
Nord	14.616.674	14.824.889	14.621.204	14.808.248	14.345.530	13.680.717
Toscana	2.552.561	2.545.014	2.474.299	2.513.312	2.372.799	2.252.697
Umbria	565.033	548.219	531.743	540.958	507.006	488.00.00
Marche	875.192	865.465	846.950	838.196	822.237	801.053
Lazio	3.357.409	3.343.551	3.332.572	3.430.631	3.315.942	3.201.691
Centro	7.350.195	7.302.249	7.185.564	7.323.097	7.017.984	6.743.533
Abruzzo	697.122	699.265	688.712	681.021	661.820	626.435
Molise	129.568	134.712	136.367	132.153	132.754	126.592
Campania	2.852.735	2.723.326	2.719.170	2.786.097	2.639.586	2.556.249
Puglia	2.148.328	2.135.211	2.150.340	2.149.870	2.095.402	1.980.385
Basilicata	244.655	228.215	224.963	221.372	220.241	214.236
Calabria	943.205	922.259	944.435	941.825	898.196	864.945
Sicilia	2.695.198	2.650.411	2.601.798	2.610.304	2.579.754	2.422.831
Sardegna	864.068	846.664	837.356	825.126	794.953	746.174
Sud	10.574.879	10.340.063	10.303.141	10.347.768	10.022.706	9.537.847
<b>Italy</b>	<b>32.541.748</b>	<b>32.467.201</b>	<b>32.109.909</b>	<b>32.479.113</b>	<b>31.386.220</b>	<b>29.962.097</b>



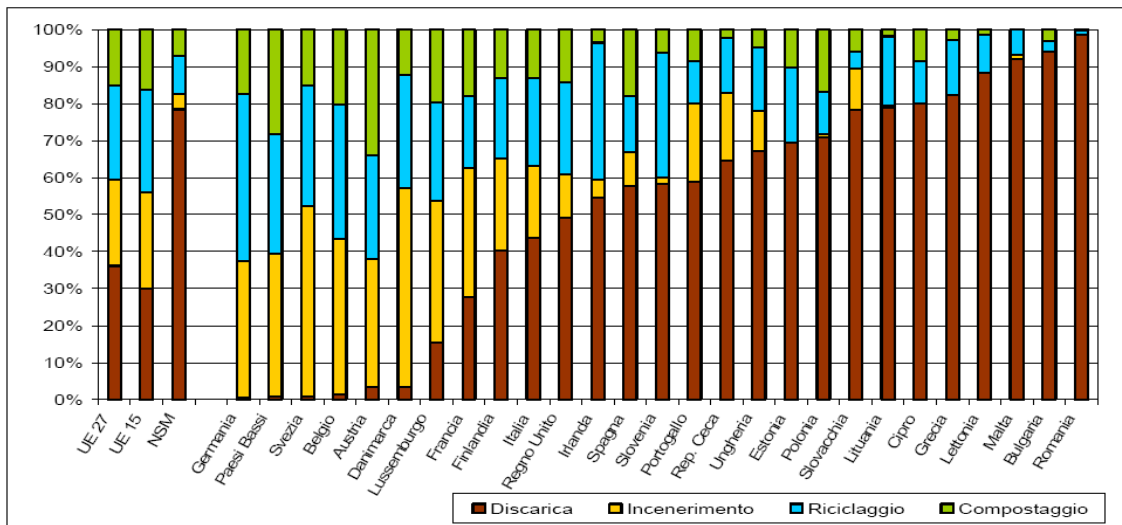
**Figure 2.5 – Solid Waste production in Italy, from 2002 up to 2012**

The pattern of waste production during years is shown in **Figure 2.5**. Due to actual economic situation, waste production was reduced during these last years. The highest waste production occurs in the north area of Italy, characterized by the highest population (27.200 inhabitants in

2012; source ISTAT). The highest per capita waste production occurs on the other hand in middle area of Italy, characterized by the lowest population.

## 2.2 Waste disposal alternatives

The **Figure 2.7** shows the waste management systems adopted by European countries in 2011: about 36% of waste was landfilled, 23% was sent to incineration plants, 26% and 15% was respectively recycled and composted/anaerobically digested. (ISPRA, 2013)



**Figure 2.7 – Solid Waste Management systems in European Countries (ISPRA, 2013)**

It is possible to notice an extreme variability in the approach of urban waste management through European countries.

Regarding waste disposal in landfill, it switches from percentages lower than one of Germany, Paesi Bassi and Sweden, up to 99% of Romania. There are several countries in which the amount of recycled material is very low and the treatment of putrescible fraction is not already developed, causing several problems within waste management.

However, as said before, landfill remains the most chosen waste management system in the world, so it is necessary to improve its configuration in order to guarantee good efficiency and safety operational conditions.

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## Chapter 3.

# REGULATIONS

There are several regulations dealing landfill design and waste disposal, both at national and European level.

### 3.1 European Directive 1999/31/EC

One of the most important European Directive on landfill siting and construction is the 1999/31/EC. The objective of the present directive is to prevent and reduce as far as possible negative effects from the landfilling of waste on the environment, on the global environment and on human health. *Article 2* defines a landfill as “...a waste disposal site for the deposit of the waste onto or into land (i.e. underground) ...”

They are classified in three categories:

- ✓ Landfills for hazardous waste;
- ✓ Landfills for non-hazardous waste;
- ✓ Landfills for inert waste;

Landfill for non-hazardous waste may be used for municipal solid waste, non-hazardous waste of any other origin which fulfils the criteria for the acceptance of waste at landfill for non-hazardous waste set out in accordance with Annex II, and stable, non-reactive waste, with leaching behavior equivalent to those of the non-hazardous waste.

Inert waste landfill sites shall be used only for inert waste.

According to *Article 5* of this Directive, “*Member States shall set up a National strategy for the implementation of the reduction of biodegradable waste going to landfills [...]*”. Lower is the amount of biodegradable organic matter landfilled, lower is the hazardousness of landfill systems, and shorter is the necessary aftercare period.

The reduction targets for the landfilling of biodegradable waste, basing on data for 1995, are:

- ✓ 75 % by 2006;
- ✓ 50 % by 2009;
- ✓ 35 % by 2016

Moreover, all emissions (leachate, gas, surface water) must be monitored and periodically sampled. The frequency of sampling could be adapted on the basis of morphology of the landfill waste and the parameters to be measured and the substances to be analyzed vary according to the composition of the waste deposited.

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According to *Article 5, Paragraph 3*, several waste categories cannot be disposed off in a landfill: liquid, explosive, corrosive, oxidizing, flammable, infectious hospital waste, veterinary waste and any other type of waste, which does not fulfill the acceptance criteria determined in accordance with *Annex II*. These criteria must be derived from considerations pertaining to:

- ✓ protection of the surrounding environment (in particular groundwater and surface water);
- ✓ protection of the environmental protection systems (e.g. liners and leachate treatment systems);
- ✓ protection of the desired waste-stabilization processes within the landfill;
- ✓ protection against human-health hazards.

*“The composition, leachability, long-term behavior and general properties of a waste to be landfilled must be known as precisely as possible [...]” (Annex II, Article 2).*

Some waste property-based criteria may be: the requirements on knowledge of total composition, limitations on the amount of organic matter in the waste, requirements or limitations on the biodegradability of the organic waste components, limitations on the amount of specified, potentially harmful/hazardous components, limitations on the potential and expected leachability of specified, potentially harmful/hazardous components and ecotoxicology properties of the waste and the resulting leachate.

The present European Directive prescribes the protection of soil and water by means of a series of bottom liners. *Article 3, Annex I* states: *“Protection of soil, groundwater and surface water is to be achieved by the combination of a geological barrier and a bottom liner during the operational/active phase and by the combination of a geological barrier and a top liner during the passive phase/post closure.”* The landfill base is formed by a mineral layer which satisfies permeability and thickness requirements, according to the waste type filling the landfill:

- landfill for hazardous waste:  $K \leq 1,0 \cdot 10^{-9} m/s$ , thickness  $\geq 5 m$
- landfill for non-hazardous waste:  $K \leq 1,0 \cdot 10^{-9} m/s$ , thickness  $\geq 1 m$
- landfill for inert waste:  $K \leq 1,0 \cdot 10^{-7} m/s$ , thickness  $\geq 1 m$

Where the geological barrier does not fulfill these conditions, it can be completed artificially and reinforced by other means. Above the geological barrier, an artificial liner and a drainage layer thick more than  $0,5 m$  are required for hazardous and non-hazardous landfill.

A final top cover must be present in order to capture biogas production and collect run-off caused by rainfall. For non-hazardous waste the top cover is constituted by, starting from the bottom:

- gas drainage layer
- impermeable mineral layer
- drainage layer  $> 0,5 m$
- top soil cover  $< 1 m$

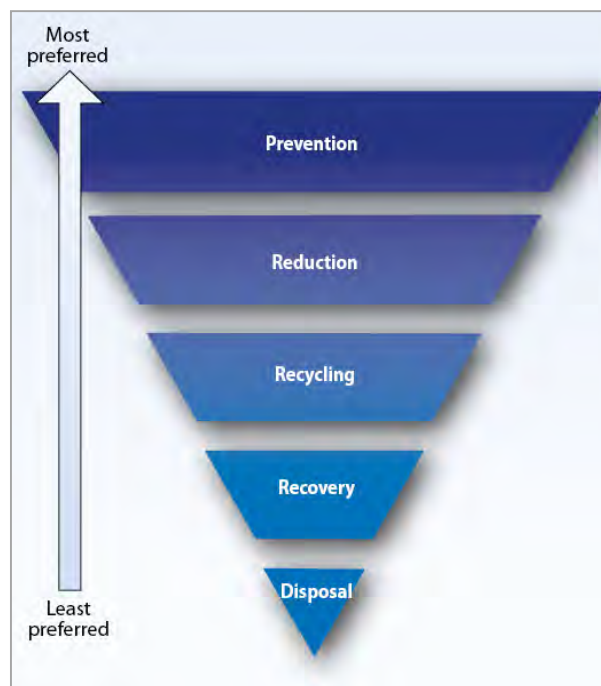
This European Directive has been complied by Italian legislation by means of the d. lgs. 36/2003.

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## 3.2 European Directive 2008/98/EC

The aim of this European Directive is the protection of the environment and the human health by the prevention or reduction of negative impact coming from waste production and management, by the reduction of global impact due to the use of natural resources and by improving its efficiency. The core of the present directive is the Waste Management Hierarchy, based on:

- Prevention
- Preparation for the reuse
- Recycling
- Energy recovery
- Disposal



**Figure 3.1 – Waste Management**

Each Member State of European Union shall comply this Hierarchy by adopting measures and actions and encourage the options that deliver the best overall environmental outcome

*Article 8* contains the Extended Producer Responsibility: “*In order to strengthen the re-use and the prevention, recycling and other recovery of waste, Member States may take legislative or non-legislative measures to ensure that any natural or legal person who professionally develops, manufactures, processes, treats, sells or imports products (producer of the product) has extended producer responsibility*”

More in general, responsibility for waste management is expressed in *Article 15*:

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*“Member States shall take the necessary measures to ensure that any original waste producer or other holder carries out the treatment of waste himself or has the treatment handled by a dealer or an establishment or undertaking which carries out waste treatment operations or arranged by a private or public waste collector [...]”*

This Directive deals moreover with hazardous waste (*Article 17, 18, 19, 20*), waste oils (*Article 21*) and bio-waste (*Article 22*).

This European Directive has been complied in Italy by means of d.lgs. 205/2010

### **3.3 The Italian Legislation: d.lgs. 36/2003**

The d.lgs. 36/03 implements in Italy the European Directive 1999/31/EC. It defines a landfill as *“...area adibita a smaltimento dei rifiuti mediante operazioni di deposito sul suolo o nel suolo, compresa la zona interna al luogo di produzione dei rifiuti adibita allo smaltimento dei medesimi da parte del produttore degli stessi, nonché qualsiasi area ove i rifiuti sono sottoposti a deposito temporaneo per più di un anno [...]”*. (*Article 2, Paragraph 1, letter g*).

Landfills are classified in three categories: (*Article 4*)

- ✓ Landfills for hazardous waste;
- ✓ Landfills for non-hazardous waste;
- ✓ Landfills for inert waste;

The present directive expresses the important concept of environmental sustainability, as the emissions level of a landfill acceptable for the environment, to be reached within a generation period.

The *Article 5, Paragraph 1* contains the objectives for the reduction of biodegradable organic matter. It states: *“Entro un anno dalla data di entrata in vigore del presente decreto, ciascuna regione elabora ed approva un apposito programma, per la riduzione dei rifiuti [...] allo scopo di raggiungere [...] i seguenti obiettivi: a) entro cinque anni dalla data di entrata in vigore del presente decreto i rifiuti urbani biodegradabili devono essere inferiori a 173 kg/anno per abitante; b) entro otto anni dalla data di entrata in vigore del presente decreto i rifiuti urbani biodegradabili devono essere inferiori a 115 kg/anno per abitante; c) entro quindici anni dalla data di entrata in vigore del presente decreto i rifiuti urbani biodegradabili devono essere inferiori a 81 kg/anno per abitante.”*

The *Article 5, Paragraph 2* carries on: *“Il programma [...] prevede il trattamento dei rifiuti e, in particolare, il riciclaggio, il trattamento aerobico o anaerobico, il recupero di materiali o energia.”*

This legislation excludes from landfilling the same materials left out by 1999/31/EC: *“a) rifiuti allo stato liquido, b) [...] Esplosivi [...], Comburenti [...] e Infiammabili [...] c) rifiuti che contengono una o più sostanze corrosive [...] in concentrazione totale maggiore o uguale a 1% d) rifiuti che contengono una o più sostanze corrosive [...] in concentrazione totale maggiore al 5% e) rifiuti sanitari pericolosi a rischio infettivo [...]”*

According to *Article 7, Paragraph 1*, waste can be disposed off in landfill only if previously treated.



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The Italian legislation provides the use of protection systems from leachate and biogas dispersion, adopting the same prescriptions of 1999/31/EC.



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## Chapter 4.

# LANDFILL

Landfill represents nowadays the most diffused method for waste disposal. (Erses et al., 2005; Vigneron et al., 2007). Two main landfill type exist: a pit type closer to groundwater and for which, due to a more difficult control, an eternal pumping is necessary; a mound type characterized by leachate migration by gravity out of landfill body. A proper landfill design must be based on the quantity and the quality of waste to be disposed off, on the physical characteristics of the site and on climatic conditions of the area of interest and it must fulfill the relative national regulations.

### 4.1 Landfill type

Traditionally, landfills have been thought of as a storage and containment systems, functioning primarily to entomb the waste. Recently, however, the focus of solid waste management has changed to regarding the landfill as a complex biological system capable of managing solid waste in a more proactive manner, acting to degrade the readily biodegradable material.

A new and promising trend in solid waste management is to operate the landfill as a bioreactor characterized by inputs (waste, rain and other infiltrations), chemical and physical reactions and outputs (leachate, biogas, other uncontrolled emissions). Bioreactor landfills are controlled systems 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.

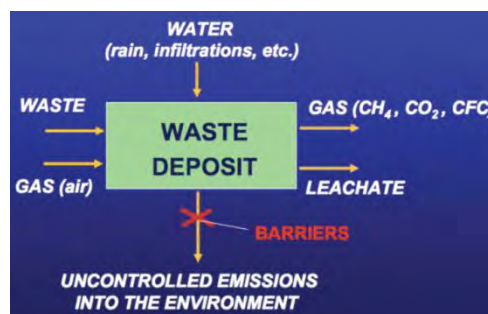


Figure 4.1 – Scheme of a landfill

The design of bioreactor landfills provides the flexibility in the location and duration of liquid and air injection, allowing for adjustment of pH, redox conditions and moisture content to create an environment conducive to microbial degradation and biological nitrogen removal. Thus, in a landfill, the active control of in situ reactions is generally restricted by the location and volume of injected liquid and air.

Liquid addition to landfills has many advantages associated with it. Leachate recirculation involves the collections and redistribution of leachate through the landfill. Moisture addition and movement

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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. Moisture is necessary to support the metabolic process, water provides the medium for chemical reactions and transport of nutrients and allows microorganisms to move about (Norbu et al., 2005). Unfortunately, achieving uniform liquid distribution is difficult because waste heterogeneities and differences in compaction within landfills create distribution challenges. Injected liquid will flow around areas with lower hydraulic conductivities and channel through the waste following preferential flow pathways formed by areas of higher hydraulic conductivities. (Berge et al., 2005).

In addition, the uniform injection of air throughout the waste is a problem due to waste heterogeneities and compaction. Air will take the path of least resistance, creating anoxic or anaerobic pockets within the waste mass.

Three main bioreactor landfill configurations exist:

- Anaerobic
- Aerobic
- Semi-aerobic

The anaerobic bioreactor landfill is a classic configuration characterized by the absence of oxygen inside waste body. It is naturally reached when waste are simply dumped away and no actions are taken for enhance air circulation and oxygen diffusion. Only moisture addition is practiced. Under these conditions, anaerobic degradation processes occur, with a consequent biogas production. As waste degradation is enhanced in anaerobic bioreactors and organic material is returned to the landfill via leachate recirculation, methane production rate increases and more volume of biogas is produced. (Berge et al., 2005). Anaerobic bioreactor landfills are more effective at degrading the solid waste than conventional anaerobic landfills; however, when compared to other types of bioreactor landfills, anaerobic systems tend to have lower temperatures and slower degradation rates. (Berge et al., 2005).

A disadvantage to operating the landfills as an anaerobic bioreactor is the accumulation of ammonia-nitrogen, which is continually returned to the landfill and it is not degraded due to the constant anaerobic conditions. An advantage is that air is not added and therefore the operational costs are less than those of an aerobic landfill system are.

The aerobic bioreactor landfill is characterized by a constant presence of oxygen inside it, ensured continuously by the entry of forced air. The aerobic degradation of organic compounds occurs, bringing to CO<sub>2</sub> and water production and it is faster than anaerobic one. The advantages of operating a landfill aerobically consist in the increased settlements, decreased metal mobility, reduced ex situ leachate treatment required and lower methane control costs. (Berge et al., 2005) Little methane is produced (if present), and this may be viewed as either an advantage or disadvantage, depending on whether methane collection and use as an energy source is desired or required. The aerobic processes generates a considerable amount of heat, leading to elevated temperatures in situ. The elevated temperatures increase evaporation, resulting in a significant loss of leachate and, therefore, there is less leachate to manage.

The semi-aerobic configuration is characterized by the presence of oxygen guaranteed by a natural convection process, due to a temperature gradient between the internal waste body and external environment.

The semi-aerobic landfill structure was developed in a joint study by Fukuoka University and Fukuoka City. A leachate-collecting pipe is set up at the floor of the landfill to remove leachate from the landfill, so that leachate will not remain where waste is deposited. Natural air is brought in from the open pit of the leachate collection pipe to the landfill layer, which promotes aerobic decomposition of waste. In other words, as the outlet of main collection pipe is always opened to air, fresh air is down in to, thereby introducing aerobic conditions around the pipes.

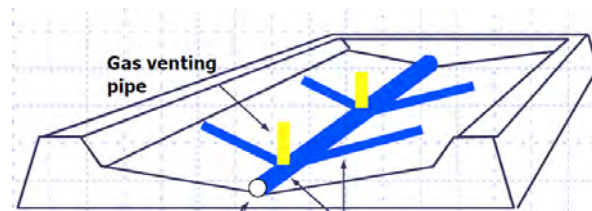


Figure 4.2 – Design of a gas venting pipe

This enables early stabilization of waste, prevents the generation of methane and greenhouse gases, which makes it effective technology in the prevention of global warming.

Generally, the air present in an aerobic environment transforms carbon within organic matter to carbon dioxide, sulfur, to sulfur ion and leads nitrogen to suffer nitrification/denitrification processes, reducing the generation of foul odor and flammable gas. Moreover, an aerobic environment increases the activity of microorganisms that decompose waste, accelerating the stabilization process.

On the other hand, in an anaerobic environment, where oxygen is not present, organic matter is transformed into volatile organic acids, such as acetic acid, and then become methane gas or carbon dioxide, while nitrogen and sulfur are transformed to ammonia, amine, hydrogen sulfide, and mercaptans, which emit foul odor and negatively affect the living environment of the surrounding area.

Faster degradation kinetics and higher temperatures characterizes a semi-aerobic landfill, in comparison with a traditional anaerobic one. Moreover lower biogas emissions and lower pollutants concentration in leachate produced, have been observed.

A graphical comparison between landfilling techniques could be presented as in **Figure 4.3** :

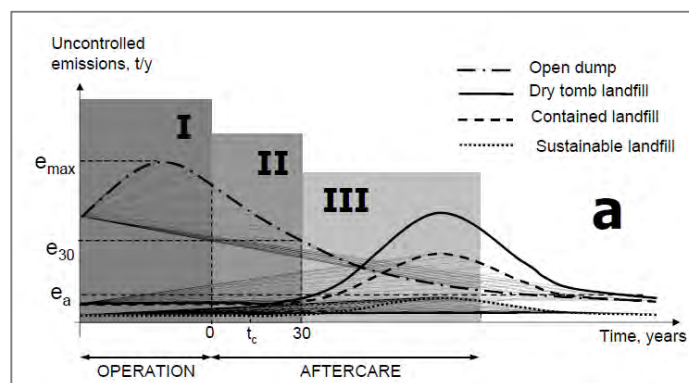


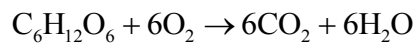
Figure 4.3 – Graphical representation of the different kind of waste disposals

A semi-aerobic landfill can be classified as a sustainable landfill because it speeds waste stabilization without translating pollution problems to future generations.

## 4.2 Degradation processes

Degradation processes occurring inside a landfill body are performed by microorganisms under specific environmental conditions.

During aerobic degradation proteins are degraded to amino acids, so to carbon dioxide, water, nitrate and sulfate, typical products of catabolism. Carbohydrates are converted into CO<sub>2</sub> and water while fats are hydrolyzed into fatty acids and glycerol. Then, through the production of Volatile Fatty Acids and alkali, they are further converted into more simple catabolites. The cellulose is degraded by means of extracellular enzymes to glucose, then used by bacteria and converted in CO<sub>2</sub> and H<sub>2</sub>O. The reaction describing the process is the following one:

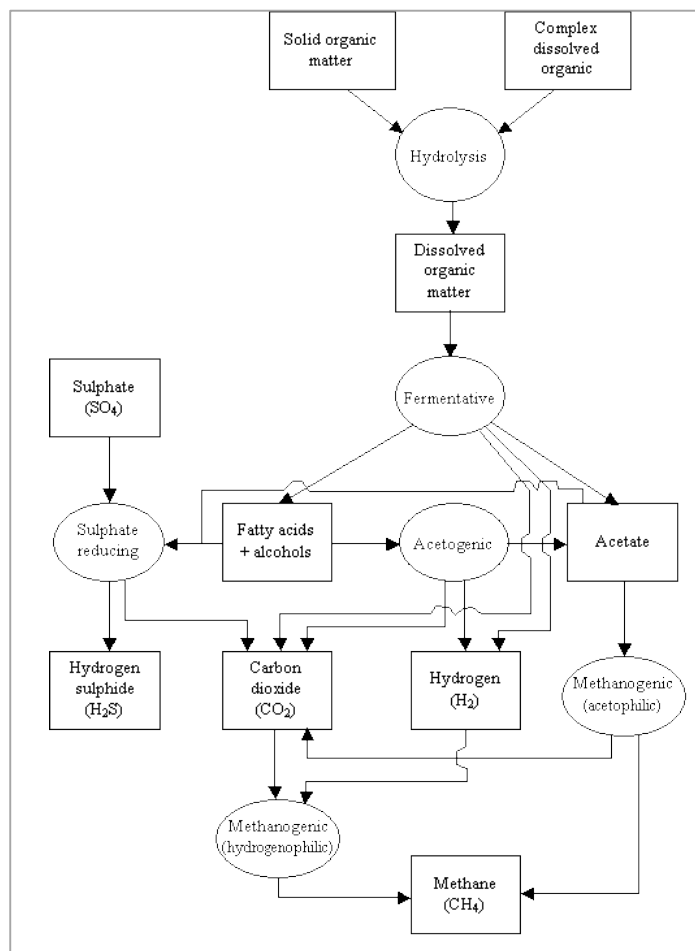


Aerobic degradation is characterized by the achievement of very high temperatures (60 – 70 °C)

□

Anaerobic processes are constituted by four step:

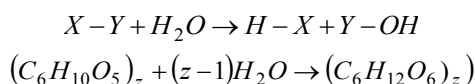
- Hydrolysis
- Acidogenic phase
- Acetogenic phase
- Methanogenic phase



**Figure 4.4 –  
Waste  
Management  
Hierarchy**

1) *Hydrolysis*. It is the reaction of a chemical compound by incorporation of water. In this process, complex particulate matter is converted into dissolved compounds with a lower molecular weight. The process requires the mediation of enzymes, such as hydrolases, excreted by fermentative bacteria. Proteins are degraded via (poly) peptides to amino acids, carbohydrates are transformed into soluble sugars (mono and disaccharides) and lipids are converted to long chain fatty acids and glycerin.

An example of a hydrolytic process is the following one:



2) *Acidogenesis*. Dissolved compounds, generated in the hydrolyzing step, are taken up in the cells of fermentative bacteria and after acidogenesis excreted as simple organic compounds like volatile fatty acids (VFA), alcohols and mineral compounds like CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, etc. Acidogenic fermentation is carried out by a diverse group of bacteria, most of which are obligate anaerobe. However, some are facultative and can also metabolize organic matter via the oxidative pathway. Few of them are listed in **Figure 4.5**:

<i>Products</i>	<i>Microorganism</i>
<i>Lactic acid</i>	<i>Bifidobacterium</i> <i>Lactobacillus</i> <i>Streptococcus</i>
<i>Alcohol</i>	<i>Aspergillus</i> <i>Leuconosotc</i> <i>Mucor</i> <i>Penicillium</i> <i>Saccharomyces</i>
<i>Butyric acid</i>	<i>Clostridium</i>
<i>Propionic acid</i>	<i>Propionibacterium</i> <i>Selenomonas</i> <i>Veillonella</i>
<i>Acidic acid</i>	<i>Clostridium</i> <i>Peptococcus</i> <i>Eubacterium</i>

**Figure 4.5 – Microorganism performing acidogenesis)**

3) *Acetogenesis*. The products of acidogenesis are converted into the final precursors for methane generation: acetatic acid, hydrogen and carbon dioxide. It is commonly an exothermic process but, if H<sub>2</sub> concentration is too high it becomes endothermic, the metabolism of other organic acids is not possible anymore and other organic acids accumulate.

4) *Methanogenesis*. During this step methane is produced by methanogenic bacteria, which can use both acetic acid and hydrogen as substrate

The reactions occurring during this phase are shown in the **Figure 4.6**:

<i>reactions</i>		
Acetat	→	CH <sub>4</sub> + CO <sub>2</sub>
4 H <sub>2</sub> +CO <sub>2</sub>	→	CH <sub>4</sub> + 2 H <sub>2</sub> O
4 HCOOH	→	CH <sub>4</sub> + 3 CO <sub>2</sub> + 2 H <sub>2</sub> O
4 CO + 2 H <sub>2</sub> O	→	CH <sub>4</sub> + 3 CO <sub>2</sub>
4 Methanol	→	3 CH <sub>4</sub> + CO <sub>2</sub> + 2 H <sub>2</sub> O
Methanol + H <sub>2</sub>	→	CH <sub>4</sub> + H <sub>2</sub> O
Ethanol + CO <sub>2</sub>	→	CH <sub>4</sub> + 2 Acetat
4 2-Propanol + CO <sub>2</sub>	→	CH <sub>4</sub> + 4 Aceton + 2 H <sub>2</sub> O

**Figure 4.6 – Reaction occurring during methanogenic phase**

The whole anaerobic degradation process occurs with a net water consumption and this is the reason why the moisture content has a primary role for maintaining the proper conditions for bacterial metabolism.

### 4.3 Sustainable landfill concept

There is no internationally accepted definition of sustainable landfill. With respect to landfills very often terms as stability, completion, end-point and threat to the environment are used together in discussions about sustainability. A selection of definition is:

- ✓ SWANA Stability Subcommittee (Barlaz, 2005): A landfill is functionally stable when the waste mass, post-closure, does not pose a threat to human health and the environment. This condition must be assessed in consideration of leachate quality and quantity; gas composition and production; cover, side-slope and liner design; site geology and hydrogeology; climate; potential receiving bodies, ecosystems and human exposure; and other factors deemed relevant on a site-specific basis.
- ✓ Anglo-Welsh Environment Agency (Environment Agency, 2005): Completion is defined as that point at which a landfill has stabilized physically, chemically and biologically to such a degree that the undisturbed contents of the site are unlikely to pose a pollution risk in the landfill's environmental setting. At completion, active aftercare pollution controls (e.g. leachate and gas management) and monitoring systems are no longer required.
- ✓ DHI (Hjelmar et al., 2005): Waste at a final storage quality provides a situation where active environmental protection measures at the landfill are no longer necessary and the leachate is acceptable in the surrounding environment.
- ✓ Technical University of Hamburg (Stegmann et al., 2003): The aftercare phase may end when the emission potential is that low that the actual emissions do not harm the environment.

Although the different definitions use slightly different wording, there seems to be a general consent that a sustainable landfill or a landfill for which it is considered safe to end the aftercare, is



a landfill that within a limited period of time reaches a state where the undisturbed contents no longer pose a threat to human health and the environment. At that point, often called completion, aftercare can be ended. It is important to notice that this is in accordance with the intention of European Legislation on waste.

The sustainable landfill management must regard its entire life, from waste disposal up to the post-closure period.

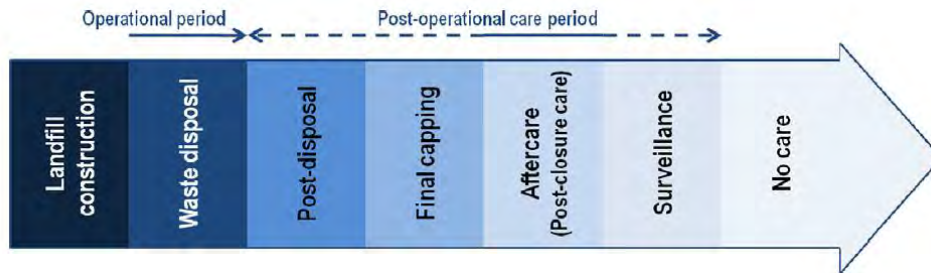


Figure 4.7 – Different management phases throughout the life-cycle of a MSW landfill. (Laner et al., 2012)

It is therefore possible to assert that a sustainable landfill has final emission lower than ordinary landfills, the emissions release occurs within a shorter period, it is possible to perform active control and prediction of emissions and, finally, its construction and maintenance is technically and economically feasible.

The mass balance is a useful tool for approaching the sustainable landfill (Cossu, 2005). With its model, it is possible to determine the effects of different alternatives for waste and landfill management. In order to comply with the sustainability concept, a landfill should reach an acceptable equilibrium with the environment within a generation time (30-40 years).

The mass balance usually considers the fate of substances entering and leaving a system in various ways.

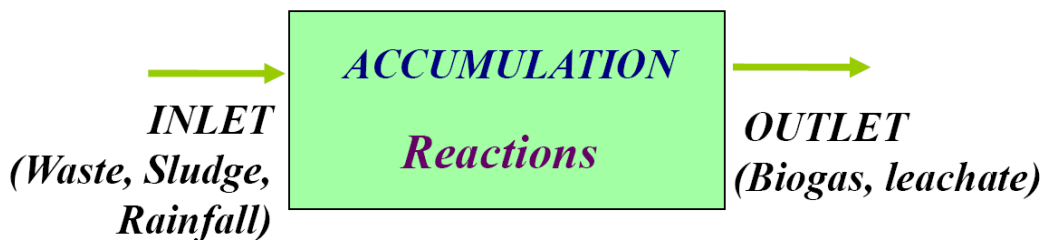


Figure 4.8 – The landfill mass flow scheme

The modeling approach to the mass balance tries to simplify the system with a Continuous Stirred Tank Reactor (CSTR), based on the assumption that the concentration of a given substance in the volume  $V$  of the landfill is always uniformly distributed in the space and, if a change in time of the concentration occurs instantaneously, the new concentration is distributed all over the system.

Considering the landfill as a reactor in which reactions and mass accumulation occur, the mass balance equation can be summarized with the **Equation 4.1**:

$$accumulation = input - output \pm reaction$$

Equation 4.1

Input in Equation XX represents the mass entering the volume from a variety of sources and different ways and it can be expressed as:

$$Input = \sum_{i=1}^n Q_i \cdot (S_s + x_s)_i \quad \text{Equation 4.2}$$

Where:

$n$  : represents the streams of waste

$i$  : represents the component of waste

$Q_i$  : is the mass flow of waste component  $i$  [t/y]

$x_s$  : is the concentration in the solid phase of  $i$ -component hardly biodegradable of waste [mg/kg<sub>waste</sub>]

$S_s$  : is the concentration in the solid phase of  $i$ -component readily biodegradable of waste [mg/kg<sub>waste</sub>]

Output in Equation XX is the mass leaving the landfill through biogas and leachate and it can be represented by the Equation XX:

$$Output = s_L \cdot q_L + s_G \cdot q_G \quad \text{Equation 4.3}$$

Where:

$q_{Lr}$  and  $q_{Gr}$  are the fractions of leachate and biogas that exit, expressed as [l/y] and [m<sup>3</sup>/y]

$s_L$  and  $s_G$  are the concentration of the contaminant in leachate and biogas, expressed as [mg/m<sup>3</sup>] and [mg/l]

Unfortunately, not all leachate and biogas exiting the landfill are collected but a fraction can escape and spread throughout the environment. For this reason it is possible to split the leachate and biogas exiting into two fractions: one that is collected and the other one which diffuses in an uncontrolled way, as shown in the following relations:

$$q_L = q_{Lr} + q_{Ld} \quad \text{and} \quad q_G = q_{Gr} + q_{Gd} \quad \text{Equation 4.4}$$

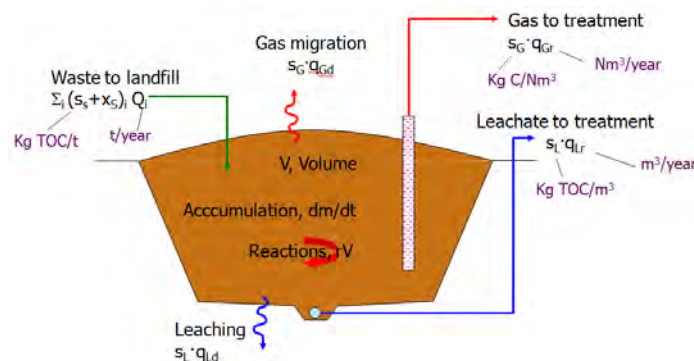


Figure 4.9 – Terms of the landfill mass balance

The accumulation term represents the increase of mass ( $m$ ) in the landfill body over time ( $t$ ), and it is expressed by means the **Equation 4.5**:

$$\text{Accumulation} = dm/dt \quad \text{Equation 4.5}$$

The accumulated mass in the landfill can undergo chemical and physical transformations and will either be mobilized and transferred to the liquid phase by means of natural lixiviation, or transformed into stable non-extractable compounds. The mobile cumulated fraction should be contained in order to avoid its uncontrolled spreading into the environment.

Reaction term is a way of leaving the system for the mass by chemical transformation into other substances. The simplest way for this process is a zero- or first-order kinetic.

$$\text{Reaction} = r \cdot V \quad \text{Equation 4.6}$$

Reaction can either occur in anaerobic environment producing biogas, or under aerobic conditions by means of air circulation inside waste body.


The total mass balance is presented in **Figure 4.10**:


***Accumulation = Inlet - Outlet - Degradation***


$$dm/dt = \sum_i (s_s + x_s)_i Q_i - s_L q_L - s_G q_G - rV - s_S Q_S$$


$$0 = \sum_i x_{Si} Q_i + \sum_i s_{Si} Q_i - (s_L q_{Lc} + s_L q_{Ld}) - (s_G q_{Gc} + s_G q_{Gd}) - rV - s_S Q_S$$

$$\underline{s_L q_{Ld} + s_G q_{Gd} + s_S Q_S} = K_X + \underline{\sum_i s_{Si} Q_i} - \underline{s_L q_{Lc} - s_G q_{Gc}} - rV$$

  
*Reduce*

  
*Reduce and contain*

  
*Reduce*

  
*Increase*

**Figure 4.10 – Mass balance**

Rearranging the mass balance equation bringing in the first half the diffused fraction of gas and leachate and leaving the rest in the second part of expression, it can be notice what action should be done in order to reduce as much as possible all uncontrolled emissions and design a landfill in a sustainable prospective.

First, reduce the amount of mass to bring to the landfill, either reducing the flow or improving its quality. Then it should increase the amount of leachate and biogas collected, avoiding its spreading into the environment, maximize the containment of the mobile accumulated fraction ( $dm/dt_{mob}$ ) and of the stabilization processes and finally maximize the increase of the reaction rate of the degradable compounds. This last action can be favored by aerobic conditions.

From a practical point of view, several options can be taken into consideration for a sustainable landfill management.

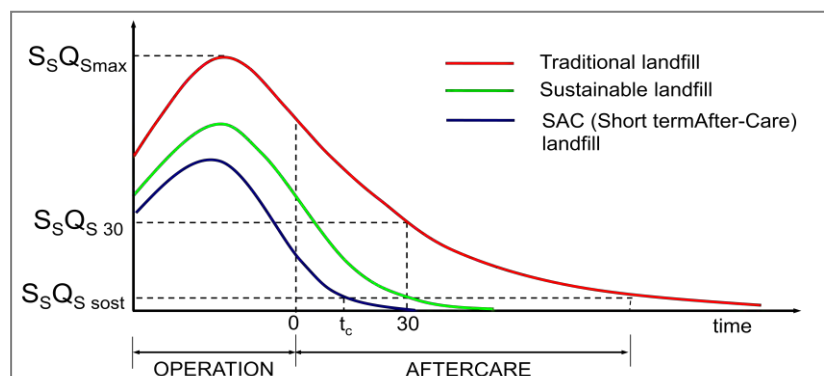
First, it is possible to act before the landfill disposal by reducing the amount of waste to be landfiling, improving the Reuse, Recovery and Recycle and by increasing the quality and stability of waste by means of mechanical and biological pre-treatments. However, in order to obtain a well-stabilized waste, the biological pre-treatments should last at least several months and this might be very expensive. It is possible, on the contrary, to act inside the landfill body, enhancing the stabilization process with either a natural or forced aeration and by increasing the amount of leachate produced moving away as much as possible all pollutants present. The leachate production increase can be obtained leaving landfill air-opened and allowing rainfall to enter waste body, but also by means of leachate recirculation, which moreover enhances the transfer of the contaminants into the liquid phase and provides a better diffusion of substrates and nutrients in the whole landfill body.

All these proposed several approaches to the environmental sustainability, based either on the modification of the characteristics of the waste to be landfilled or on the modification of the landfill construction and operation procedures, such as aerobic or semi-aerobic landfill, flushing and leachate recirculation, come together in the more general idea of multi-barrier landfill which provides the extension of the concept of barrier from the simple physical control of the emission to the waste characteristics and the landfill operation (Cossu, 1995).

According to the multi-barrier concept the landfill barriers are constituted by:

- Quality of waste: a well-stabilized waste produces very low pollutants concentration ;
- Quality of the site: the geological and hydrogeological situation has to ensure safety in the long term against possible emissions;
- Landfill concept: semi-aerobic, aerobic, aerated landfill;
- Landfill drainage & liner

A sustainable management of a landfill aims to reduce the duration of emissions which, on the other hand, may last centuries for a traditional contained landfill, as shown in the **Figure 4.11**:



**Figure 4.11 – Long-term landfill accumulation**

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## Chapter 5.

# THE ROLE OF NITROGEN INSIDE A LANDFILL

Nitrogen is one of the main component present in landfill leachate, coming from the nitrogen content of the waste (mainly proteins contained in yard wastes and food wastes). As the proteins are hydrolyzed and fermented by microorganisms, ammonia nitrogen is produced (ammonification process). Its concentration depends on the rate of solubilization and/or leaching from the waste. It constitutes an important nutrient for metabolic processes but if too abundant, it may cause eutrophication problems, so its removal is necessary.

During last year's a new bioreactor concept for landfill is establishing, characterized by the leachate recirculation (Bilgili et al., 201Sanchez), which causes nevertheless an increase of ammonia concentration, implying so a long-term impact problem.

In landfill leachate, the most of the ammonia-nitrogen species is in the form of the ammonium ion ( $\text{NH}_4^+$ ), because pH levels are generally less than 8,0 (Berge et al., 2005). Dissolved unionized ammonia (predominant at pH higher than 10) is more toxic to anaerobic degradation processes than ammonium ion, but it should not be present in significant concentrations in a landfill, which pH never reaches high values. **Figure 5.1** provides the distribution of ammonia and ammonium as function of pH.

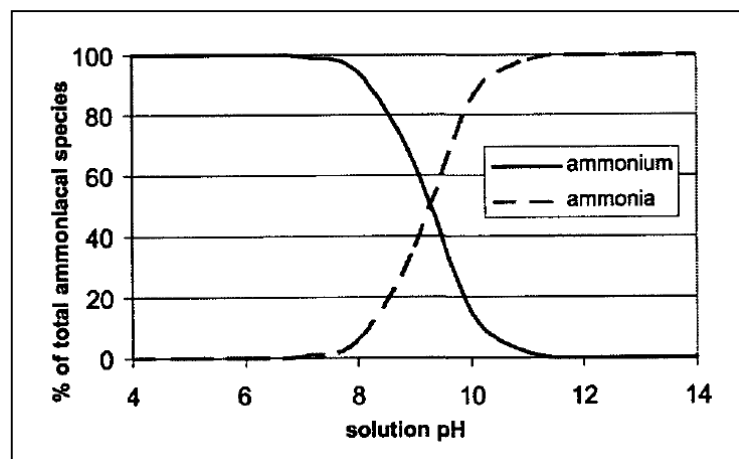
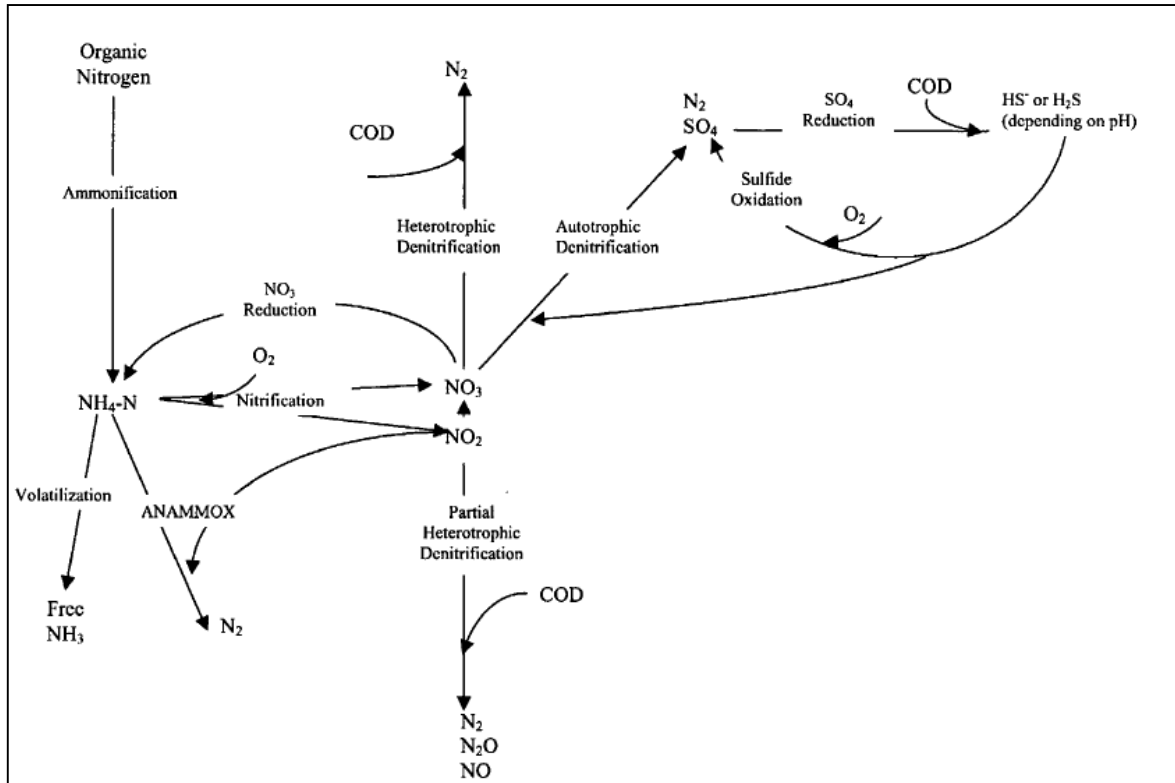


Figure 5.1 – Nitrogen form in solution at 25°C at various pH levels

### 5.1 Nitrogen involving processes

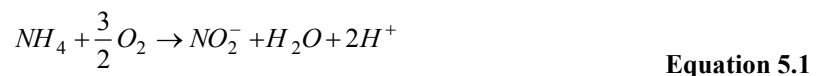
The heterogeneous nature of solid waste complicates the nitrogen cycle in bioreactor landfills, thus, within landfill, there may be many nitrogen transformation processes occurring simultaneously.

Processes commonly found in wastewater treatment plants and in soils, such as ammonification, sorption, volatilization, nitrification, denitrification and anaerobic ammonium oxidation (ANAMMOX), may all occur in bioreactor landfills, as shown in **Figure 5.2**.



**Fig. 5.2 – Potential pathways of nitrogen transformation and/or removal in bioreactor landfill (Berge et al., 2005)**

The two main reaction involving nitrogen compounds are nitrification and denitrification. Nitrification is a two-step aerobic process in which ammonia-nitrogen/ammonium is microbially oxidized to nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) via obligate aerobe, autotrophic, chemolithotrophic microorganisms.



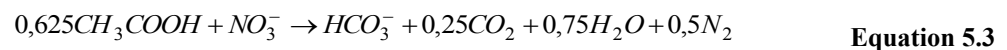
Because nitrification is an aerobic process, it is almost nonexistent in conventional landfills and in bioreactor landfills in which air is not added. In those systems nitrification is restricted in the upper parts of a landfill, where air may infiltrate.

It is performed by several kind of autotrophic bacteria: among them, the most easily cultivable are Nitrosomonas and Nitrobacter, with the growth rate of Nitrosomonas considered as the rate-limiting step and thus the most critical from a design perspective. Because ammonia oxidation is the rate-limiting step, it is often used as the overall rate of nitrification. (Berge et al., 2005). Autotrophic microorganism can use inorganic compounds as electron donor and acceptor and nitrifiers, in

particular, obtain carbon from dissolved CO<sub>2</sub> and energy from oxidation of ammonia and nitrite. Nitrification process consume alkalinity and pH decreases, but nitrifying microorganisms are quite sensitive to pH, which should remain in the range 6-9. Due to the heterogeneity of waste mass within a landfill, oxygen may become limiting for nitrifiers in areas containing large amount of organic carbon due to the competition with heterotrophs. Under oxygen-limiting conditions, autotrophic nitrification may produce nitric (NO) and nitrous oxide (N<sub>2</sub>O), that are potent greenhouse gases. Due to this fact, it is suspected that in situ nitrification may be optimized when operated in landfills containing older waste, with a low organic carbon content.

Nitrification process results sensible also to temperature conditions. Sanchez-Monedero et al., (2001) reported that nitrification did not occur when temperature rose above 40°C, while Juteau et al., (2004), found that nitrification did not occur under thermophilic conditions.

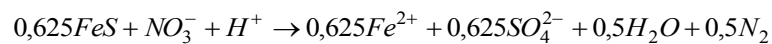
Denitrification is a process producing nitrogen gas (N<sub>2</sub>) starting from nitrate (NO<sub>3</sub><sup>-</sup>). It is usually an heterotrophic process occurring when sufficient carbon source, used as electron donor, is available: If not, partial denitrification may occur, which may lead to the production of harmful intermediates (N<sub>2</sub>O and NO). (Chen et al., 2009). Typically, in situ denitrification occurs in anoxic bioreactor landfills, but, due to the potential presence of anoxic pockets in aerobic bioreactor landfills, it may also occur in aerobic landfills. It is expressed by the **Equation 5.3**



Typically, denitrifying bacteria are heterotrophic facultative anaerobes, 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

In contrast, autotrophic denitrification will occur in environments with low organic carbon source and the presence of inorganic sulfur material, used as electron donor. The nitrate removal mechanism produces sulphate, which concentration increase may have an adverse effect on methane production rates due to the competition with sulfidogens.

**Equation 5.4** and **Equation 5.5** represents an example of autotrophic denitrification. (Vigneron et al., 2007; Chen et al., 2009; Sun et al., 2012)



**Equation 5.4**

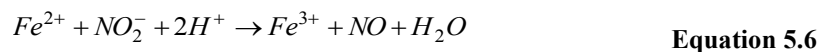


**Equation 5.5**

During the autotrophic denitrification the nitrate decrease is usually coupled with an increase in sulfate concentration. (Berge et al., 2006).

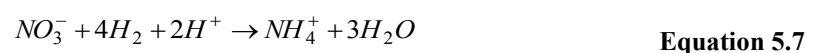
Vigneron et al., (2007) considered denitrification processes by increasing nitrate and nitrite concentration through their injection inside the bioreactor, during both the acidogenic and methanogenic phase. The results obtained can be summarized in the following points:

- ✓ Denitrification occurring during the acidogenic phase, when easily biodegradable carbon was detected as VFA, was predominantly heterotrophic, while nitrate injected during the last methanogenic phase where converted to nitrogen gas through a autotrophic denitrification, with a consequent sulphate production, according to the Equation 3;
- ✓ Nitrate injection during the acidogenic phases delays the methane production;
- ✓ The accumulation of intermediates (N<sub>2</sub>O, NO) after nitrate injection during acidogenic phase is very low;
- ✓ NO accumulation instead occurs after nitrite injection, which can inhibit the entire waste degradation; consequently the recirculation of a nitrified leachate could inhibit the denitrification process. NO is an intermediate of denitrification, but its accumulation is often linked to a chemical denitrification. A chemical reaction which may occur is expressed by **Equation 5.6**:



In this case nitrate is reduced by iron, which instead is oxidized;

- ✓ The presence of H<sub>2</sub>S inside waste body can inhibit the N<sub>2</sub> production, enhancing instead the DNRA (Dissimilatory Nitrate Reduction to Ammonium) process, due to which nitrogen is converted into NH<sub>4</sub><sup>+</sup> and it is not released outside the landfill:



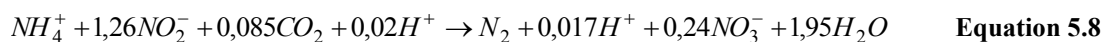
The presence of H<sub>2</sub>S may have caused a decrease of the oxido-reduction potential ORP, resulting in the incapacity of nitrate conversion by denitrification.

N<sub>2</sub> concentration can decrease also due to its assimilation by microorganism (nitrogen fixation). The DNRA process predominate in anaerobic sludge digesters, anoxic sediments and the rumen, all of which are carbon-rich, nitrate poor environment (Price et al., 2003).

The autotrophic denitrification based on sulfur compounds has been receiving more attention recently (Oh et al., 2001). The sulfur acts as an electron donor, while nitrogen is reduced. When both sulfur and organic matter are present, mixotrophic conditions occurs and under these conditions a better nitrogen and TOC removal is performed. But, as said above, if the sulfur compounds concentration results too high, it causes the N<sub>2</sub> inhibition, enhancing instead the DNRA process.

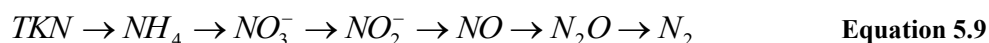


Another important process involving nitrogen compounds which may occur inside a landfill, is the ANAMMOX process (Anaerobic Ammonia Oxidation). It constitutes an important contribution for nitrogen removal from solid matrix of waste (Valencia et al., 2011). The development of ANAMMOX bacteria occurs under anaerobic conditions but can be enhanced by injection of small quantity of oxygen. In fact, ANAMMOX bacteria need nitrite ( $\text{NO}_2^-$ ) for their development, and these nitrite can derive from an incomplete nitrification process due to limited oxygen concentration.



Being the growth rates of the ANAMMOX bacteria extremely slow, this process is generally favorable in environments in which retention time is long and operation is stable.

In order to close the nitrogen cycle, it is important to investigate some sub-products of nitrification and denitrification reactions. It is well known in fact that, starting from hydrolytic process of organic nitrogen, the following series of composts occurs:



Of particular interest results the production of NO and  $\text{N}_2\text{O}$ .

Nitrous oxide  $\text{N}_2\text{O}$  is a persistent trace gas in the atmosphere with a particular high global warming potential (GWP). Its mean life-time in the atmosphere is estimated to be 114 years and its 100 year global warming potential is about 298 times that of  $\text{CO}_2$  (Harborth et al., 2013; Sun et al., 2013). Due to its long residence time into atmosphere it can react with ozone present. In fact it is mainly removed from the atmosphere by photochemical reactions in the stratosphere and thus its emission is currently the most important ozone-depleting emission. (Ravishankara et al., 2009). Its global average concentration reached a level of 323 ppb in 2010, which is 20% above the pre-industrial concentration (WMO, 2011).

The waste management sector is a large global anthropogenic source for GHG emissions, about 2,8 % of the global anthropogenic emissions based on 100-year GWP (IPCC, 2007).  $\text{N}_2\text{O}$  fluxes have been reported relatively higher from MSW landfills. At the Ammassuo landfill in Finland,  $\text{N}_2\text{O}$  fluxes were found to be at least 1-2 order of magnitude higher than the maximum  $\text{N}_2\text{O}$  fluxes from northern European agricultural soils and boreal forests (Rinne et al., 2005). Nonetheless, the contribution of  $\text{N}_2\text{O}$  to the total greenhouse warming potential of MSW landfill emissions is rather small (about 3%). Moreover its emissions from MSW landfills are typically characterized by a large spatial variability due to the heterogeneous nature of landfill sites (Zhang et al., 2008).

Nitrous oxide is a common by-product of nitrification and an intermediate product of denitrification process (Zhang et al., 2009); Its production is also caused by other degradation process of nitrogen compounds, such as Anammox process, autotrophic denitrification and DNRA.

The common heterotrophic denitrification process, if combined with the addition of nitrate/nitrite or with a leachate recirculation characterized by a low ratio C/N, can lead to production of nitrous nitrogen  $\text{N}_2\text{O}$ , as intermediate of denitrification process itself (Chen et al., 2009).

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It is at this point necessary to understand what are the most influencing factors for N<sub>2</sub>O production. Sun et al., (2013) asserts that the presence of N<sub>2</sub>O inside leachate depends from:

- ✓ organic substance content: low content of organic substance may make incomplete the denitrification process bringing to the store of N<sub>2</sub>O
- ✓ presence of oxygen: oxygen shortage makes incomplete nitrification process bringing to N<sub>2</sub>O production

So it is possible to conclude that the recirculation of a fresh leachate can inhibit or reduce the production of N<sub>2</sub>O.

Another important nitrogen compound to evaluate is NO which constitute an intermediate of the denitrification process. Generally its production is favorite by a low pH and its storage inhibits methanogenic processes more than N<sub>2</sub>O and NO<sub>3</sub>.

Vigneron et al., (2007) individuate another reason for N<sub>2</sub>O and NO accumulation: when nitrate/nitrite are injected inside the waste body during the methanogenic phase, not being easily biodegradable organic substance (VFA), the complete denitrification is delayed and its intermediates accumulate.

## 5.2 Nitrogen mass balance

The nitrogen mass balance can be developed starting from the following differential equation:

$$V \frac{dN}{dT} = -k_L Q_L N - k_R V N \quad \text{Equation 5.10}$$

Where:

$V$  is the volume occupied by waste

$N$  is the TKN of solid waste

$k_L$  is the kinetic constant expressing the relation between the nitrogen removed by means of leachate

$Q_L$  is the produced leachate flow

$k_R$  is the kinetic constant expressing the relation between transformed nitrogen and TKN of solid waste

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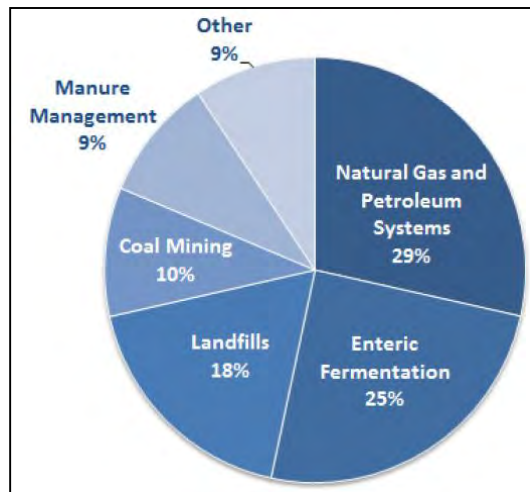
## Chapter 6.

### THE LANDFILL BIOGAS

A major part of municipal solid waste disposed of in landfills consists of organic carbon, which is partly microbiologically degradable resulting in greenhouse gas emissions such as methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). Usually 90% of the carbon degraded in a bioreactor landfill is converted into landfill gas, while only 10% remains in the dissolved organic load of the leachate. CH<sub>4</sub> is more powerful greenhouse gas than CO<sub>2</sub>. Over a period of 100 years, the global warming potential for CH<sub>4</sub> is 25 because of its stronger molar absorption coefficient for infrared radiation and longer atmospheric residence time (12±3 years). (Kumar et al., 2014).

The global atmospheric concentration of CH<sub>4</sub> has increased from a pre-industrial value of about 715 up to 1.732 ppb in the early 1990s, and was 1.774 ppb in 2005 (Solomon et al., 2007).

Worldwide, CH<sub>4</sub> emission from the waste sector is about 18% of the global anthropogenic CH<sub>4</sub> emission, with landfills being the main source estimated to release between 35 and 69 Tg CH<sub>4</sub> per year to the atmosphere. (Solomon et al., 2007).



**Figure 6.1: Methane emissions by source.**  
[www.epa.gov/climatechange/ghgemissions/usinventoryreport.html](http://www.epa.gov/climatechange/ghgemissions/usinventoryreport.html)

Biogas produced in landfills is the result of physical, chemical and microbial processes that occur in the waste. These processes are sensitive to their environment, and, therefore, there are a number of factors affecting the microbial population and thus the biogas generation. (Aguilar-Virgen et al., 2014).

Cellulose is the most important carbon source for methanogenesis in landfills, however it is not an easily biodegradable material under anaerobic conditions. (Erses et al., 2008). In fact, cellulose and hemicellulose, whose half-lives are about 15 years, contribute to 90% of total methane produced.

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The GHGs generated by the landfills are directly emitted to the atmosphere thereby creating the problems of global warming, risk of fire and explosion in landfills and sanitation for locals. When a waste is subjected to open dumping, a number of problems like:

- ✓ direct emission of GHGs to the atmosphere
- ✓ significant loss of valuable nutrients (N, P and K) from the waste
- ✓ unrecovered possible kind of energy source
- ✓ diminishing the possibility of recycling the recyclable material
- ✓ pollution of ground water by seepage of leachate
- ✓ sanitary and health hazards in the surrounding area

are created, due to natural and long term decay of the wastes.

These problems can be solved by using Sanitary or Engineered Landfills that can efficiently recover biogas.

Harnessing the power of landfill gas (LFG) energy provides environmental and economic benefits to landfills, energy users, and the community. In particular, LFG energy projects:

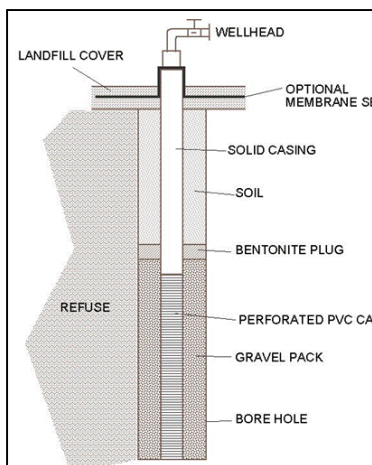
- ✓ Reduce emissions of greenhouse gases that contribute to global climate change.
- ✓ Offset the use of non-renewable resources, such as coal, oil, and natural gas.
- ✓ Help improve local air quality.
- ✓ Provide revenues for landfills and energy cost savings for users of LFG energy.
- ✓ Create jobs and economic benefits for communities and businesses.

Landfill owners, energy service providers, businesses, state agencies, local governments, communities, and other stakeholders interested in developing this valuable resource can work together to develop successful LFG energy projects. The EPA Landfill Methane Outreach Program (LMOP) encourages and facilitates the development of environmentally and economically sound LFG energy projects by partnering with stakeholders and providing a variety of information, tools, and services. It is a voluntary assistance program that helps to reduce methane emissions from landfills by encouraging the recovery and beneficial use of landfill gas as an energy resource.

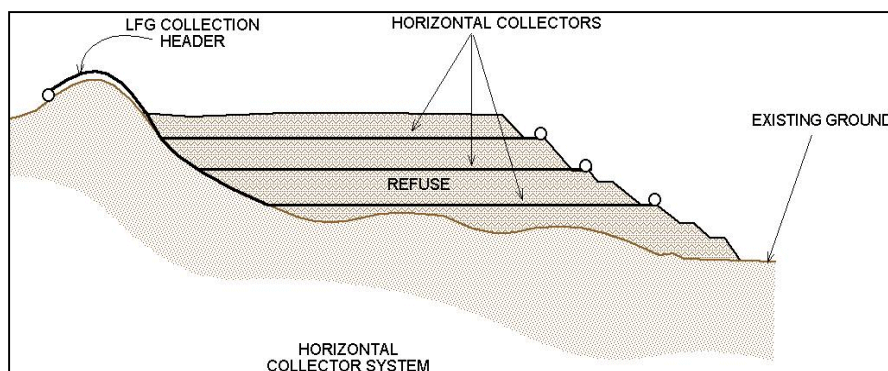
By joining LMOP, companies, state agencies, organizations, landfills and communities gain access to a vast network of industry experts and practitioners, as well as to various technical and marketing resources that can help with LFG energy project development.

LFG contain methane that can be captured and use to fuel power plants, manufacturing facilities, vehicles, homes and more.

The most common method of LFG collection involves drilling vertical wells in the waste and connecting those wellheads to lateral piping that transports the gas to a collection header using a blower or vacuum induction system. Another type of LFG collection system uses horizontal piping laid in trenches in the waste. These systems are useful in deeper landfills and in areas of active filling. Some collection systems involve a combination of vertical wells and horizontal collectors.



**Figure 6.2: Typical LFG extraction well**



**Figure 6.3: Typical LFG collection system with Horizontal Trenches**

After collection, LFG can either be flared or used in an energy recovery system to combust the methane and other trace contaminants. Using LFG in an energy recovery system usually requires some treatment of the LFG to remove excess moisture, particulates, and other impurities. The type and extent of treatment depends on site-specific LFG characteristics and the type of energy recovery system employed. Boilers and most internal combustion engines generally require minimal treatment (e.g., dehumidification, particulate filtration, and compression). Some internal combustion engines and many gas turbine and microturbine applications also require siloxane removal using adsorption beds after the dehumidification step.

The majority (more than 70 percent) of the LFG energy projects that generate electricity do so by combusting the LFG in internal combustion engines. The three most commonly used technologies, internal combustion engines, gas turbines, and microturbines, can accommodate a wide range of project sizes. Gas turbines are more likely to be used for large projects, usually 5 MW or larger. Internal combustion engines are well-suited for 800 kW to 3 MW projects, but multiple units can be used together for projects larger than 3 MW. Microturbines, as their name suggests, are much smaller than turbines, with a single unit having between 30 and 250 kW in capacity, and thus are generally used for projects smaller than 1 MW. Small internal combustion engines are also available for projects in this size range. An LFG energy project may use multiple units to accommodate a landfill's specific gas flow over time. For example, a project might have three internal combustion engines, two gas turbines, or an array of 10 microturbines, depending on gas flow and energy needs.

LFG energy CHP applications, also known as cogeneration projects, provide greater overall energy efficiency and are growing in number. In addition to producing electricity, these projects recover and beneficially use the heat from the unit combusting the LFG. LFG energy CHP projects can use internal combustion engine, gas turbine, or microturbine technologies.

Less common LFG electricity generation technologies include a few boiler/steam turbine applications, in which LFG is combusted in a large boiler to generate steam used by the turbine to create electricity. A few combined cycle applications have also been implemented. These combine a gas turbine that combusts the LFG with a steam turbine that uses steam generated from the gas

turbine's exhaust to create electricity. Boiler/steam turbine and combined cycle applications tend to be larger in scale than the majority of LFG electricity projects that use internal combustion engines.

Direct use of LFG is often a cost-effective option when a facility that could use LFG as a fuel in its combustion or heating equipment is located within approximately five miles of a landfill; however distances of 10 miles or more can also be economically feasible in some situations.

The creation of pipeline-quality, or high-Btu, gas from LFG is becoming more prevalent. In this process, LFG is cleaned and purified until it is at the quality that can be directly injected into a natural gas pipeline. Also growing in popularity are projects in which LFG provides heat for processes that create alternative fuels (e.g., biodiesel or ethanol). In some cases, LFG is directly used as feedstock for an alternative fuel (e.g., compressed natural gas [CNG], liquefied natural gas [LNG], or methanol). Only a handful of these projects are currently operational, but several more are in the construction or planning stages. LFG has also found a home in a few greenhouse operations.

## 6.1 Biogas production model

A mathematical model useful for predicting the biogas production based on the kinetic model comes from Gompertz Growth Equation. This model has sigmoid shape with a clear inflection point. It was used to determine the cumulative volume of biogas produced from the bioreactors according the **Equation 6.1**: (Lay et al., 1998; Sandip et al., 2012).

$$BG = BGP \cdot \exp \left\{ - \exp \left[ \frac{R_m \cdot e}{BGP} (\lambda - t) + 1 \right] \right\} \quad \text{Equation 6.1}$$

Where:

$BG$  is the cumulative biogas yield  $\left[ \frac{ml}{gVS} \right]$

$t$  is the digestion time  $[d]$

$BGP$  is the biogas yield potential  $\left[ \frac{ml}{gVS} \right]$

$R_m$  is maximal daily biogas yield  $\left[ \frac{ml}{gVS \cdot d} \right]$

$\lambda$  is bacteria growth lag time  $[d]$

$e$  is mathematical constant (= 2,718)

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## Chapter 7.

### LANDFILL S.An.A.

The landfill S.AN.A. is characterized by three management phases. The first one semi-aerobic, in which oxygen injection and diffusion in waste body are guaranteed by means convective circulation of air due to a thermal gradient between external environment and waste body, the second one anaerobic, during which biogas production occurs and, finally, a third one characterized by either forced or convective injection of air. Each one of these three phases has a well-defined role.

During semi-aerobic phase, degradation of biodegradable organic matter is enhanced, so the production of volatile fatty acids is reduced and the acidogenic phase is shorted during the following anaerobic phase; during anaerobic phase biogas production is enhanced for energetic aims; in the third and last phase the most hardly degradable organic substances are degraded, left from the first two phases.

The aim of this innovative landfill model consists in reducing, as much as possible, the post-operational phase, enhancing the degradation of organic matter under anaerobic conditions and increasing the biogas production during the anaerobic phase for a energy use.

Due to what just said, landfill S.AN.A. corresponds to a sustainable management model. The most innovative aspect is represented by the first semi-aerobic phase.

In the Figure xx, one can notice that the polluting load results minimum in the case of a semi-aerobic landfill.

#### 7.1 State of the art

Several laboratory practices have been performed during the last two decades for assessing the influence of aeration and waste management on degradation rate and chemical parameters of municipal solid waste.

Lay et al., (1998) utilized a laboratory-scale landfill bioreactor for understanding the developments of bacteria population and methanogenic activity within a waste mass. The examination revealed that the methane production rate of the columns incubated with leachate recycling was greater than that of without leachate recycling.

O'Keefe et al., (2000) studied the influence of aeration on treatment of municipal solid waste in simulated landfill cells and assessed aeration performed on landfill reactor resulted in acceptable volatile solids reduction

Sekmann et al., (2011) investigated the effects of aeration rate on solid waste decomposition in aerobic, leachate recirculated landfill. The results showed that aeration accelerates the waste stabilization rate in landfilling.

Cossu et al., (2003) carried out a laboratory test using six bioreactors simulating different landfill concept. The degradation rates resulted higher under aerobic conditions while the traditional anaerobic landfill showed the highest level of emissions, with high concentration of BOD, COD and

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ammonia; moreover biogas production was delayed by the initial acid phase of biodegradation. The combination of pre-treatment, semi-aerobic conditions and flushing seemed to optimize the advantages presented by the different individual option, achieving a more marked oxidation of organics and nitrogen.

Cossu et al., (2005) applied a mass balance model in a small scale using bioreactor columns, managed in aerobic, semi-aerobic and anaerobic conditions. The carbon and nitrogen removal were significantly influenced by management method. Aerobic and semi-aerobic increased degradation rate of waste.

Sandip et al., (2012) investigated the process to increase methane production rate and reduce the biostabilisation time for municipal solid waste in simulated anaerobic bioreactor landfill. One among the parameters considered was the aeration rate. The test showed that aerobic process reduced the risk of inhibition due to volatile fatty acids accumulation in early stage of anaerobic degradation. It enhanced the separation of acid formation phase and methane fermentation phase, reduced the acid production time, optimized the microorganism's growth environment and accelerated the stabilization rate of solid waste.

Zhang et al., (2012) studied the role of aerobic pretreatment prior to landfilling. The results indicated a reduction of the degradation time and a lower COD of the generated leachate. The degradation rate constant  $k$  in the aerobic stage was higher than that in the anaerobic stage.

Sponza et al., (2005) assessed the effects of shredding of wastes on treatment of municipal solid wastes in simulated anaerobic reactors. The size reduction of the particles and the resulting enlargement of the available specific surface can support the biological processes, so the shredding resulted an effective method of improving waste degradation, leading to a higher pH value of leachate produced. On the contrary, compaction did not result a very suitable method for waste degradation, since long stabilization time was required.

Consequently, starting from literature data seen so far, one can assess that the benefits associated with leachate recirculation and/or landfill aeration have been well documented.

The S.An.A. test aims to conjugate the already proved advantages of leachate recirculation and aeration on waste degradation and methane production, and study the different modality of air injection in order to assess the most effective and viable one also from an economic point of view.

## **7.2 Experimental Survey**

In the following paragraphs, it will be presented the experimental procedure developed according to the aims of the present research.

The raw material used for the experimental survey was constituted by 200 kg of urban solid waste. It was characterized by a large fraction of putrescible material, then plastic and cellulosic material, finally by a small fraction of metal and inert.

Waste have been sieved through the sieve 80 mm and only the undersieve was considered. The remained waste, effectively used for the research were 107,6 kg.





**Figure 7.1 – Raw Urban Solid Waste used for experimental survey**

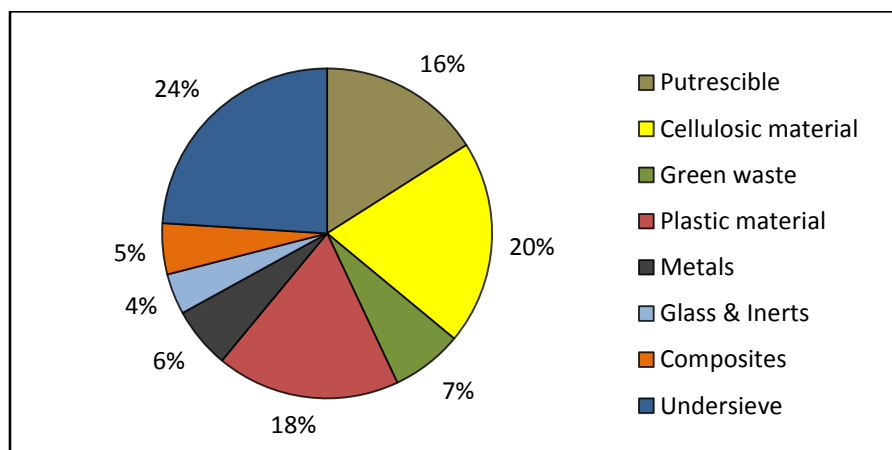


**Figure 7.2 –Sieve #80 mm**



**Figure 7.3 –Sieved Urban Solid Waste used for experimental survey**

A product analysis was performed on the sieved material and the results are shown in the **Figure 7.4:**



**Figure 7.4 – Product analysis of waste material used for S.An.A. test**

The bioreactor was constructed using six 24-cm-diameter polymethyl methacrylate (Plexiglas®) pipe with a total height of 106 cm, loaded with urban solid waste. The bulk density of the compacted waste was 0,5 t/m<sup>3</sup>.

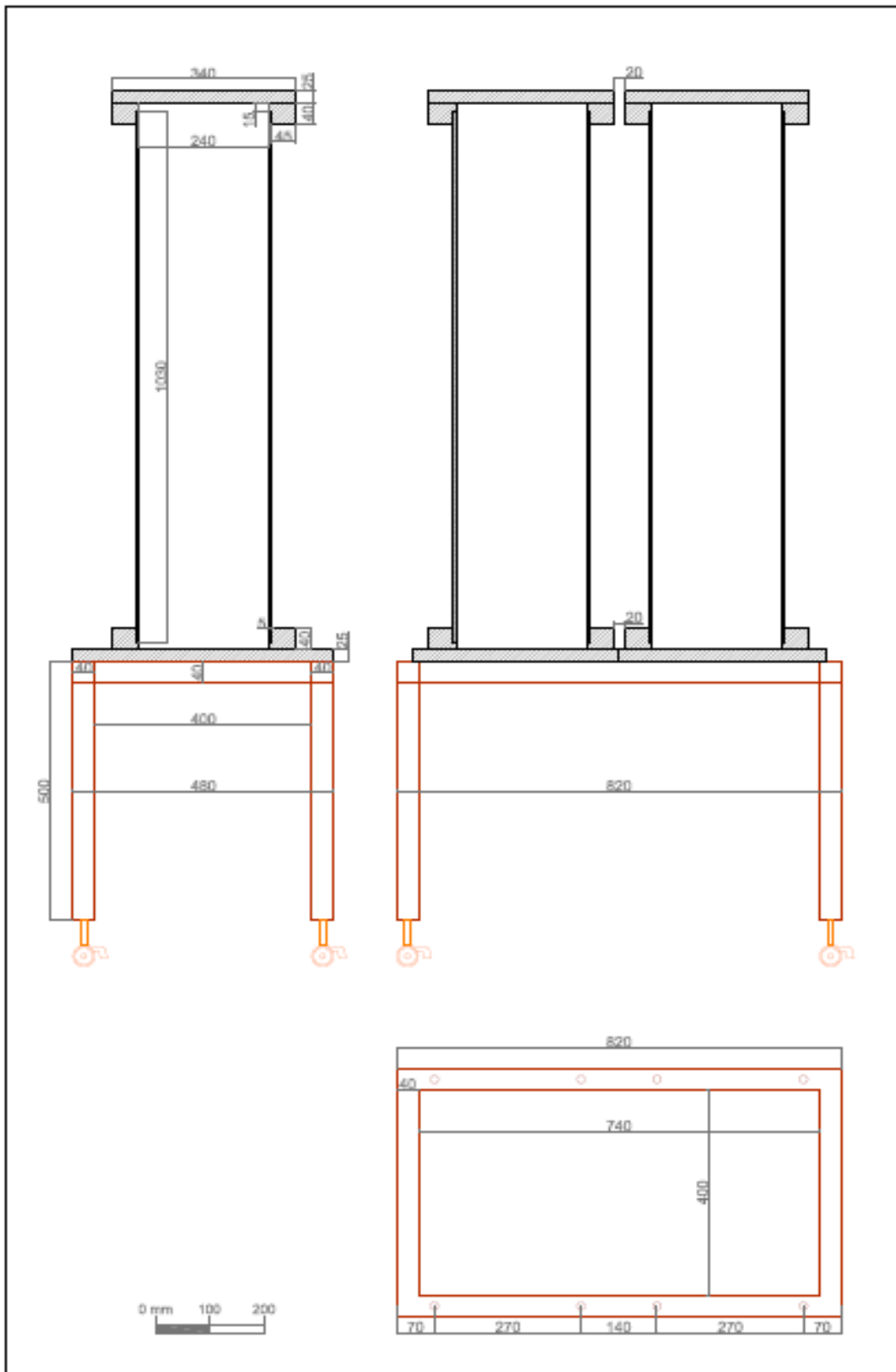


Figure 7.5 –Design characteristics of columns

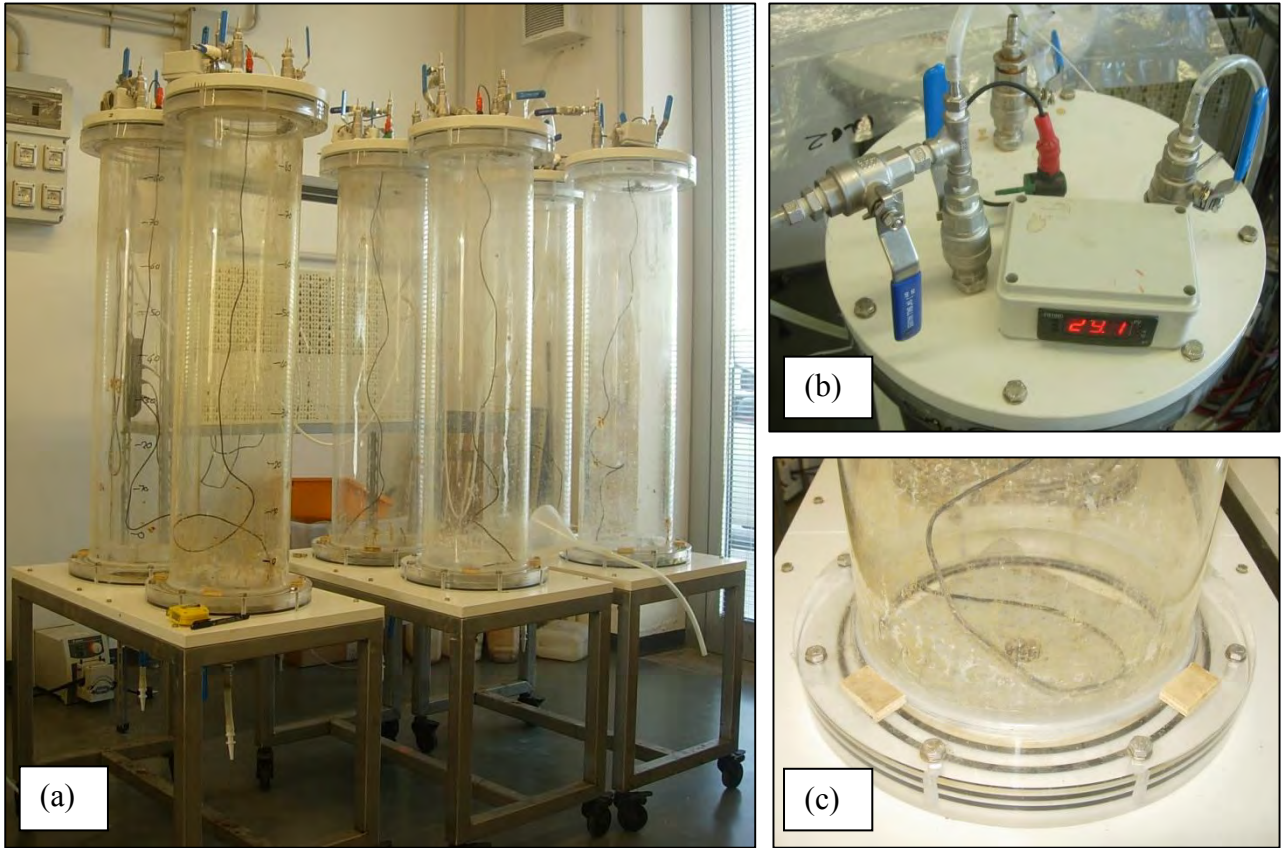


Figure 7.6 – (a) Columns before filling; (b) Upper part of the column; (c) Bottom of the column

A 10-cm thick gravel layer was placed at the bottom of each column as a drainage layer. The gravel is greater than 2 cm in size.



Figure 7.7 – Gravel

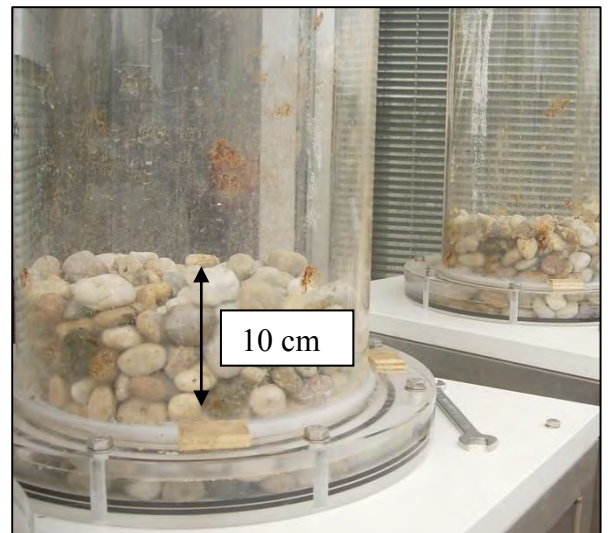


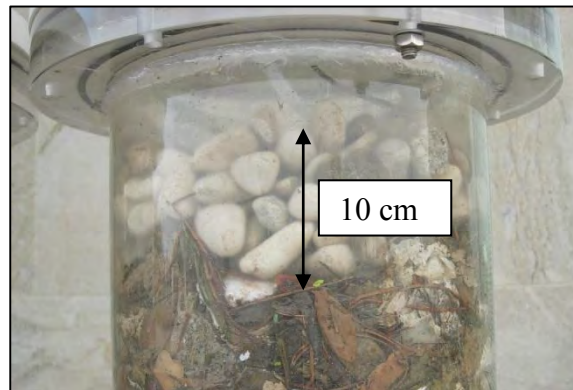
Figure 7.8 – Gravel at the base of each column

Waste were inserted in each column with a density of  $0,5 \text{ t/m}^3$  and according to the amount displayed in **Table 7.1**:

**Table 7.1 – Waste mass in each column**

Column	Amount [Kg]
1	18,4
2	18,4
3	18,4
4	18,4
5	15,6
6	18,4

A 10 cm thick layer of the same gravel was placed on the top of the loaded waste to facilitate the even distribution of recirculated leachate.



**Figure 7.9 – Gravel at the top of columns**

In the end, columns appeared as shown in **Figure 7.10**:



**Figure 7.10 – Final configuration of columns**

The upper end of columns is equipped with three valves providing for the introduction of air into the reactor, sampling and extraction of gas, as well as introduction of water and recirculation.

To channel air into the waste body, a vertical PVC tube with side perforations was installed at the center of the waste layer; this system guarantees the uniform distribution of air throughout the column. Gas generated from each column was collected by connecting a Tedlar bag to the gas port of the column.

Temperature monitoring was performed by means of Thermo Systems TS100 temperature probes installed inside the reactor.

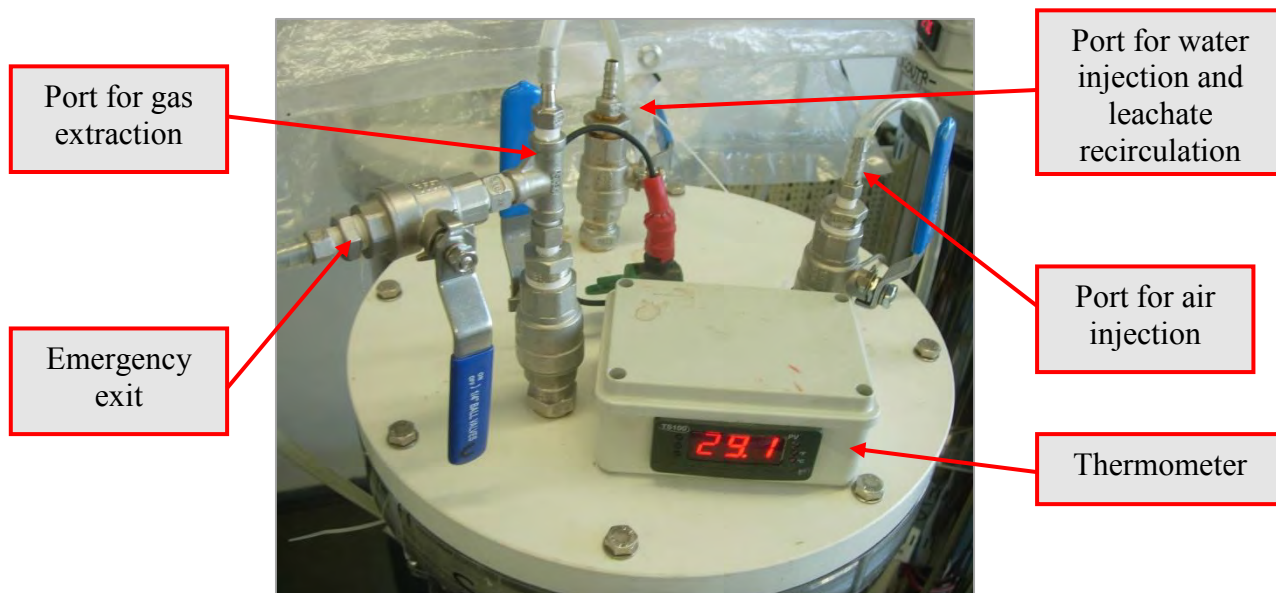


Figure 7.11 – Top of the column

A leachate collection port was located at the bottom of each column for leachate extraction and collection.



Figure 7.12 – Leachate extraction port

The columns were organized according to management criteria. The columns 1, 2, 3, 4 were managed as S.An.A., while the other two columns (5 and 6), were maintained always in anaerobic conditions as controlled bioreactors.

At the beginning of the experiment water was added into each column to adjust the moisture content of the waste and promote the leachate production. Six liters of water were added to columns 1, 2 and 6, while five liters of water were added to columns 3, 4 and 5 in order to reach 60% of moisture content.

The amount of water needed for reaching a given moisture content was calculated by solving the **Equation 7.1** and **Equation 7.2** :

$$\begin{cases} M_S + M_{WA} + M_{WI} = M_{TOT} & \text{Equation 7.1} \\ M_{TOT} \cdot \%_{MOISTURE} = M_{WA} + M_{WI} & \text{Equation 7.2} \end{cases}$$

Where:

$M_S$  is the dry mass of waste (=Total Solids)

$M_{WA}$  is the amount of water that must be added to waste for reaching a given moisture content

$M_{WI}$  is the water already present in the waste body

$M_{TOT}$  is the total mass of waste after water addition.

$\%_{MOISTURE}$  is the moisture content to reach

The two equations are reworked and put together, obtaining the **Equation 7.3**:

$$M_{WA} = \frac{M_{WI} \cdot \left( \frac{1}{\%_{MOISTURE}} - 1 \right) - M_S}{\left( 1 - \frac{1}{\%_{MOISTURE}} \right)} \quad \text{Equation 7.3}$$

Before calculating the amount of water to add, it was necessary to measure the dry mass content of waste, i.e. the Total Solids. Three waste samples were put in a furnace for evaporation of pore water at 105 °C for twelve hours. The sample were weighted before and after the evaporation by means of an analytic balance.

Then, the same three dried samples were put inside a muffle furnace at 550 °C for four hours and Volatile Solids were obtained. The results are showed in **Table 7.2**:

**Table 7.2 – Total Solids and Volatile Solids of waste**

Sample	Total Solids [%]	Volatile Solids [%]
1	55	33,2
2	54,8	34,2
3	56	30,9
Average	55,5	32,7

After reaching the proper water content in each column, the first leachate was pulled out on 4<sup>th</sup> July and analyzed. The results are reported in **Table 7.3**:

**Table 7.3 – Chemical analysis on the first leachate**

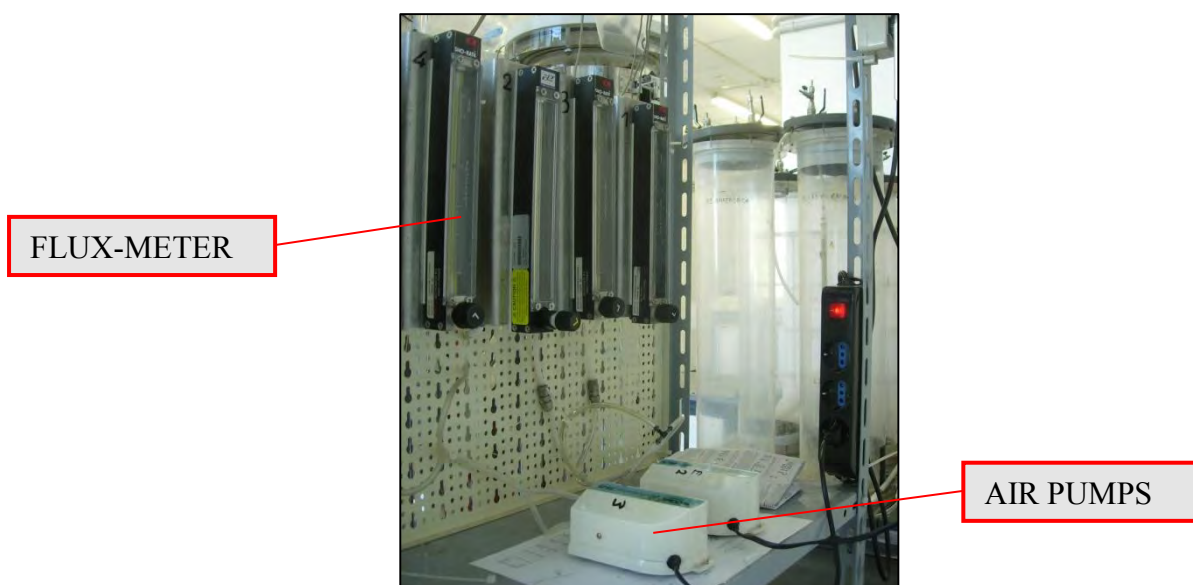
	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
pH	5,35	5,21	5,39	5,27	5,22	5,27
BOD <sub>5</sub> [mgO <sub>2</sub> /l]	27.431					
COD [mgO <sub>2</sub> /l]	30.000					
TOC [mgC/l]	9.130					
TKN [mgN/l]	886					
NH <sub>3</sub> [mgN/l]	402,4	275,8	387,1	364,3	266,3	368
Alkalinity [mgCaCO <sub>3</sub> /l]	448	182	602	391	199	494
VFA [mg/l]	2.212,8	2.166	2.227	2.170,8	2.155	2.128
SO <sub>4</sub> <sup>-2</sup> [mg/l]	2.262					
Sulfide [mg/l]	52					
Cl <sup>-</sup> [mg/l]	3.140					
Cd [µg/l]	< 10					
Cr [µg/l]	289					
Cu [µg/l]	779					
Fe [µg/l]	63.869					
Mg [µg/l]	10.922					
Ni [µg/l]	583					
Pb [µg/l]	64					
Zn [µg/l]	11.522					

As one can notice, waste material is very biodegradable with high content of organic matter. The general acidic condition expressed by pH values, is due to very high concentration of Volatile Fatty Acids and low amount of alkalinity. Regarding metals content, iron was the most present, while cadmium the least one.

After the filling and the closure of columns, aeration started in the columns 1, 2, 3 and 4.

The flux of air supplied to columns was changed during testing period in order to increase the degradation rate of waste.(**Table 7.6**).

Air was introduced by a Prodac Air Professional pump 360 and the inlet airflow was regulated and adjusted by a Sho-Rate GT1135 flow-meters, as shown in **Figure 7.13**:



**Figure 7.13 – Aeration instruments**

Analysis were performed on leachate pulled out from columns since 4<sup>th</sup> July 2014, according to the scheme presented in **Table 7.4**:

**Table 7.4 – Chemical analysis on the first leachate**

Analysis Type		pH	COD	BOD <sub>5</sub>	NH <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	TKN	FOS/TAC	Sulfide	Chloride	Sulfate	Metals
Frequency	Since 04/07 To 08/08												
	Since 25/08												

■ Daily      ■ Three time a week      ■ Once a month  
■ Once a week      ■ Twice a month

The analysis were performed according the method IRSA-CNR 29/2003 for liquid samples, while the solid samples were analyzed according to the methods showed in **Table 7.5**:

**Table 7.5 – Methods for analyzing solid samples**

Leaching test 24h in distilled water	UNI EN 12457-2
Total solids, Volatile Solids	IRSA-CNR Q 64/84 vol.2 n.2
Ammonia nitrogen	IRSA-CNR Q 64/86 vol.3 n.7 mod.
TKN	IRSA-CNR Q 64/85 vol.3 n.8 mod.
TOC	UNI EN 13137
Cd	EPA n. 3050B/96 + 6010C/07
Cr (VI)	EPA n. 3050B/96 + 6010C/07
Cu	EPA n. 3050B/96 + 6010C/07



Fe	EPA n. 3050B/96 + 6010C/07
Mg	EPA n. 3050B/96 + 6010C/07
Ni	EPA n. 3050B/96 + 6010C/07
Zn	EPA n. 3050B/96 + 6010C/07

It must be borne in mind that during the period 09/08 – 24/08 the columns remained closed and no analysis was performed.

The biogas produced by each column was collected into Tedlar® sampling bags featuring a single polypropylene fitting that is used for both filling the bag and removing the sample for analysis. The fitting contains both a syringe port with PTFE-lined septum and a hose connection and acts as a valve for hose connection.



**Figure 7.14 – Tedlar sampling bag**



**Figure 7.15 – Instruments for emptying the biogas sampling bags**

Once or twice a day was measured biogas volume and its volumetric concentration of O<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> by means of a portable analyzer (Eco-Control LFG20). LFG20 permits simple and precise measurements of CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> in a sample drawn by an internal pump at 200 ml per minute, using an electrochemical cell for oxygen measurement and Infra Red (IR) technique for methane and carbon dioxide measurement.

Leachate daily pulled out from columns was totally re-circulated, except when it was used as sample for chemical analysis. It was chosen to take 250 ml or 150 ml as samples, according to the kind of analysis to carry out.



**Figure 7.15 – LFG20 for biogas measurements**



**Figure 7.16 – Samples of leachate taken from columns for chemical analysis (08/10/14)**

Temperature is a very important factor for methane production. Methanogenic bacteria include both mesophilic groups working at around 40°C and termophilic groups whose maximum activity occurs at 70°C.

In order to ensure optimal environmental conditions, thermo-regulated insulation system covering all reactors lateral surface were fitted up on columns and set at 40°C on 7<sup>th</sup> August, about one month later the beginning of the test and before the change to the anaerobic phase (**Figure 7.17** and **Figure 7.18**).



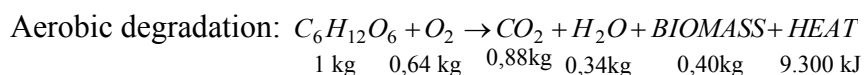
**Figure 7.17 – Thermal covers**

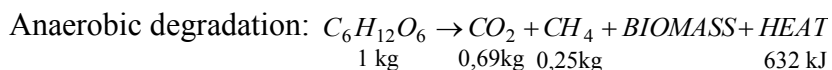


**Figure 7.18 – Columns with thermal covers**

The anaerobic degradation processes always occur at lower temperature conditions respect the aerobic ones.

By comparing anaerobic and aerobic degradation processes of glucose, the following balance occurs (Christensen, Kjeldsen, 1989):





Therefore the anaerobic reactions are weakly exothermic and the heat generation constitutes about 7% of that achievable by an aerobic reaction.

The S.An.A. test was planned into three distinct phases: Semiaerobic, Anaerobic and Aerobic. In the present thesis work, only the semi-aerobic and the anaerobic phases were investigated but the considered period (03/07 – 14/11) can be split up in three parts:

- Since 03/07 to 08/08, the S.An.A. columns were all aerated according to the fluxes listed in Table 7.6, so they remained in the semi-aerobic conditions;
- Since 08/08 to 24/10 the S.An.A. columns were managed in a different manner from each other, according to the trend of parameters of each column;
- Since 24/10 to 14/11 all columns were maintained in anaerobic conditions

**Table 7.6 – Aeration program during the test**

Period			Int [l/d]	Cont [l/d]	Int [l/d]	Cont [l/d]	Anaerobic	Anaerobic
Since	To	Days	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
03/07	14/07	12	14	14	14	14	0	0
14/07	16/07	2	28	28	28	28	0	0
16/07	08/08	23	50	50	50	50	0	0
08/08	27/08	19	0	0	0	0	0	0
27/08	10/09	14	50	50	0	0	0	0
10/09	23/09	13	0	50	0	0	0	0
23/09	07/10	14	0	50	0	50	0	0
07/10	23/10	16	0	50	0	100	0	0
24/10	10/11	17	0	0	0	0	0	0
Total days		130						

For intermittent columns (C1 and C3) aeration was performed only for twelve hours and then stopped for the rest of the day, while in continuous columns (C2 and C4) the aeration was performed during all the day.



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## Chapter 8.

# **SCIENTIFIC PAPER: *Nitrogen mass balance and biogas production in innovative Semiaerobic – Anaerobic – Aerobic (S.An.A.) landfill***

### 8.1 Introduction

Conventional landfilling is a commonly used method for the disposal of Municipal Solid Waste, which represent an important source of air, water and soil contamination. The need for alternative waste management techniques to better utilizes the waste and minimize its adverse environmental impact, led to an increasing interest in landfill bioreactors that allow accelerating municipal solid waste decomposition and reducing the post-operational phase of a landfill. (Sun et al., 2012; Xu et al., 2014).

Nitrogen is one of the most critical compound that can be found in a landfill. It is mainly found as ammonia or ammonium ion (according the pH of the system), but usually, due to the weakly acidic conditions characterizing a landfill environment, the ammonium ion is the prevalent form. Its removal usually occurs through nitrification and autotrophic denitrification processes, which require respectively aerobic and anoxic conditions.

Due to the anaerobic conditions typically present in a traditional landfill, nitrification process is inhibited and ammonia may accumulate up to toxic levels. (Berge et al., 2006; Sun et al., 2012). On the contrary, the alternating aerobic and anaerobic conditions characterizing a bioreactor landfill can enhance the removal of nitrogen compounds and reduce the risk of contamination for the surrounding environment.

The management of a landfill must comply with the sustainability concept, meaning that landfill should reach an acceptable equilibrium with environment within a generation time (30 – 40 years). In order to apply this fundamental concept it is necessary to choose the proper technologies and tools, review the existing regulations and set targets which allow to reach an high final storage quality of materials.

The bioreactor landfills can be characterized by liquid and air injection, allowing for adjustment of pH, redox conditions and moisture content and creating a suitable environment for degradation processes. Moisture is necessary to support the metabolic process, transport nutrients and allow microorganisms to move about (Norbu et al., 2005), while oxygen speeds up the degradation processes (Cossu et al., 2003; Ritzkowsky, 2013).

So far, several studies have been performed on positive influence of aeration and leachate recirculation on degradation rate of municipal solid waste (Cossu et al., 2003; Cossu et al., 2005; Lay et al., 1998; O’Keefe et al., 2000; Raga et al., 2013; Sandip et al., 2012; Sekmann et al., 2011; Sponza et al., 2005; Zhang et al., 2012), but only few of them have pointed on the effects produced

on the biogas production and its composition. Xu et al., (2014) investigated simulated hybrid bioreactor landfill by means of two laboratory-scale columns filled with 13,2 kg of MSW and having a bulk density of 0,6 t/m<sup>3</sup>. The hybrid column was aerated with 120 l/d at intermittent way until the pH of leachate resulted seven, then it was maintained under anaerobic conditions. The experiment revealed a sensible increase of methane production in hybrid bioreactor, four hundred times greater than that in the anaerobic bioreactor.

Cossu et al., (2005) planned a test on four bioreactors landfill columns and applied a mass balance model in a small scale. Two columns were pre-aerated continuously with an airflow of 4,4 l/kg/d. The results assessed that a strong beginning aeration encourages carbon removal and methane production.

Higher methane production was obtained also by Sandip et al., (2012) after the pre-aeration during a simulated bioreactor test.

Few of these results are listed in the **Table 8.1**:

**Table 8.1 – Aeration fluxes from literature**

	<b>Air injected [l/d/kg]</b>	<b>Days of aeration [d]</b>	<b>Total methane produced [l/kgTS]</b>
<b>Cossu et al., (2005)</b>	4,4	21	-
<b>Xu et al., (2014)</b>	9,1	72	31,9
<b>Sandip et al., (2012)</b>	-	14	32,2
<b>Sekman et al.,( 2011)</b>	144	150	-
	432		
	864		
	1440		

The objective of the present study is to apply the innovative S.An.A. waste management system, in order to conjugate the already proved advantages of leachate recirculation and aeration with methane production, and study the different modality of air injection for assessing the most effective and viable one, also from an economic point of view.

The S.An.A. landfill is characterized by three different management phases: semi-aerobic, anaerobic and aerobic. During the semi-aerobic phase air is injected into the waste mass in order to simulate the natural convection caused by the temperature gradient between the external environment and the landfill body. The main objective of this first phase is the reduction of volatile fatty acids in order to enhance and anticipate the methane production during the next anaerobic phase. In the last aerobic phase, air is forced into waste body for degradation of most refractory compounds. The S.An.A. system provides also for either partial or total leachate recirculation for ensuring better nutrient distribution and proper moisture content.

This management system could fulfill the sustainability concept for a landfill, because it should reduce the post-closure period

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## 8.2 Materials and methods

### 8.2.1 Waste samples

The raw material used for the experimental survey was constituted by 200 kg of urban solid waste, which were sieved at #80 mm. The undersieve material obtained, was used for filling the reactors and its amount was 107,6 kg totally.

Waste composition analysis was carried out considering the following categories: putrescible, cellulosic materials, green waste, plastic materials, metals, glass and inert, composites and undersieve. (Figure 8.1).

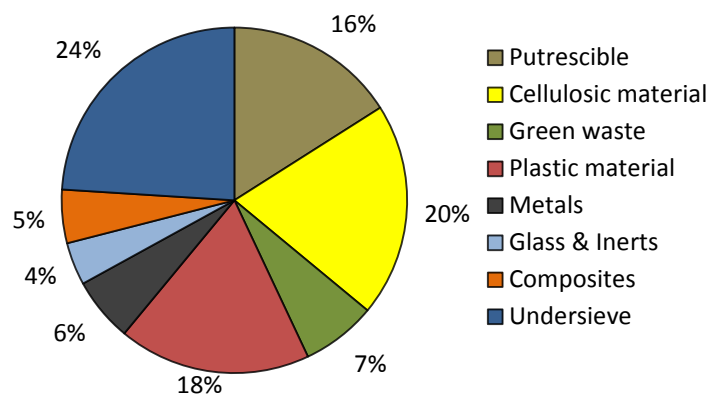


Figure 8.1 – Waste composition analysis of raw waste

### 8.2.2 Equipment

Six reactors were set up for the experiment. The bioreactors were fulfilled using six 24-cm-diameter polymethyl methacrylate (Plexiglas®) pipe with a total height of 106 cm, loaded with urban solid waste, which were inserted in each column with a density of 0,5 t/m<sup>3</sup> and according to the amount displayed in Table 8.2:

Table 8.2 – Waste mass in bioreactors

Column	Amount of waste [Kg]	
C1	18,4	
C2	18,4	
C3	18,4	
C4	18,4	
C5	15,6	
C6	18,4	

A 10-cm thick gravel layer was placed at the bottom of each column as a drainage layer. The gravel is greater than 2 cm in size. A 10 cm thick layer of the same gravel was placed on the top of the loaded waste to facilitate the even distribution of recirculated leachate.

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The upper end of columns is equipped with three valves providing for the introduction of air into the reactor, sampling and extraction of gas, as well as introduction of water and recirculation.

To channel air into the waste body, a vertical PVC tube with side perforations was installed at the center of the waste layer; this system guarantees the uniform distribution of air throughout the column. Gas generated from each column was collected by connecting a Tedlar bag to the gas port of the column.

Temperature monitoring was performed by means of Thermo Systems TS100 temperature probes installed inside the reactor.

A leachate collection port was located at the bottom of each column for leachate collection.

In the end, columns appeared as shown in **Figure 8.2**:



**Figure 8.2 – Final configuration of columns**

The air was introduced by a Prodac Air Professional pump 360 and the inlet airflow was regulated and adjusted by a Sho-Rate GT1135 flow-meters. The biogas produced by each column was collected into Tedlar® sampling bags featuring a single polypropylene fitting that is used for both filling the bag and removing the sample for analysis. The fitting contains both a syringe port with PTFE-lined septum and a hose connection.

### **8.2.3 Management of bioreactors**

The S.An.A. Test was planned into three distinct phases: Semiaerobic, Anaerobic and Aerobic. In the present thesis work, only the semi-aerobic and the anaerobic phases were investigated but the considered period (03/07 – 10/11) can be split up into three parts:

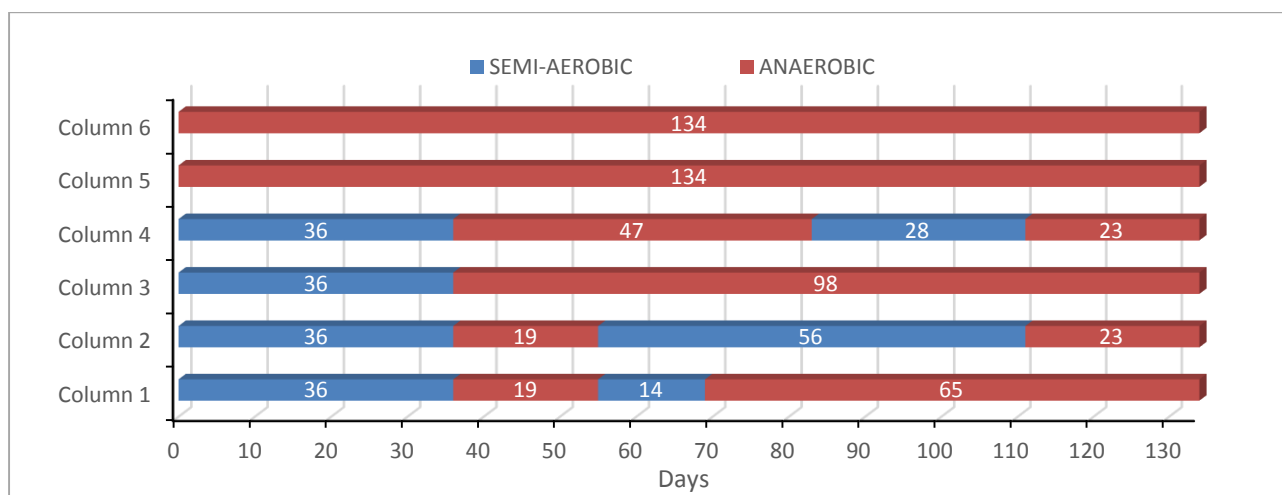
- Since 03/07 to 08/08, the S.An.A. columns were all aerated according to the fluxes showed in Table XX, so they remained in the semi-aerobic conditions;



- Since 08/08 to 24/10 the S.An.A. columns were managed in a different manner from each other, according to the trend of parameters of each column;
- Since 24/10 to 10/11 all columns were maintained in anaerobic conditions

The columns 1, 2, 3, 4 were managed as S.An.A., while the other two columns (5 and 6), were maintained always in anaerobic conditions as controlled bioreactors.

After the filling and the closure of columns, aeration was started in the columns 1, 2, 3 and 4. The **Figure 8.3** shows the duration of semi-aerobic and anaerobic phases in all columns:



**Figure 8.3 – Aeration program during the test**

Aeration was performed into two modalities: the bioreactors C1 and C3 were aerated intermittently, while bioreactors C2 and C4 were aerated continuously. The intermittent aeration was performed by injecting the daily air flux for twelve hours and then stopping, while for the continuous aeration, the daily air flux was injected for all the day.

The volume of air supplied to columns was changed during testing period, in order to increase the degradation rate of waste. The **Table 8.3** lists the inlet air flux:

**Table 8.3 – Aeration rate**

Period			Int [l/d]	Cont [l/d]	Int [l/d]	Cont [l/d]	Anaerobic	Anaerobic
Since	To	Days	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
03/07	14/07	12	14	14	14	14	0	0
14/07	16/07	2	28	28	28	28	0	0
16/07	08/08	23	50	50	50	50	0	0
08/08	27/08	19	0	0	0	0	0	0
27/08	10/09	14	50	50	0	0	0	0
10/09	23/09	13	0	50	0	0	0	0
23/09	07/10	14	0	50	0	50	0	0
07/10	23/10	16	0	50	0	100	0	0
24/10	10/11	17	0	0	0	0	0	0
Total days		130						

At the beginning of the experiment, water was added into each column to adjust the moisture content of the waste and promote the leachate production. Six liters of water were added to columns 1, 2 and 6, while five liters of water were added to columns 3, 4 and 5 in order to reach 60% of moisture content.

Leachate recirculation was performed daily during the whole test. Leachate daily pulled out from columns was totally re-circulated, except when it was used as sample for chemical analysis. It was chosen to take 250 ml or 150 ml as samples, according to the kind of analysis to carry out.

Once or twice a day was measured biogas volume and its volumetric concentration of O<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> by means of a portable analyzer (Eco-Control LFG20).

#### 8.2.4 Analytical procedures

The dry mass content of waste and the Volatile Solids were measured. (**Table 8.4**)

**Table 8.4 – Total Solids and Volatile Solids of waste**

Sample	Total Solids [%]	Volatile Solids [%]
1	55	33,2
2	54,8	34,2
3	56	30,9
<i>Average</i>	<b>55,5</b>	<b>32,7</b>

Analysis were performed on leachate pulled out from columns since 4<sup>th</sup> July 2014, according to the IRSA-CNR 29/2003 methods.

pH, COD, BOD<sub>5</sub>, TOC, TKN, N-NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were evaluated on leachate samples during the whole test with different frequencies, while TOC, TKN, N-NH<sub>4</sub><sup>+</sup> and metals were analyzed on solid waste sample at the beginning of the test, according to the methods listed in **Table 8.5**

**Table 8.5 – Methods for analysis on solid samples**

Method for solid samples	
Leaching test 24h in distilled water	UNI EN 12457-2
Total solids, Volatile Solids	IRSA-CNR Q 64/84 vol.2 n.2
Ammonia nitrogen	IRSA-CNR Q 64/86 vol.3 n.7 mod.
TKN	IRSA-CNR Q 64/85 vol.3 n.8 mod.
TOC	UNI EN 13137
Cd	EPA n. 3050B/96 + 6010C/07
Cr (VI)	EPA n. 3050B/96 + 6010C/07
Cu	EPA n. 3050B/96 + 6010C/07
Fe	EPA n. 3050B/96 + 6010C/07
Mg	EPA n. 3050B/96 + 6010C/07
Ni	EPA n. 3050B/96 + 6010C/07
Zn	EPA n. 3050B/96 + 6010C/07

The results of the analysis were always compared with the correspondent values found in literature, indicating the optimum parameters for methane production, as shown in **Table 8.6**.

**Table 8.6 – Optimum parameters for methane production**

Parameter	Optimal range	Source
Temperature [°C]	30-40	Christensen et al., (1996)
	35-40	Yuen et al., (1995)
	35	Cossu et al., (2005)
pH	6-8	Zehnder et al., (1982)
	6,7-7,4	Lay et al., (1998)
	6,4-7,2	Chung et al., (1998)
	6,5-8,2	Sekman et al., (2011)
	6,65-7,41	Sandip et al., (2012)
Alkalinity [mgCaCO <sub>3</sub> /l]	1.000-5.000	Agdag et al., (2005)
	2.000-3.500	Sekman et al., (2011)
Volatile Fatty Acids [mgCH <sub>3</sub> COOH/l]	< 1.400	Wang et al., (1999)
Ammonia [mgN-NH <sub>3</sub> /l]	< 3.000	McCarty and McKinney, (1961)

These optimal ranges were taken into account as reference for passing from the semi-aerobic phase to the anaerobic one.

A mathematical model of biogas production based on the kinetic model from Gompertz growth equation was used. This model has sigmoid shape with a clear inflection point. It was used to determine the cumulative volume of gas produced from the bioreactors according to the **Equation 8.1**. (Lay et al., 1998; Sandip et al., 2012).

$$BG = BGP \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{BGP}(\lambda - t) + 1\right]\right\} \quad \text{Equation 8.1}$$

Where *BG* is the cumulative biogas yield [ml/gVS], *t* is the digestion time [d], *BGP* is the biogas yield potential [ml/gVS], *R<sub>m</sub>* is maximal daily biogas yield [ml/gVS/d], *λ* is bacteria growth lag time [d] and *e* is mathematical constant (=2,718).

### 8.3 Results and discussion

The following results include 140 days of S.An.A. test, starting from 4<sup>th</sup> July.

#### Leachate pH

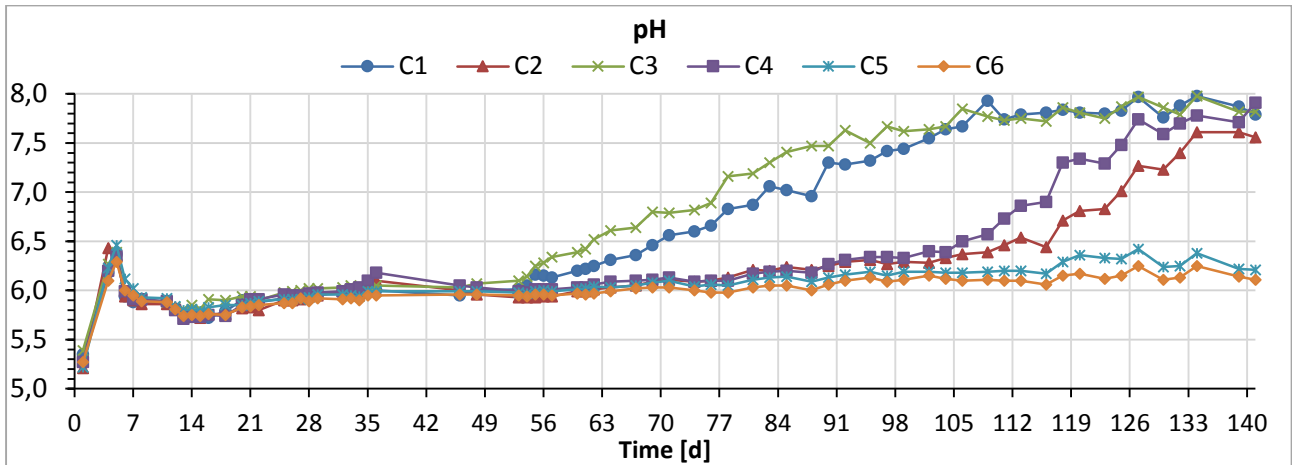


Figure 8.4 – pH trend

Figure 8.4 presents the change of pH during the experiment. The pH values in all bioreactors dropped to about 5,7 in the first two weeks, indicating that the accumulation of organic acids occurred .

Leachate pH of the Column 1 and Column 3, aerated in an intermittent way, began to slowly increase at day 50 and continued to increase rapidly up to 7,8 on day 110.

In Column 2 and Column 4, aerated in a continuous way, leachate pH remained low (<6,5) up to day 110, and then start to increase faster, respectively up to 7,4 and 7,7 on day 132, later respect intermittent columns.

Column 5 and Column 6 remained always in acidic or slight acidic conditions and pH never increase over 6,5.

The conversion of S.An.A. columns to anaerobic conditions occurred at pH listed in **Table 8.7**:

Table 8.7 – pH values at the conversion to anaerobic phase

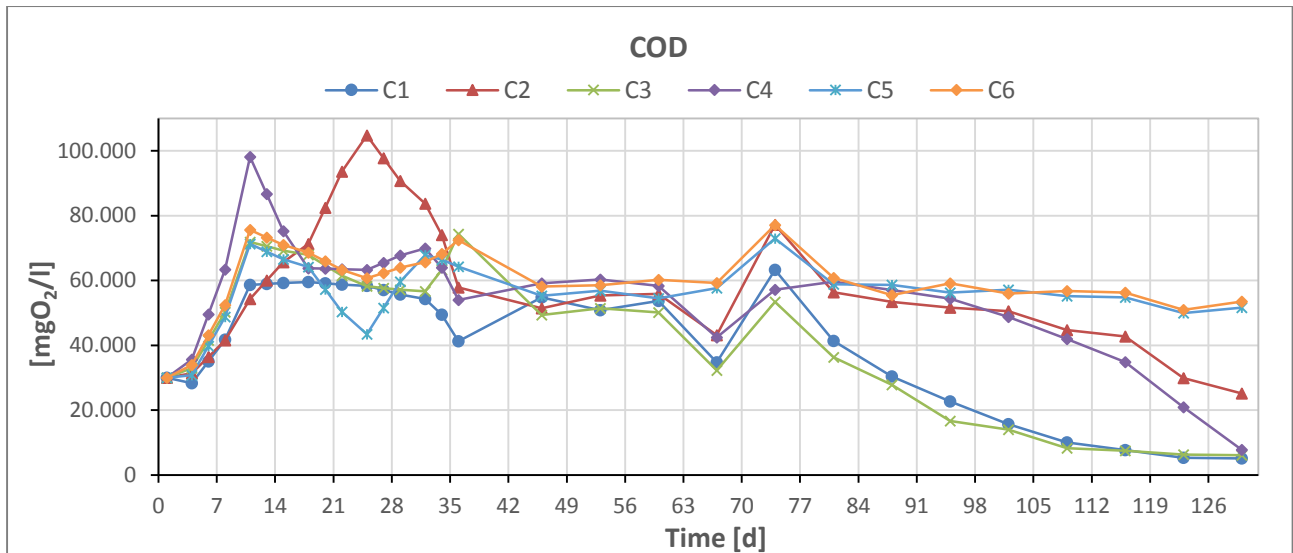
Columns	C1	C2	C3	C4
pH	6,46	6,46	6,25	6,5

Bioreactor C3 began to produce methane at the lowest pH respect the other columns. It was tried to pass C4 at pH 6,1, but it did not produce methane, so it was decided to report the column to aerobic conditions up to pH 6,5. From these analysis it seems that methane generation occurs at pH>6,25 and can continue up to pH 8.

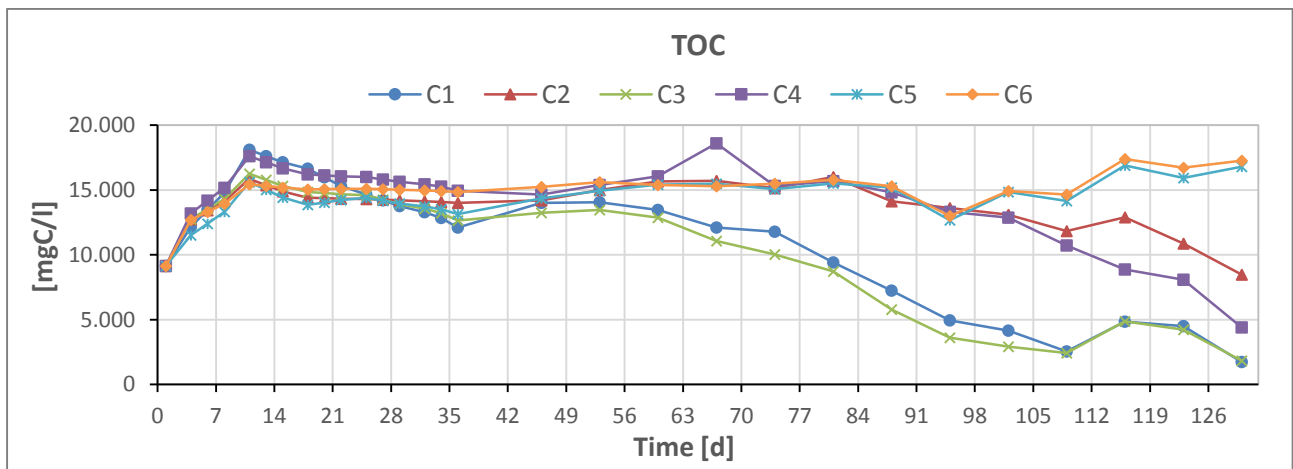
The pH resulted well influenced by aeration modality. The intermittent aeration speeded up the pH increase in C1 and C3, shortening the acidic phase and anticipating the methane generation.

## Dissolved organic matter

The parameters concerning organic substance were analyzed and are reported in **Figure 8.5** and **Figure 8.6**:



**Figure 8.5 – COD trend**



**Figure 8.6 – TOC trend**

In each column, the leachate showed an increasing trend of COD and TOC during the first two weeks of test.

After the reaching of a proper water content, the hydrolysis process starts, breaking the complex organic molecules into smaller organic compounds and increasing the more easily degradable organic material (COD)

The maximum COD value were recorded in C1, C2, C3, respectively at day 18, 25, 36, and in C4, C5, C6 at day 11. The C2 had the highest COD of 104.000 mgO<sub>2</sub>/l.

Afterwards, the aerobic (in the presence of oxygen) and anaerobic (in the absence of oxygen) degradation processes began to reduce the organic biodegradable material. In particular, this reduction resulted strong in the C1 and C3, weaker in the C2, C4 and control columns ( C5 and C6). In fact, as generally known, aerobic conditions aid and speed up the degradation process (Sekman et al., 2011; Sang et al., 2009; Erses et al., 2008). Hydrolysis of complex organics in the presence of oxygen enhances biodegradation rate and convert organic carbon in the waste mass to mostly carbon dioxide and water, with stabilized humid material remaining.

In C1 and C3, intermittent aerated, COD dropped quickly from day 74, while in C2 and C4, continuous aerated, remained relatively high (about 50.000 mgO<sub>2</sub>/l) up to day 120 and then began to decrease more rapidly.

The similar trend of TOC shows a well visible increase for all columns, followed by a decrease. One can notice that the highest increase occurring for C1, intermittent aerated, suggests that the intermittent aeration accelerated solubilization/depolymerization of the solid waste into leachate.

In C1, C2, C3 and C4, TOC reached values of 16.650, 15.850, 16.250, and 17.600 mgC/l respectively on day 11 and then decreased to 1.740 and 1.840 mgC/l in C1 and C3, to 8.480 and 4.400 mgC/l in C2 and C4 on day 130. It remained very high in control columns.

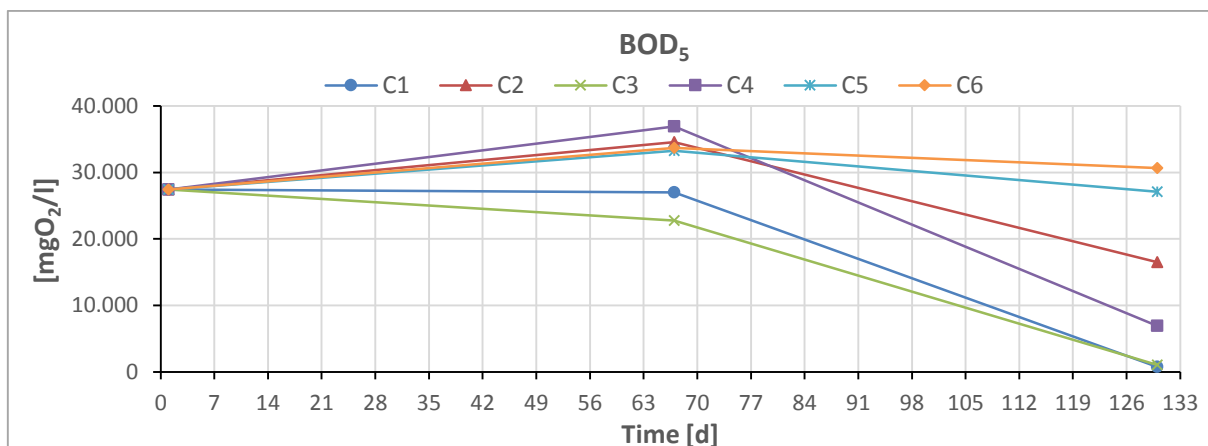
Another important parameter to consider is BOD<sub>5</sub>/COD ratio of the leachate, indicating the amount of biodegradable compounds. According to Sekman et al., (2011), BOD<sub>5</sub>/COD ratio between 0,02 and 0,13 implies that the leachate has a low biodegradability, while according to Kjeldsen et al., (2002), ratio between 0,4 and 0,8 implies high biodegradability.

In this research the initial BOD<sub>5</sub>/COD ratio results very high, as shown in **Table 8.8**:

**Table 8.8 – Initial BOD<sub>5</sub>/COD ratio**

COD [mgO <sub>2</sub> /l]	BOD <sub>5</sub> [mgO <sub>2</sub> /l]	BOD <sub>5</sub> /COD
30.000	27.431	0,91

During the S.An.A. experimentation BOD<sub>5</sub>/COD ratio decreased a lot in C1 and C3 but remained high in C2 and C4 where the slowly biodegradable material increased. In C5 and C6 the ratio decreased in the first period, but then remained constant. The ratio decrease was due to the increase of slowly biodegradable matter, while BOD<sub>5</sub> remained relatively high.



**Figure 8.7 – BOD<sub>5</sub> trend**

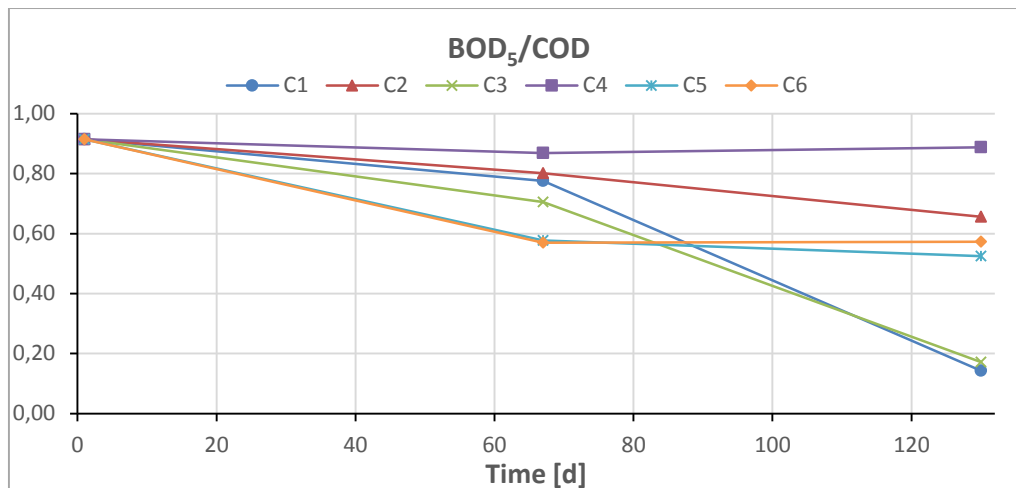


Figure 8.8 – BOD<sub>5</sub>/COD ratio

The strong decrease of COD and TOC in C1 and C3 verified that intermittent aeration is practical for accelerative stabilization of waste and for enhancing methane production. Two reasons can be suggested for explaining the fact:

- With intermittent aeration, for the same daily inlet airflow, the injection time halves and the inlet pressure of the flux increases, enhancing the oxygen diffusion;
- The alternation of aerobic and anaerobic periods makes more dynamic the transition of the aerobic and anaerobic microbial population forming a diverse microbial community. Sang et al., (2009) carried out a test on landfill bioreactor both in anaerobic and aerobic conditions, performing the aeration in continuous and intermittent manner. They found a very rich bacterial population within the reactor characterized by intermittent aeration. In particular they found methanogens, such as *Methanobacteriales* (H<sub>2</sub>-utilizing groups) and *Methanosarcinales* (acetate-utilizing group); during the test *Methanobacteriales* were gradually replaced by *Methanosarcinales*, suggesting that the main degradation pathway was acetotrophy for methanogenesis. Aerobic bacteria resulted subjected to stressful conditions due to the presence of anaerobic periods, so during aerobic conditions, the degradation process resulted faster.

## Nitrogen compounds

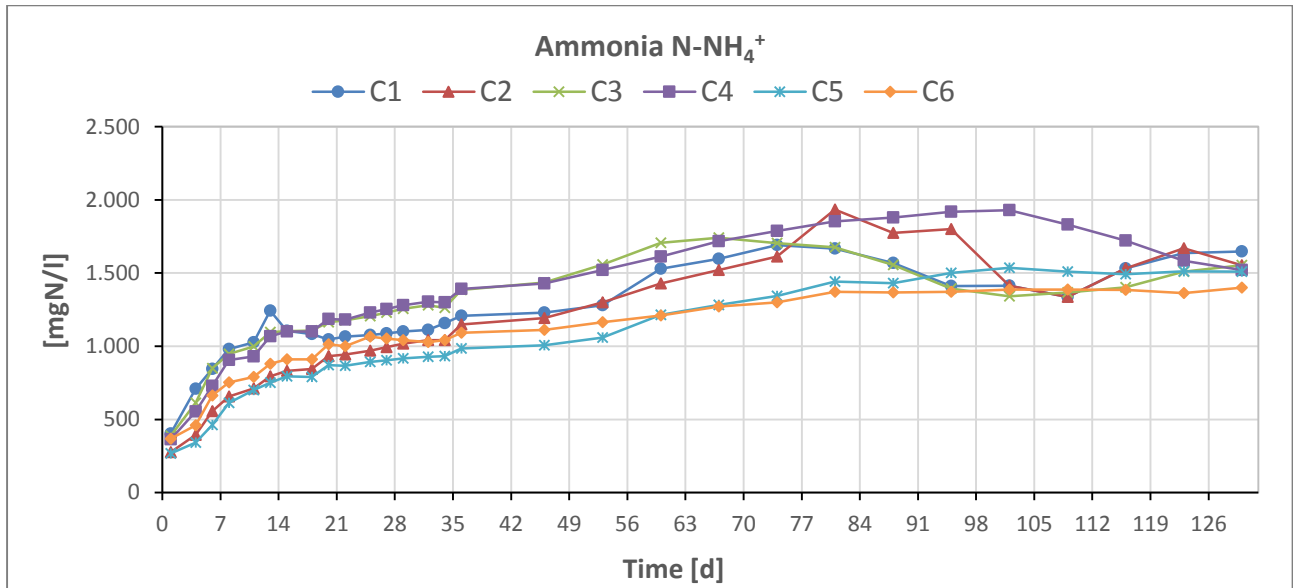


Figure 8.9 – Ammonia trend

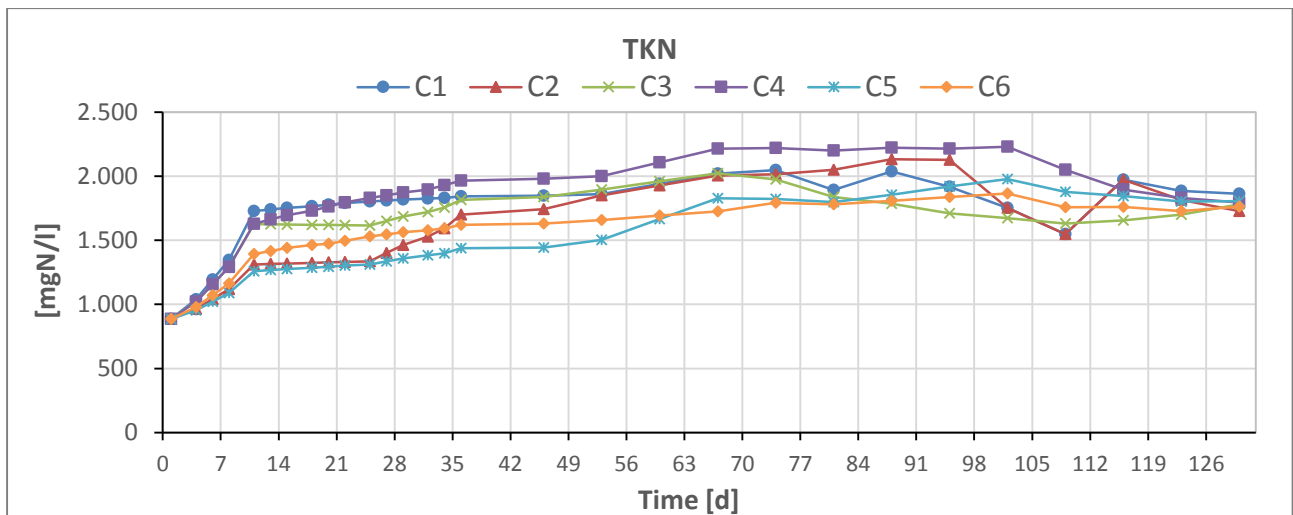


Figure 8.10 – TKN trend

As shown in **Figure 8.9**, ammonia nitrogen concentration accumulated in all bioreactors and in C1, C2, C3, C4 and C5 reached more than 1.500 mgN/l. Only in C6 remained below 1.400 mgN/l.

The accumulation was probably enhanced by hydrolytic process and by daily leachate recirculation. The increased ammonia concentration intensify the toxicity of the leachate. Pohland et al., (1987) stated that concentrations between 200 and 1.500 mg/l have not adverse effects on anaerobic process, concentrations ranging from 1.500 to 3.000 mg/l were shown to have inhibitory effects at higher pH levels, and concentrations above 3.000 mg/l were very toxic.

However Calli et al., (2005) have shown that NH<sub>3</sub>-N levels up to 6.000 mg/l could be tolerated in anaerobic bioreactors. In the presents study, at the end of the first phase, ammonia concentration did not reach toxic effects.



In the case of S.An.A. Test, nitrification and denitrification processes did not verified, probably due to insufficient oxygen supply for nitrifying bacteria. Neither nitrate ( $\text{NO}_3^-$ ) nor nitrite ( $\text{NO}_2^-$ ) were detected, and this fact contributed to ammonia accumulation.

About on day 110, ammonia nitrogen began to decrease in C2, C4, C5, C6, probably due to flushing effect. This one, caused by the leachate extraction and consequent injection of equal volume of fresh water, became more important with the decrease of hydrolysis, which, on the other hand, increased the ammonia concentration.

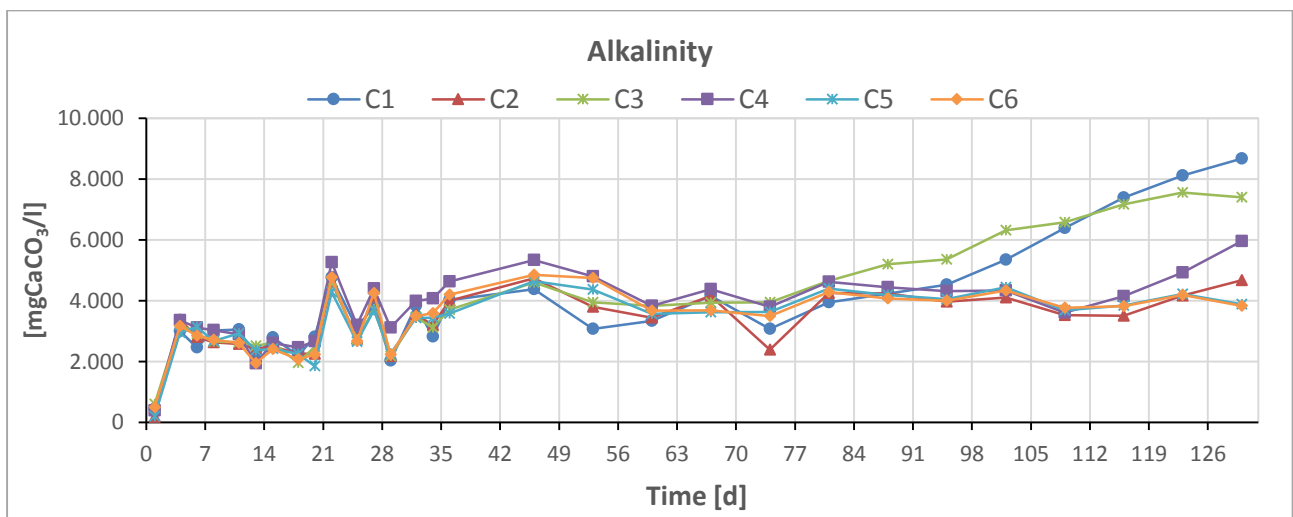
TKN had a similar trend of ammonia-nitrogen. After a slight increase due to the ammonia accumulation, it remained constant and then slightly decreased. Its constancy was due to the simultaneous decrease of organic carbon and increase of ammonia.

### FOS/TAC

*FOS/TAC* expresses the ratio between two important parameters, FOS and TAC, representing respectively Volatile Fatty Acids (in term of acetic acid) and alkalinity (in term of calcium carbonate). It has been developed in Germany as controlling parameter for anaerobic digestion processes and give an indication of the stability of the system, whose pH must be always near neutral values, in order to avoid the partial or complete inhibition of biogas production.

In the S.An.A. Test *FOS/TAC* was used for giving an indication about the equilibrium between acids and buffer capacity of the system, from which greatly depends the biogas production of the system itself. According to Farquhar et al., (1973), the methane production of an anaerobic degradation system requires a ratio between VFAs and alkalinity (which can be expressed as *FOS/TAC* ratio) lower than 0,8.

Alkalinity and VFA values of leachate samples of anaerobic and aerobic landfill reactors are given in **Figure 8.11-8.12**.



**Figure 8.11 – Alkalinity trend**

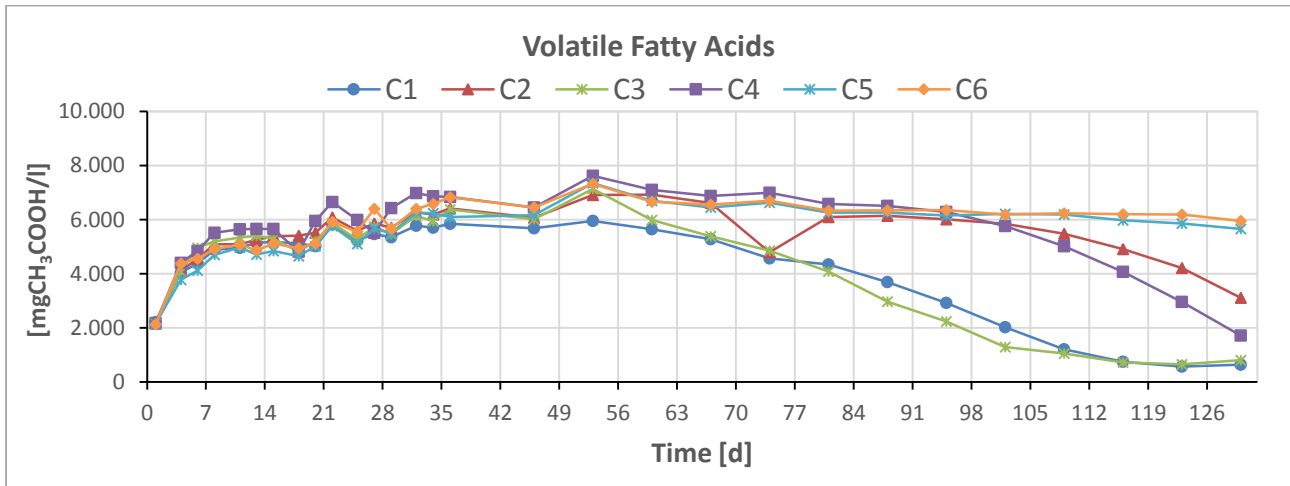


Figure 8.12 – Volatile Fatty Acids trend

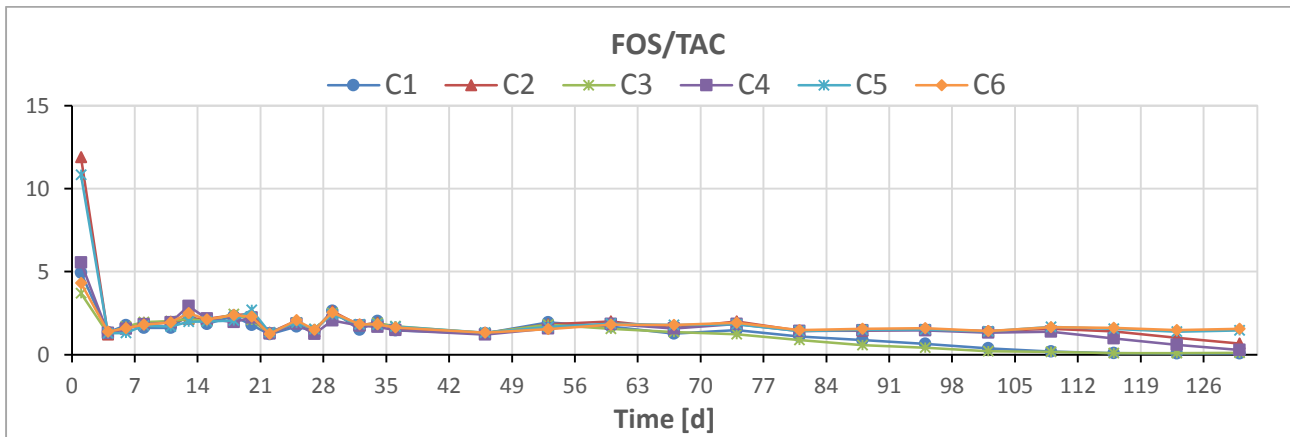


Figure 8.13 – FOS/TAC trend

Alkalinity remained quite constant in the first two months of test, and then increased in all S.An.A. columns. C1 and C3 were characterized by a quicker increase, up to 8.600 and 7.400 mgCaCO<sub>3</sub>/l respectively, while C2 and C4 reached concentrations of 4.000 mgCaCO<sub>3</sub>/l

The VFA concentration in the leachate of all bioreactors showed similar trend with COD concentrations. It increased at the beginning of test within 50 days, up to about 7.000 mgCH<sub>3</sub>COOH/l, as a result of accumulation of organic acids due to hydrolysis and acidogenesis.

The VFA concentration then reduced as the daily biogas production increased because the methanogenic bacteria, which utilized the VFA as a substrate to produce biogas and new cells. They decreased very rapidly in C1 and C3 at day 70, in C2 and C4 remained constant up to day 100 and then quickly decreased, while in C5 and C6 remained high for whole test at about 6.200 mgCH<sub>3</sub>COOH/l.

FOS/TAC remained constantly greater than one up to day 80 for C1 and C3, and up to day 120 for C2 and C4, then it dropped to values lower than 0,8 since day 90 for intermittent columns and since day 120 for continuous columns. In the control columns it was always greater than 1,5, due to the well-developed acidic conditions.

## Leachable compounds

Another important component detected and monitored was chloride. Chloride is a non-degradable conservative parameter which concentration change is commonly used to assess the variation of leachate dilution and washout effects (Sekman et al., 2011; Erses et al., 2008; Siddiqui et al., 2013). According to Ehrig and Scheelhaase (1993) there is no observable difference in chloride concentration between acidogenic and methanogenic phases. The chloride is generally washed out from the landfill via leachate recirculation and drawing. Leachate recirculation only, would lead to chloride removal less than that dissolved in the leachate, and thus, leachate chloride increase.

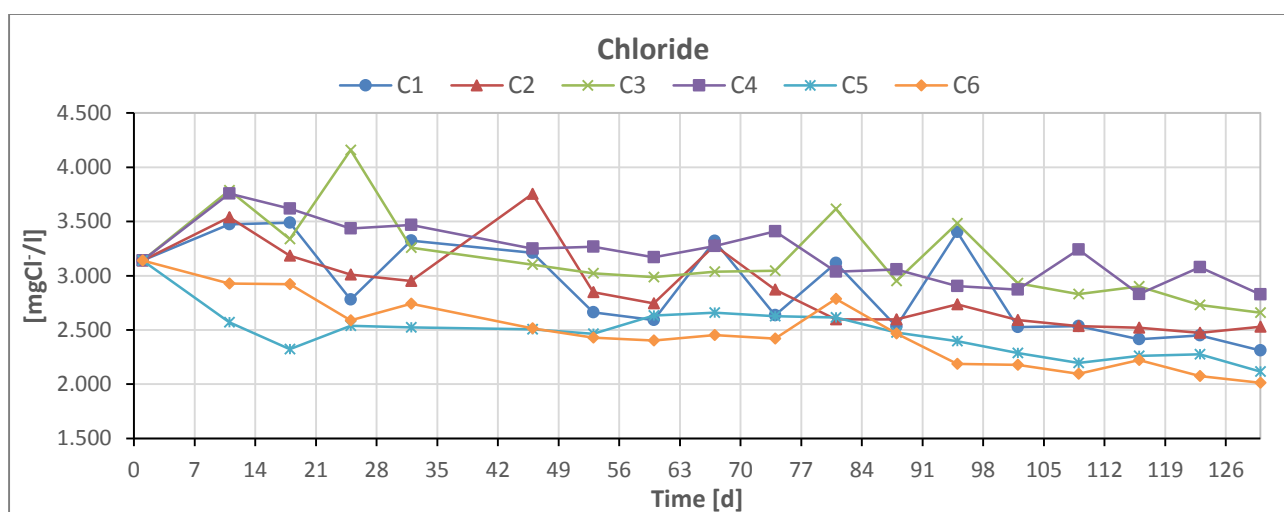


Figure 8.14 – Chloride trend

From **Figure 8.14** it is possible to notice a slight increase of chloride in C1, C3 and C4, while a decrease in the control ones (C5 and C6). Sekman et al., (2011), observed a simultaneous increase of pH and chloride because, as a result of the increase in pH, the dissolution of chloride increases and thus the chloride concentration in leachate increases.

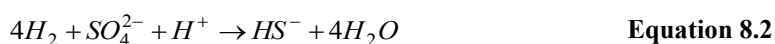
In the first month of S.An.A. test, pH remained generally low (<6), in particular in the control columns, and so chloride concentration slowly decreased, confirming the thesis of Sekman et al., (2011).

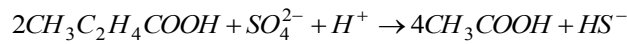
Since day 70 the chloride concentrations slightly decreased, showing an oscillating trend in C1 and C3. (See **Figure 8.14**).

The initial concentration of sulphate in the anaerobic and aerobic reactors were 2.261 mg/l.

It is possible to notice a general decrease in all columns, probably due to sulphur-reducing bacteria, strictly anaerobic, that converts, after sulphate reduction, hydrogen, acetic acid and volatile fatty acids. Although the first four columns were aerated during the first phase, the presence of anaerobic zones inside waste mass allowed anyway the development of sulphur-reducing bacteria.

The chemical reactions are expressed by means of the **Equation 8.2-8.4**:





Equation 8.4

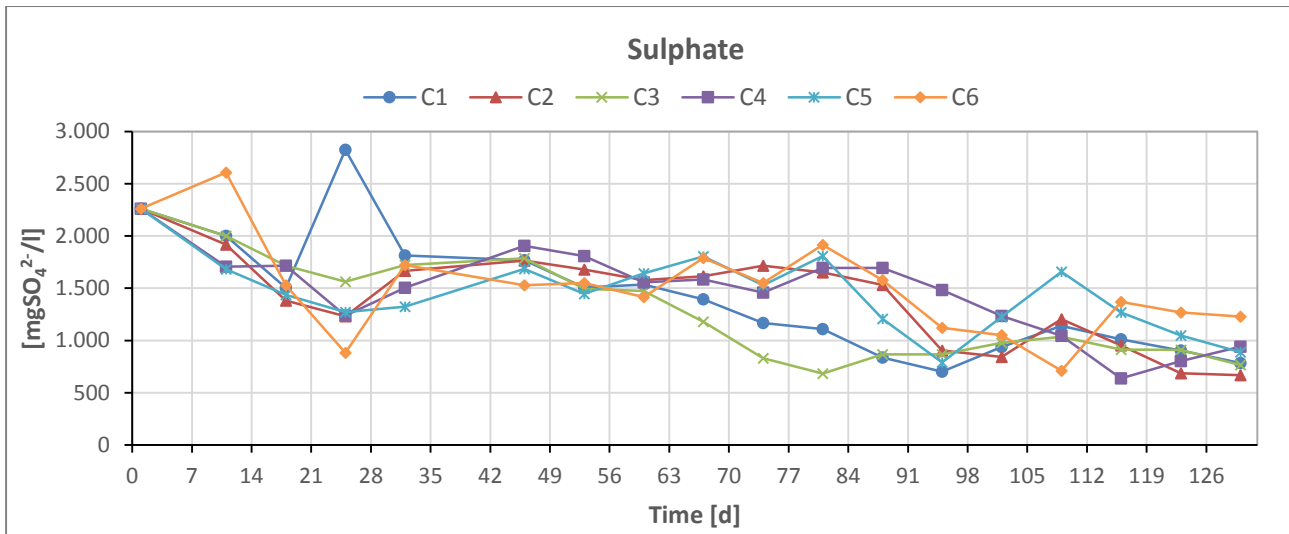


Figure 8.15 – Sulphate trend

Since day 70 in C1 and C3, characterized by methanogenic conditions, the sulphate decrease was partly due to the flushing, partly due to the sulphate-reducing bacteria which convert sulphate to sulfide, consuming acetic acid and hydrogen. In C2 and C4, still under aerobic conditions up to day 112, the sulphate decrease results slower, probably only due to the flushing, while in C5 and C6, after a feeble increase, sulphate decreases due to the presence of sulphate-reducing bacteria.

On day 112 the remained aerations in C2 and C4 were stopped because they reached proper pH values ( $\geq 6,5$ ), as shown in **Figure 8.4**. From that moment, all columns were in anaerobic conditions and the Second Phase of S.An.A. test was reached by all columns.

At the end of the semi-aerobic phase it was possible to carry out a final count of the oxygen supplied to each S.An.A. column since the beginning of the experimentation. The result is shown in **Figure 8.17**:

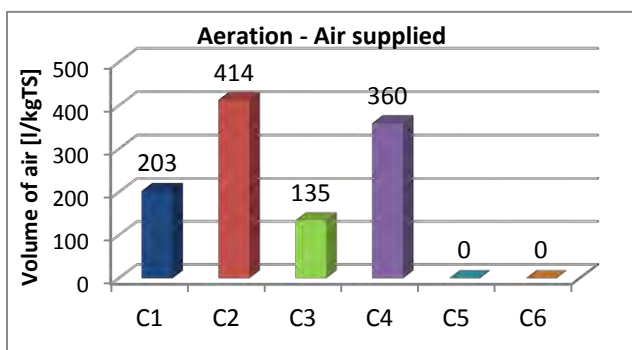


Figure 8.16 – Air supplied to columns

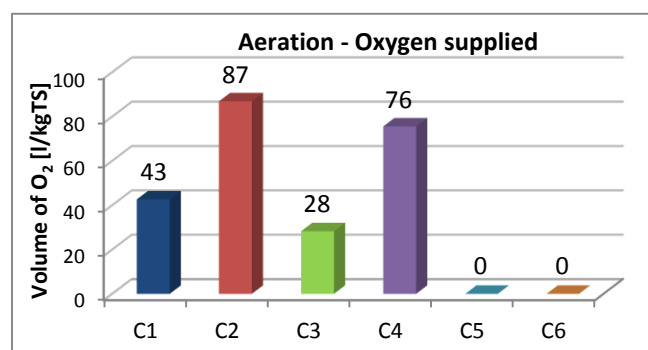


Figure 8.17 – Oxygen supplied to columns

As one can notice, C2 and C4 received the highest amount of air because they were aerated longer than the other two columns. The aeration was continued in reply to the worse trend of parameters characterizing these two columns. In fact the continuous aeration led to lower performance than the intermittent one, forcing to acting differently.

## Biogas production

The amount of methane generation per kilogram of organic matter stabilized is taken as an indicator of waste stabilization degree (Sponza et al., 2004).

Gas production started for the S.An.A. columns soon after the passage to anaerobic phase. Biogas production was relatively low during the first three-four days after the closure of aeration, presumably due to the time taken for acclimatization of the methanogenic bacteria, but then increased and methanogenic conditions were rapidly established, which was confirmed by the change in biogas composition to about 55-60% CH<sub>4</sub> and 30-35% CO<sub>2</sub> by volume.

VFAs were quickly metabolized to methane and carbon dioxide and their decrease was consistent with the increase in gas production.

Landfill gas concentrations and methane production rates of the bioreactors are presented in **Figure 8.18** and in **Figure 8.19**. The highest methane concentration measured in the biogas of the control anaerobic columns C5 and C6 were respectively 23% and 15,5% on day 55, then methane concentration gradually went down. The maximum methane production rate per dry mass of waste (Total Solids) was as low as 0,18 l<sub>CH<sub>4</sub></sub>/d/kgTS and 0,08 l<sub>CH<sub>4</sub></sub>/d/kgTS respectively for C5 and C6, over the 140 days of experiment.

The anaerobic bioreactors never reached a stable methane production phase during the whole test period, largely due to the stable acidic conditions that mummified the waste mass. The total methane produced in C5 and C6 was respectively 0,551 l/kgTS and 0,282 l/kgTS.

In the S.An.A. columns (C1, C2, C3 and C4), after pH reached 6,5 air injection was stopped and the system was switched to an anaerobic bioreactor. C1 and C3 were converted to anaerobic conditions earlier than C2 and C4 and the methane concentration began to rapidly increase to over 50% within a short time and remained around 55% throughout the test. The methane production rate peaked on day 96 at 2,15 l/d/kgTS in C1 and on day 103 at 2,045 l/d/kgTS in C3.

C2 and C4 were definitively converted to anaerobic conditions on day 112 (while C1 and C3 on day 70 and 36 respectively).

Overall, the total methane generated by C1 was 37,23 l/kgTS. The other columns (C2, C3 and C4) are still producing methane so it is not possible give a definitive result. (**Table 8.9**)

**Table 8.9 – Methane production by S.An.A. bioreactors**

	Days of pre-aeration	Volume of oxygen injected [l <sub>O<sub>2</sub></sub> /kgTS]	Methane production period [d]	Maximum daily methane production [l/d/kgTS]	Total methane production at day 139 [l/kgTS]
S.An.A. C1	50	43,00	91	2,150	37,23
S.An.A. C2	92	87,65	49	1,228	11,02
S.An.A. C3	36	28,51	105	2,045	58,24
S.An.A. C4	64	76,24	77	1,858	23,64
S.An.A. C5	0	0,00	24	0,180	0,55
S.An.A. C6	0	0,00	21	0,079	0,28

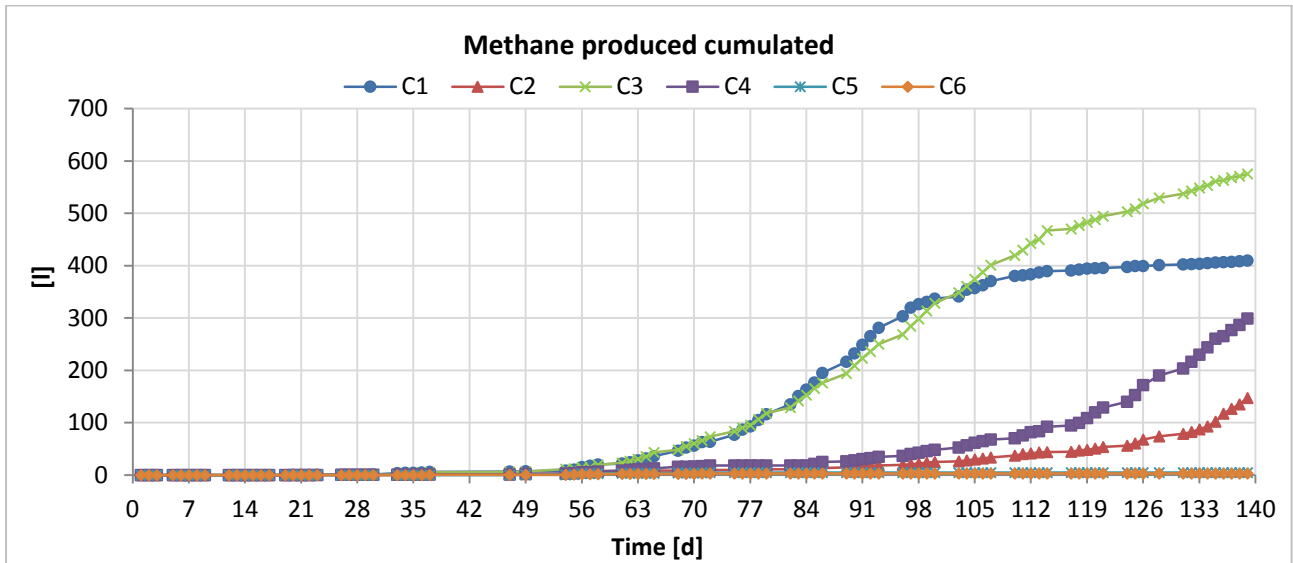


Figure 8.18 – Methane produced cumulated

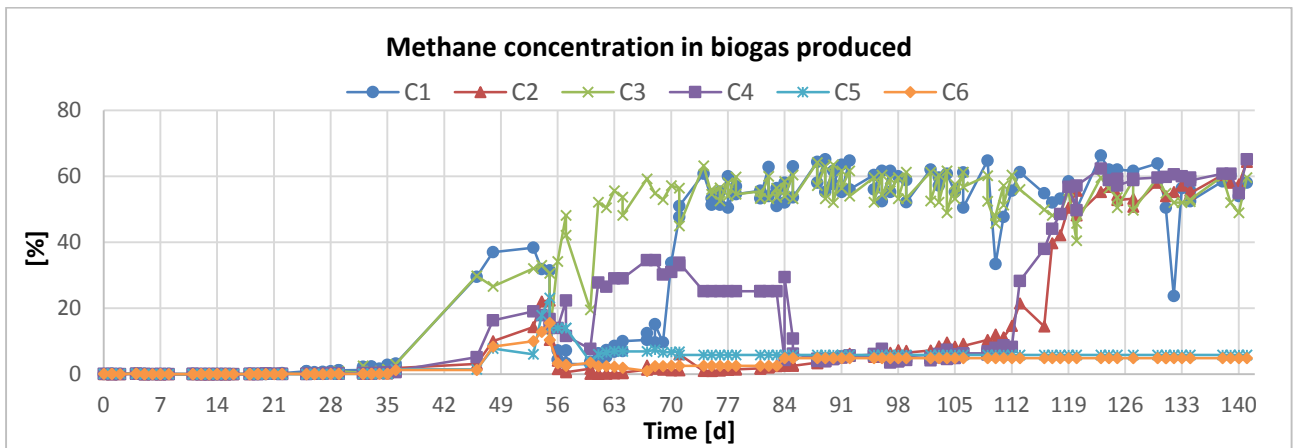


Figure 8.19 – Concentration of methane produced

The results obtained relative to methane production can be compared with those found in literature. Xu et al., (2014) performed a bioreactor test and valued the methane production after a pre-aeration period.

Table 8.10 – Methane production by bioreactors

Days of pre-aeration	Volume of oxygen injected [l <sub>O<sub>2</sub></sub> /kgTS]	Methane production period [d]	Maximum daily methane production [lCH <sub>4</sub> /d/kgTS]	Total Methane production [l/kgTS]	Total Methane production in anaerobic bioreactors [l/kgTS]
72	273,27	228	0,427	31,90	0,99

As one can notice, the total methane production after a pre-aeration period is greater than that obtained by an anaerobic bioreactor, confirming that a pre-aeration improves the methane generation and increases the its production rate.

However, by comparing these values with those obtained by S.An.A. test, it is possible to notice that the methane generated by C1 and C3 results greater than that produced by Xu et al., (2014), despite the total volume of oxygen injected is lower. Therefore, although the pre-aeration facilitates and increase the methane generation, it should not be excessive, otherwise the organic substance may be degraded too much and it may not be available anymore for methane production.

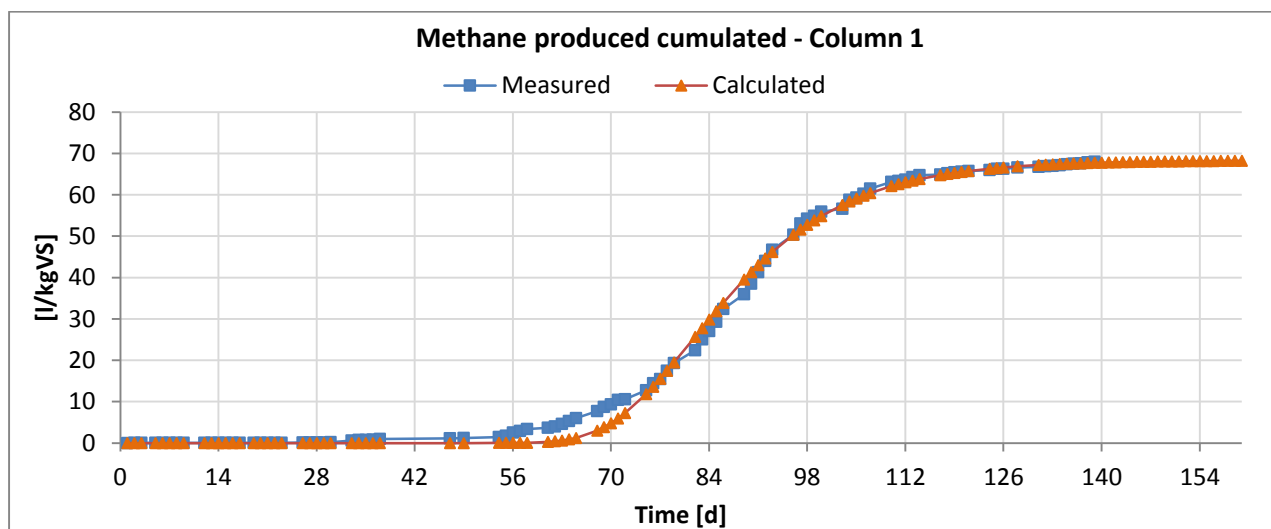
It is so necessary to understand which is the right oxygen flux per kg of Total Solids to inject, in order to improve the methane generation and, on the other hand, to not reduce the available organic substance. For example, C1 was aerated 15 days more than C3 and this fact affected negatively the total methane generation, which resulted less than C3. Besides, C2 and C4 were aerated for a longer period than C1 and C3 and COD started to decrease sensibly during the pre-aeration phase, so probably, the total methane production at the end of the test will result lower than C1 and C3

Another fundamental aspect is the injection modality of air. From S.An.A. test it seems clear that the intermittent aeration, characterizing C1 and C3, with the same daily inlet flux of C2 and C4, promotes methane production, more than a continuous aeration. Sang et al., (2009) verified that intermittent aeration is practical for accelerative stabilization of landfills with less energy consumption because it forms a diverse microbial community within bioreactor, more dynamic than that in the traditional anaerobic systems.

The modified Gompertz Equation was applied on data of biogas production. The model parameters were calculated by minimizing the difference between the values measured and calculated and are listed in **Table 8.11**

**Table 8.11– Calculated parameters of modified Gompertz Model**

	BGP [l/kgVS]	R <sub>m</sub> [l/kgVS/d]	λ [d]
<b>C1</b>	68,3	2	69,7
<b>C2</b>	1.029	2,9	190,7
<b>C3</b>	109,7	1,7	68,5
<b>C4</b>	2.362,2	8,6	175



**Figure 8.20 – Gompertz Model on C1**

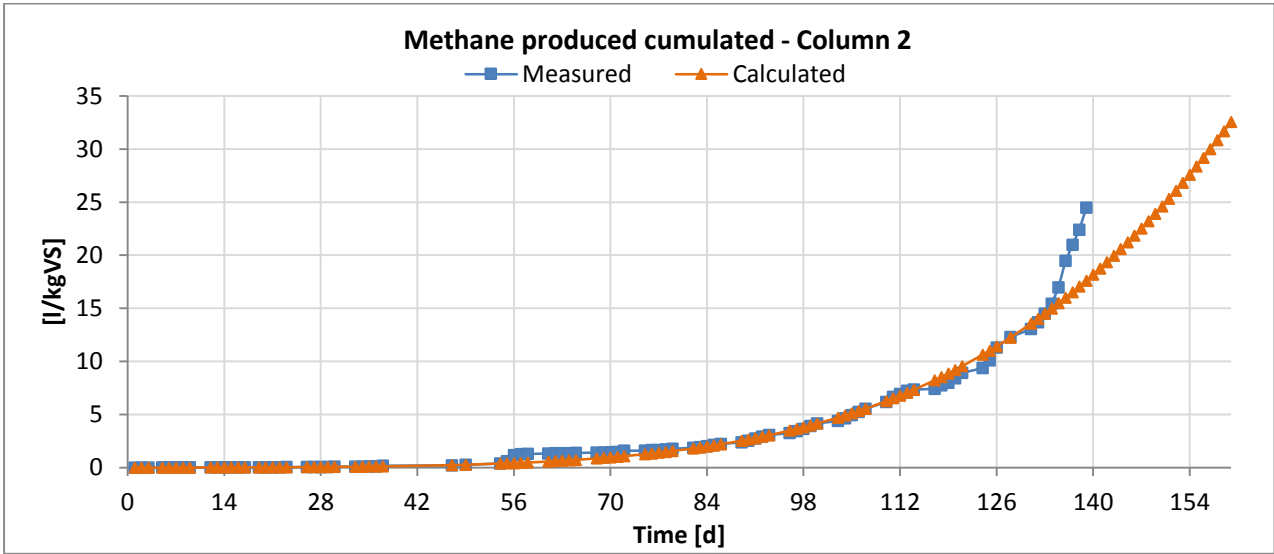


Figure 8.21 – Gompertz Model on C2

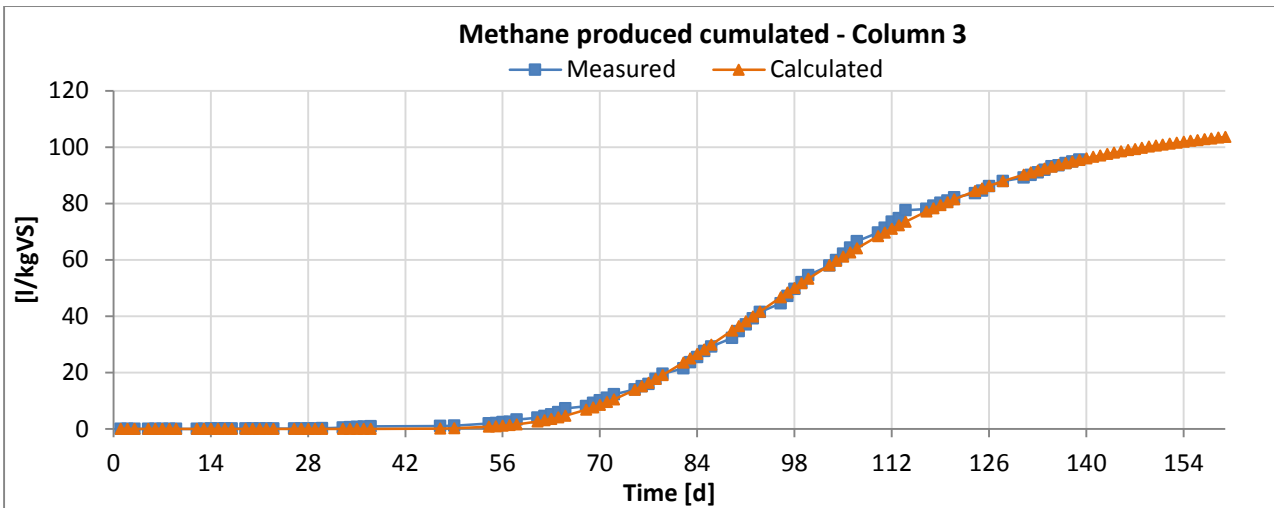


Figure 8.22 – Gompertz Model on C3

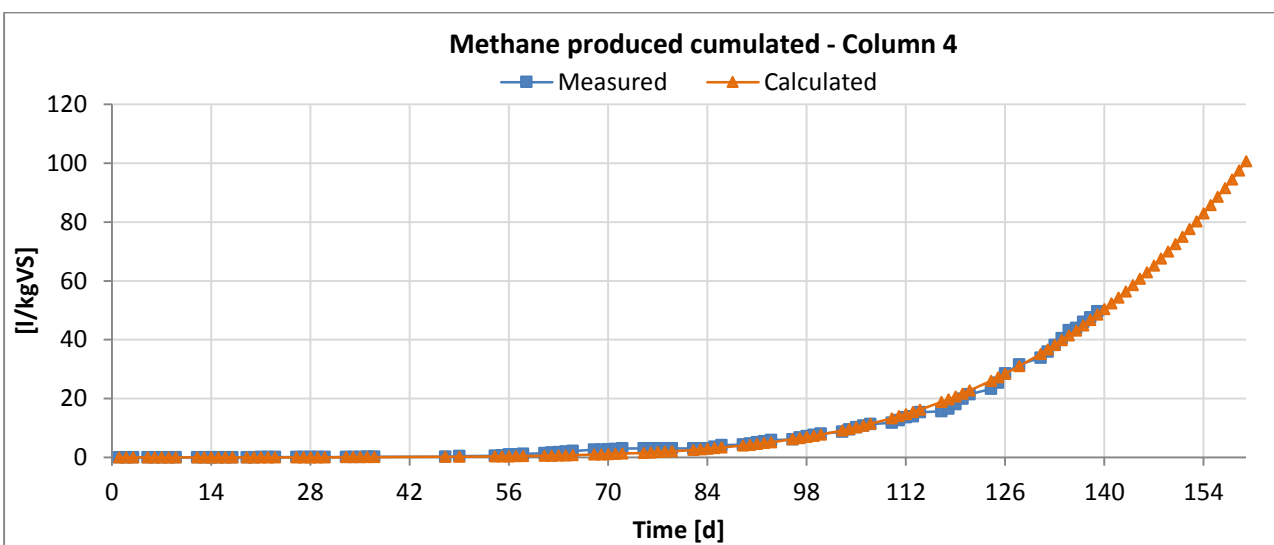


Figure 8.23 – Gompertz Model on C4



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As one can notice, the Modified Gompertz Model well fits the data on methane generation, in particular for C1 and C3. The methane production for C1 results almost finished, because the curve shows a plateau; on the other hand C3 is still producing and C2 and C4 are only in the initial phase of methane generation, so they are characterized by a high production rate.

Regarding the Gompertz Model parameters, C3 shows a higher biogas yield potential than C1, probably, as said above, thanks to the lower amount of oxygen injected. C2 and C3 shows the highest biogas yield potential, but these values are not definitive, so they cannot be taken into account for a significant comparison; it is necessary to wait until these biogas productions will stop and the correspondent curves will reach a plateau.

The maximal daily biogas yield was higher in C1 than C3, meaning that C1 was characterized by greater biogas generation rate than C3, producing daily greater volume of methane; in spite of all that, at the end of the test, the total amount resulted lower than C3, probably due to the higher organic material consumed during the longer pre-aeration phase.

Unfortunately, it is not possible at this point to consider  $R_m$  for C2 and C4, being both at the beginning of the methanogenic phase.

Bioreactors C2 and C4 exhibited some retardation in terms of biogas production at the beginning, because the acidogenesis period lasted for a long time, so the bacteria growth lag time  $\lambda$  resulted very high. On the contrary, C1 and C3 were both characterized by a lower  $\lambda$ , meaning that methane production started earlier.

Control bioreactors C5 and C6 produced insignificant amount of methane, so it was considered useless to apply Gompertz Model.

It will be possible to obtain better results at the end of anaerobic phase, when methane production will stop. For each column, the methane generation rate and the its total production will be calculated and compared with the others. At that point the Gompertz Model will be apply for obtaining the final parameters.

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## Nitrogen mass balance

Nitrogen mass balance was performed on TKN in term of mgN/kgTS.

$$TKN_{ACC} = TKN_S - TKN_L \quad \text{Equation 8.5}$$

Where  $TKN_S$  is the initial nitrogen mass into the waste,  $TKN_L$  is the nitrogen mass removed via leachate extraction and  $TKN_{ACC}$  is the nitrogen mass remained into the waste. Unfortunately it was not possible to take into account the nitrogen mass escaped via biogas, in the form of ammonia gas or nitrogen gas ( $N_2$ ).

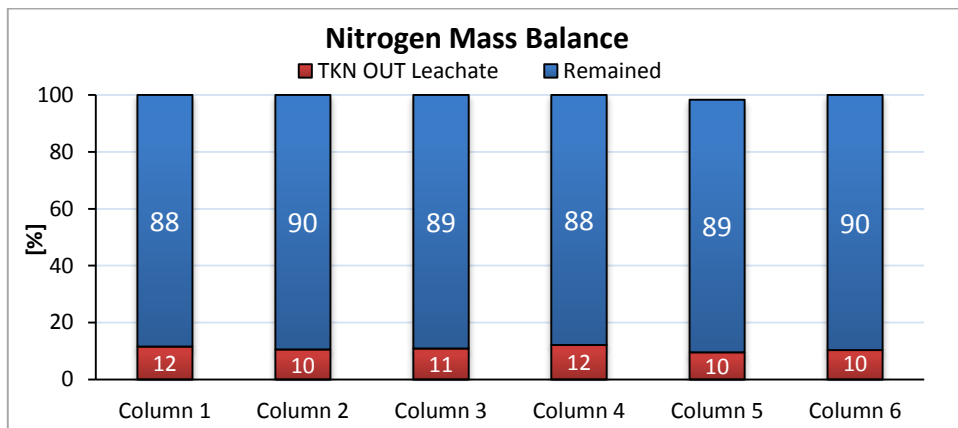


Figure 8.24 – Nitrogen mass balance

As it is possible to notice large amount of nitrogen remained into the solid mass of waste, while only about 10 % was removed.

It is necessary to consider also losses of mass from different sources, such as ammonia and nitrogen ( $N_2$ ) under the gas form that could be escaped and were not recorded. Therefore, for this reason, the final nitrogen remained should be a little bit lower than that calculated.

## Carbon mass balance

Carbon mass balance was performed on TOC in term of gC/kgTS, by considering the initial carbon content of waste ( $TOC_S$ ), the carbon removed by leachate extraction ( $TOC_L$ ) and the carbon removed by biogas as  $CH_4$  and  $CO_2$  ( $TOC_G$ ).

$$TOC_{ACC} = TOC_S - TOC_L - TOC_G \quad \text{Equation 8.6}$$

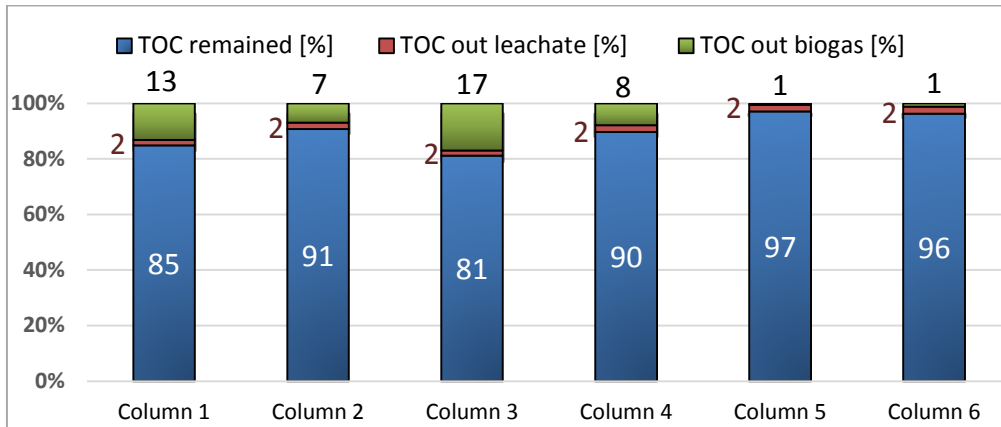


Figure 8.25 – Carbon mass balance

As one can notice, the carbon removed in C1 and C3 resulted greater than in C2 and C4. In any case biogas represents the medium by which the majority of degradation products escape, as affirmed by Scheelhase et al., (1997). However the most of carbon escaped in biogas was removed as carbon dioxide, as shown by Figure 8.26:

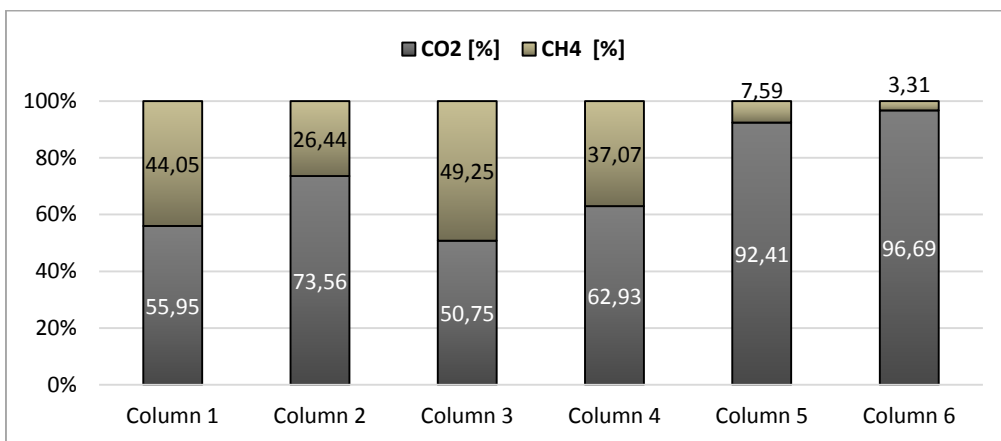


Figure 8.26 – Percentage of carbon removal

The contribution given by leachate is very low due to the low amount of liquid weekly pulled out.



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## 8.4 Conclusions

The S.An.A. landfill management system proved to be rather effective in relation to the degradation of organic material, but with different efficiency levels. The volume of oxygen injected and, in particular, the aeration modality, affected a lot the trend of parameters. The intermittent aeration demonstrated its positive effects on pH pattern, on Volatile Fatty Acids reduction and on the following methane production.

From the test it turned out that a short but strong aeration produces better effects than a long but faint one. In fact, if aeration lasts too much, it removes organic substance for the following methane production.

The methane produced resulted satisfying for the columns aerated intermittently. It is possible to establish a relation between the inlet air flux and the daily methane generation rate, and between the total volume of oxygen injected and the total methane produced. If the total volume of oxygen introduced results too much, the total methane produced is less; on the other hand, if the inlet air flux increases, the methane generation rate increases, as occurred in this test for bioreactor C1 (**Table 8.10**).

The methane started to be produced at pH 6,5 for C1 (aerobic intermittent), C2 and C4 (aerobic continuous), at pH 6,25 for C3 (aerobic intermittent) and the generation continued also at pH 8,0. So it is possible to affirm that is not suitable to convert bioreactors to anaerobic conditions having pH lower than 6,25.

It was not possible to close completely the nitrogen mass balance. First because the S.An.A. test is not yet concluded, second because during the whole test both nitrate and nitrite remained lacking, or however, under the determination limit of the instrument. This fact, together with the ammonia accumulation into the leachate, lead to conclude that nitrification process never occurred, probably due to not enough oxygen injected.

For this reason, further experiments should be performed with intermittent aeration and the inlet daily oxygen flux should be increased for better stimulate the degradation of nitrogen compounds.



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## REFERENCES

- Agdag, O.N., Sponza, D.T., (2005). Effect of alkalinity on the performance of a simulated landfill bioreactor digesting organic solid wastes. *Chemosphere* 59, 871-879.
- Aguilar-Virgen, Q., Taboada-Gonzalez, P., Ojeda-Benitez, S., (2014). Power generation with biogas from municipal solid waste: Prediction of gas generation with in situ parameters. *Renewable and Sustainable Energy Reviews* 30, 412-419.
- Barlaz, M., (2005). Personal Communication.
- Berge, N.D., Reinhart, D.R., (2005). The fate of Nitrogen in Bioreactor Landfills. *Environmental Science and Technology* 35, 365-399.
- Berge, N.D., Reinhart, D.R., Dietz, K., Townsend, T., (2006). In situ ammonia removal in bioreactor landfill leachate. *Waste Management* 26, 334-343.
- Bilgili, M.S., Demir, A., Varank, G., (2012). Effect of leachate recirculation and aeration on volatile fatty acid concentrations in aerobic and anaerobic landfill leachate. *Waste Management Resource* 30 (2), 161-170.
- Bogner, J., Ahmed, M.A., Diaz, C., Faaij, A., Gao, Q., Hashimoto, S., Mareckova, K., Pipatti, R., Zhang, T., (2007). Mitigation Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. *Waste Management, In Climate Change 2007*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Calli, B., Mertoglu, B., Inanc, B., Yenigun, O., (2005). Methanogenic diversity in anaerobic bioreactors under extremely high ammonia levels. *Enzyme and Microbial Technology* 37, 448-455.
- Chen, Y.C., Wu, S.W., Wu, W.X., Sun, H., Ding, Y., (2009). Denitrification capacity of bioreactors filled with refuse at different landfill ages. *Journal of Hazardous Materials* 172, 159-165.
- Christensen, T.H., Kjeldsen, P., (1989). *Biochemical Processes in Landfills*. In: Christensen, T.H., Cossu, R., Stegmann, R., (Eds), *Sanitary Landfilling: Process, Technology and Environmental Impact*. Academic Press, London.
- Christensen, T.H., Kjeldsen, P., Lindhardt, B., (1996). *Gas-Generating Processes in Landfills In Landfillin of Waste: Biogas*. E & FN Spon, London. ISBN 0 419 19400 2.

- 
- Chugh, S., Clarke, W., Pullammanappallil, P., Rudolph, V., (1998). Effect of recirculated leachate volume on MSW degradation. *Waste Management*, 564-573.
- Cossu, R., (1995). The multi-barrier landfill and related engineering problems. In "Proceedings of Sardinia '95". Fifth International Waste Management and Landfill Symposium. S. Margherita di Pula, Cagliari, Italy, 2-6 October. CISA Publisher, Vol. I, 3-28.
- Cossu, R., Raga, R., Rossetti, D., (2003). The PAF model: an integrated approach for landfill sustainability. *Waste Management* 23, 37-44.
- Cossu, R., Raga, R., Vettorazzi, G., (2005). Carbon and nitrogen mass balance in some landfill models for sustainability assessment. In "Proceedings Sardinia 2005". Tenth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 3-7 October.
- Cossu, R., (2005). The sustainable landfilling concept. In "Proceedings of Sardinia 2005". Tenth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 3-7 October.
- Ehrig, H.J., Scheelhaase, T., (1993). Pollution potential and long term behaviour of sanitary landfills. In "Proceedings of Sardinia 93". Fourth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 11-15 October.
- Erses, A.S., Fazal, M.F., Onay, T.T., Craig, W.H., (2005). Determination of solid waste sorption capacity for selected heavy metals in landfills. *Journal of Hazardous Materials B121*, 223-232.
- Erses, A.S., Onay, T.T., Yenigun, O., (2008). Comparison of aerobic and anaerobic degradation of municipal solid waste in bioreactor landfill. *Bioresource Technology* 99, 5418-5426.
- Farquhar, G.J., Rovers, F.A., (1973). Gas production during refuse decomposition. *Water, Air and Soil Pollution* 2, 483-495.
- Harborth, P., Fub, R., Munnich, K., Flessa, H., Fricke, K., (2013). Spatial variability of nitrous oxide and methane emissions from an MBT landfill in operation: Strong N<sub>2</sub>O hotspots at the working face. *Waste Management* 33, 2099-2107.
- Hjelmar, O., Hansen, J.B., (2005). Sustainable landfill: the role of the final storage quality. In "Proceedings Sardinia 05". Tenth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 3-7 October 2005.



- 
- Hoornweg, D., Bhada-Tata, P., (2012). What a waste: a global review of Solid Waste Management. Urban Development Series Knowledge Papers. Urban Development & Local Government Unit, The World Bank.
- ISPRA, (2013). Rapporto Rifiuti Urbani. Edizione 2013.
- Juteau, P., Tremblay, D., Ould-Moulaye, C.B., Bisailon, J.G., Beaudet, R., (2004). Swine waste treatment by self-heating aerobic thermophilic bioreactors. *Water Research* 38, 539-546.
- Kjeldsen, P., Barlaz, M.A., Rooker, R., Baun, A., Ledin, A., Christensen, T.H., (2002). Present and long-term composition of MSW landfill leachate: a review. *Environmental Science and Technology* 32 (4), 297-336.
- Kumar, A., Sharma, M.P., (2014). Estimation of GHG emission and energy recovery potential from MSW landfill sites. *Sustainable Energy Technologies and Assessments* 5, 50-61.
- Laner, D., Crest, M., Scharff, H., Morris, J.W.F., Barlaz, M.A., (2012). A review of approaches for a long-term management of a municipal solid waste landfill. *Waste Management* 32, 498-512
- Lay, J.J., Li, Y.Y., Noike, T., (1998). Developments of bacterial population and methanogenic activity in a laboratory-scale landfill bioreactor. *Water Resource* 32, 3673-3679.
- Mc Carty, P.L., McKinney, R.E., (1961). Volatile acid toxicity in anaerobic digestion. *Journal, Water Pollution Control Federation* 33, 223-232.
- Mc Carty, P.L., McKinney, R.E., (1961). Salt toxicity in anaerobic digestion. *Journal, Water Pollution Control Federation* 33, 399-415.
- Norbu, T., Visvanathan, C., Basnayake, B., (2005). Pretreatment of municipal solid waste prior to landfilling. *Waste Management* 25, 997-1003.
- Oh, S.E., Yoo, Y.B., Young, J.C., Kim, I.S., (2001). Effect of organics on sulfur-utilizing autotrophic denitrification under mixotrophic conditions. *Journal of Biotechnology* 92, 1-8.
- O'Keefe, D.M., Chynoweth, D.P., (2000). Influence of phase separation, leachate recycle and aeration on treatment of municipal solid waste in simulated landfill cells. *Bioresource Technology* 72, 55-66.
- Ozturk, I., (1999). Anaerobic biotechnology and Its Application in Waste Treatment (in Turkish). *Water Foundation Journal*, Istanbul.
- Price, G.A., Barlaz, M.A., Hater, G.R., (2003). Nitrogen management in bioreactor landfills. *Waste Management* 23, 675-688.

- 
- Raga, R., Cossu, R., (2013). Bioreactor tests preliminary to landfill in situ aeration: A case study. *Waste Management* 33, 871-880.
- Ravishankara, A.R., Daniel, J.S., Portmann, R.W., (2009). Nitrous oxide (N<sub>2</sub>O): the dominant ozone-depleting substance emitted in the 21<sup>st</sup> century. *Science* 326, 123-125.
- Rinne, J., Pihlatie, M., Lohila, A., Thum, T., Aurela, M., Tuovinen, J.-P., Laurila, T., Vesala, T., (2005). Nitrous oxide emissions from a municipal landfill. *Environmental Science and Technology* 39, 7790-7793.
- Ritzkowski, M., Stegmann, R., (2013). Landfill aeration within the scope of post-closure care and its completion. *Waste Management* 33, 2074-2082.
- Sanchez-Monedero, M.A., Roig, A., Paredes, C., Bernal, M.P., (2001). Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC, and maturity of composting mixtures. *Bioresource Technology* 76, 301-308.
- Sandip, M., Kanchan, K., Ashok, B., (2012). Enhancement of methane production and bio-stabilisation of municipal solid waste in anaerobic bioreactor landfill. *Bioresource Technology* 110, 10-17.
- Sang, N.N., Soda, S., Inoue, D., Sei, K., Ike, Michihiko, (2009). Effects of intermittent and continuous aeration on accelerative stabilization and microbial population dynamics in landfill bioreactors. *Journal of Bioscience and Bioengineering* 108, 336-343.
- Scharff, H., (2006). The role of sustainable Landfill In Future Waste Management Systems.
- Scheelhaase, T., Bidlingmaier, W., (1997). Effect of mechanical biological pretreatment of residual waste and landfilling. In "Proceedings Sardinia 97", Sixth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, Vol I, CISA, pp. 397-408.
- Sekman, E., Top, S., Varank, G., Bilgili, M.S., (2011). Pilot-scale investigation of aeration rate effect on leachate characteristics in landfills. *Fresenius Environmental Bulletin* 20.
- Siddiqui, A.A., Richards, D.J., Powrie, W., (2013). Biodegradation and flushing of MBT wastes. *Waste Management* 33, 2257-2266.
- Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M.M.B., Miller, H.L., Chen, Z., (2007). *Climate Change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report on the Intergovernmental Panel on Climate Change.*

- 
- Sponza, D.T., Agdag, O.N., (2004). Impact of leachate recirculation and recirculation volume on stabilization of municipal solid wastes in simulated anaerobic bioreactors. *Process Biochemistry* 39, 2157-2165.
- Sponza, D.T., Agdag, O.N., (2005). Effects of shredding of wastes on the treatment of municipal solid wastes (MSWs) in simulated anaerobic recycled reactors. *Enzyme and microbial technology* 36, 25-33.
- Stegmann, R., Heyer, K.-U., Hupe, K., Ritzkowski, M., (2003). Discussion of criteria for the completion of landfill aftercare. In "Proceedings of Sardinia 2003", Ninth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 6-10 October 2003, CISA.
- Sun, F., Wu, S., Liu, J., Li, B., Chen, Y., Wu, W., (2012). Denitification capacity of a landfilled refuse in response to the variations of COD/NO<sub>3</sub>-N in the injected leachate. *Bioresource Technology* 103, 109-115.
- Sun, Y., Wang, Y.N., Sun, X., Wu, H., Zhang, H., (2013). Production characteristics of N<sub>2</sub>O during stabilization of municipal solid waste in an intermittent aerated semi-aerobic bioreactor landfill. *Waste Management* 33, 2729-2736.
- Valencia, R., Van der Zon, W., Woelders, H., Lubberding, H.J., Gijzen, H.J., (2011). Anammox: An option for ammonium removal in bioreactor landfill. *Waste Management* 31, 2287-2293.
- Vigneron, V., Ponthieu, M., Barina, G., Audic, J.M., Duquennoi, C., Mazéas, L., Bernet, N., Bouchez, T., (2007). Nitrate and nitrite injection during municipal solid waste anaerobic biodegradation. *Waste Management* 27, 778-791.
- Wang, Q., Kuninobu, M., Kakimoto, K., Ogawa, H.I., (1999). Upgrading of anaerobic digestion of waste activated sludge by ultrasonic pretreatment. *Bioresource Technology* 68, 309-313.
- Xu, Q., Jin, Z., Ma, Z., Tao, H., Ko, J.H., (2014). Methane production in simulated hybrid bioreactor landfill. *Bioresource Technology* 168, 92-96.
- Yuen, S.T.S., Styles, J.R., McMahon, T.A., (1995). An active landfill management by leachate recirculation: a review and an outline of a full-scale project. In "Proceedings of Sardinia 95", Fifth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 2-6 October 1995. CISA, pp. 403-418.
- Zehnder, A.B.J., Ingvorsen, K., Marti, T., (1982). Microbiology of methanogen bacteria in anaerobic digestion. *Proceedings of the 2<sup>nd</sup> International Symposium of Anaerobic Digestion*, Travemunde, 6-11 September 1981. Elsevier Biomedical Press, BV, Amsterdam, The Netherlands, pp. 45-68.

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Zhang, H.H., He, P.J., Shao, L.M., (2008). N<sub>2</sub>O emissions from municipal solid waste landfills with selected infertile cover soils and leachate subsurface irrigation. *Environmental Pollution* 156, 959-965.

Zhang, H., He, P., Shao, L., (2009). N<sub>2</sub>O emissions at municipal solid waste landfill sites: Effects of CH<sub>4</sub> emissions and cover soil. *Atmospheric Environment* 43, 2623-2631.

Zhang, Y., Yue, D., Nie, Y., (2012). Greenhouse gas emissions from two-stage landfilling of municipal solid waste. *Atmospheric Environment* 55, 139-143.

# ANNEXES

## Metals

Table A.1-6 – Metals into the leachate

		LEACHATE-COLUMN 1							
Days		Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Fe [µg/l]	Mg [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
1	04/07	10	289	779	63.869	10.922	583	64	11.522
32	04/08	< 10	42,6	196,0	19.300,0	9.633,0	703,0	< 30	1.683,0
67	08/09	10	25,5	225,0	17.333,0	4.767,0	460,0	24,4	700,0
95	06/10	< 10	46,3	215,0	10.350,0	1.160,0	232,0	45.3	377,0

		LEACHATE-COLUMN 2							
Days		Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Fe [µg/l]	Mg [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
1	04/07	10	289	779	63.869	10.922	583	64	11.522
32	04/08	< 10	55,0	204,0	20.667,0	11.733,0	750,0	< 10	2.653,0
67	08/09	10	24,2	41,0	43.933,0	11.400,0	660,0	10,0	723,0
95	06/10	< 10	< 30	103,0	49.667,0	7.933,0	653,0	< 10	195,0

		LEACHATE-COLUMN 3							
Days		Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Fe [µg/l]	Mg [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
1	04/07	10	289	779	63.869	10.922	583	64	11.522
32	04/08	< 10	41,3	156,0	41.533,0	9.067,0	760,0	< 10	820,0
67	08/09	10	29,4	261,0	33.100,0	4.733,0	380,0	10,0	320,0
95	06/10	< 10	48,0	213,0	9.517,0	767,0	225,0	47,7	480,0

		LEACHATE-COLUMN 4							
Days		Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Fe [µg/l]	Mg [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
1	04/07	10	289	779	63.869	10.922	583	64	11.522
32	04/08	< 10	76,7	197,0	28.133,0	12.333,0	1.197,0	< 10	2.503,0
67	08/09	10	38,7	39,0	61.133,0	11.600,0	1.020,0	10,0	417,0
95	06/10	< 10	43,3	104,0	43.333,0	8.333,0	773,0	< 10	323,0

		LEACHATE-COLUMN 5							
Days		Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Fe [µg/l]	Mg [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
1	04/07	10	289	779	63.869	10.922	583	64	11.522
32	04/08	< 10	97,7	353,0	12.533,0	11.433,0	717,0	< 10	2.346,0
67	08/09	10	51,7	73,3	25.600,0	10.233,0	767,0	10,0	1.397,0
95	06/10	< 10	46,3	209,0	2.780,0	7.166,0	657,0	78,8	1.067,0

Days		LECHATE-COLUMN 6							
		Cd [ $\mu\text{g/l}$ ]	Cr [ $\mu\text{g/l}$ ]	Cu [ $\mu\text{g/l}$ ]	Fe [ $\mu\text{g/l}$ ]	Mg [ $\mu\text{g/l}$ ]	Ni [ $\mu\text{g/l}$ ]	Pb [ $\mu\text{g/l}$ ]	Zn [ $\mu\text{g/l}$ ]
1	04/07	10	289	779	63.869	10.922	583	64	11.522
32	04/08	< 10	44,3	310,0	15.200,0	11.767,0	777,0	< 10	2.347,0
67	08/09	10	27,1	81,3	25.800,0	11.100,0	787,0	10,0	1.697,0
95	06/10	< 10	< 30	158,0	14.400,0	9.367,0	717,0	37,3	1.507,0

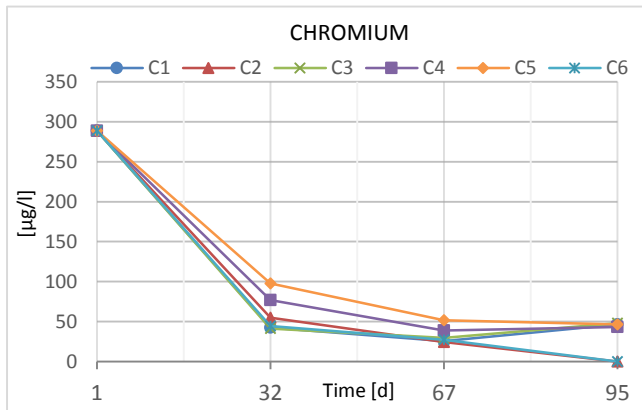


Figure A.1 –Chromium into the leachate

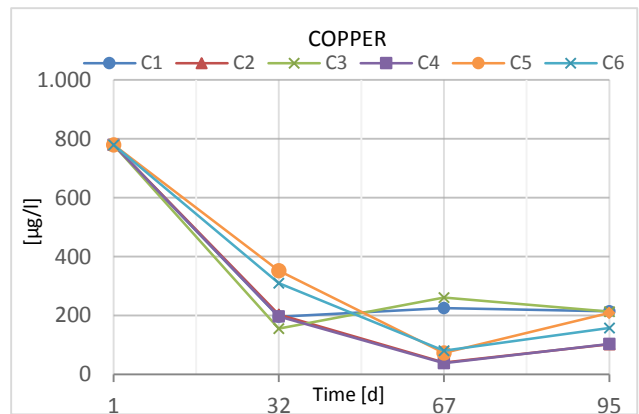


Figure A.2 –Copper into the leachate

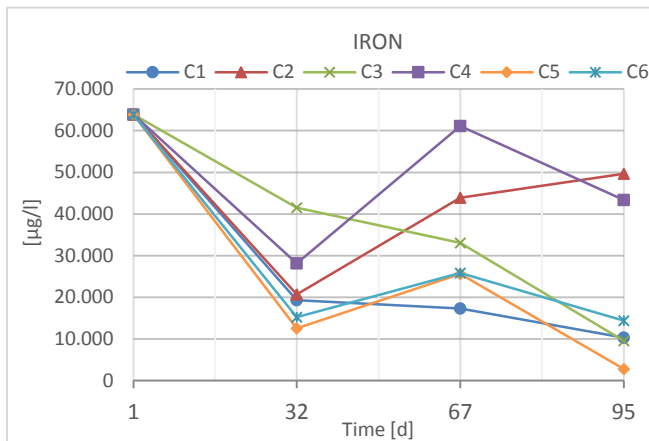


Figure A.3 –Iron into the leachate

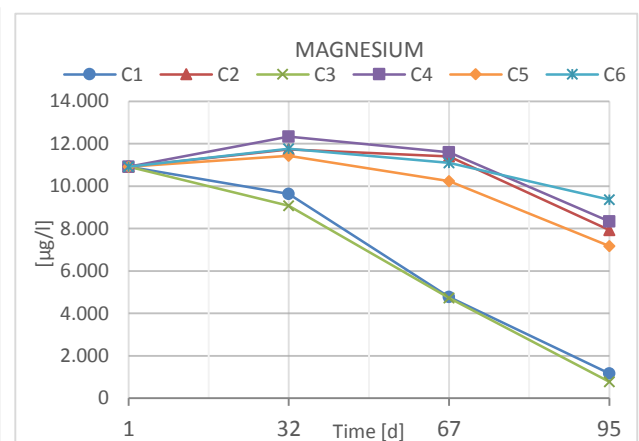


Figure A.4 –Magnesium into the leachate

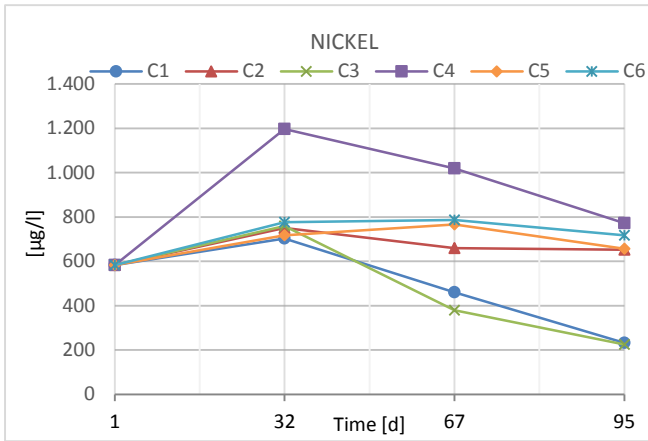


Figure A.5 –Nickel into the leachate

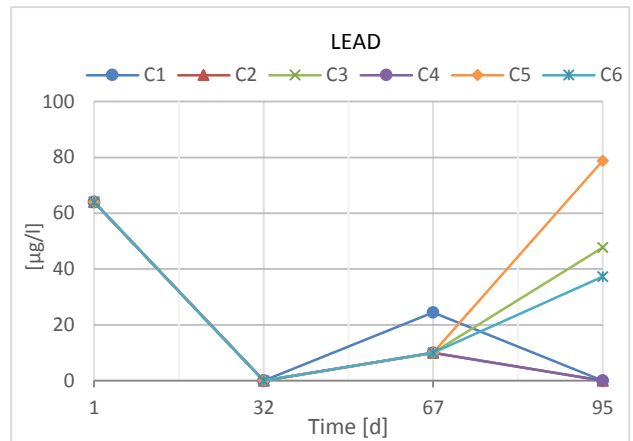


Figure A.6 –Lead into the leachate

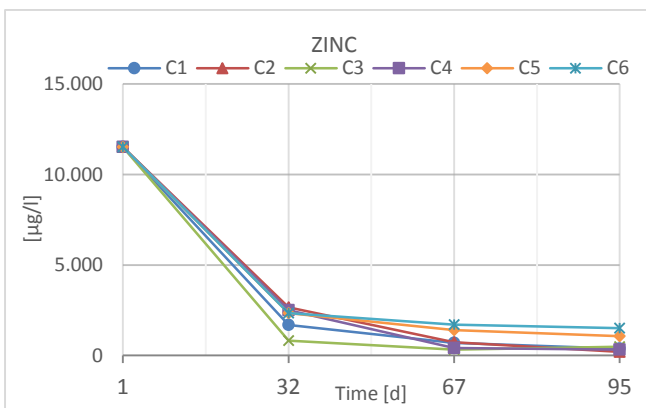


Figure A.7 –Zinc into the leachate

Table A.7 – Metals from the leaching test

	LEACHING TEST - L/S=10							
	Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Fe [µg/l]	Mg [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
Leached S1	< 10	176	172	7.959	2.664	181	34	4.795
Leached S2	< 10	238	190	10.689	2.677	180	41	4.562
Average	10	207	181	9.324	2.670,5	180,5	37,5	4.678,5

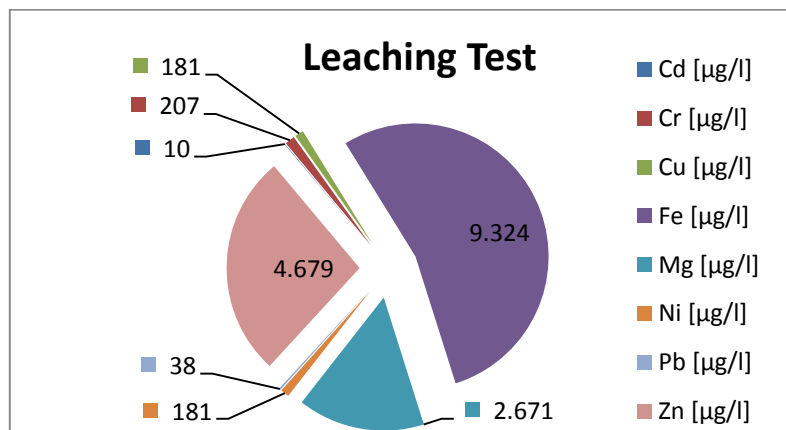


Figure A.8 – Metal content from leaching Test

Table A.8 – Metals within the solid mass of waste

	METAL CONTENT OF SOLID WASTE							
	Cd [mg/Kg]	Cr [mg/Kg]	Cu [mg/Kg]	Fe [mg/Kg]	Mg [mg/Kg]	Ni [mg/Kg]	Pb [mg/Kg]	Zn [mg/Kg]
<b>Solid 1</b>	<0,5	21,50	28,70	2.670,00	75,90	11,70	7,70	83,40
<b>Solid 2</b>	0,57	23,60	28,00	2.326,00	67,30	12,10	12,00	86,20
<b>Average</b>	0,57	22,55	28,35	2.498,00	71,60	11,90	9,85	84,80

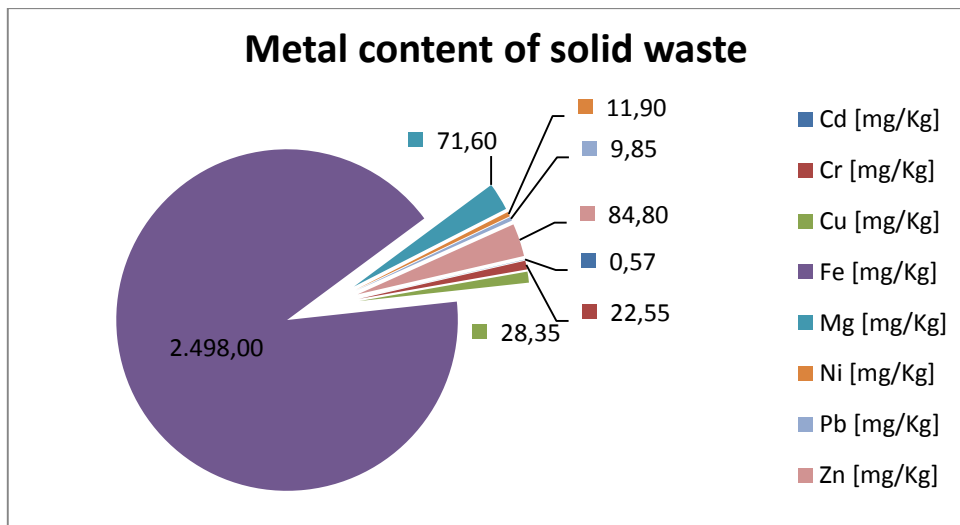


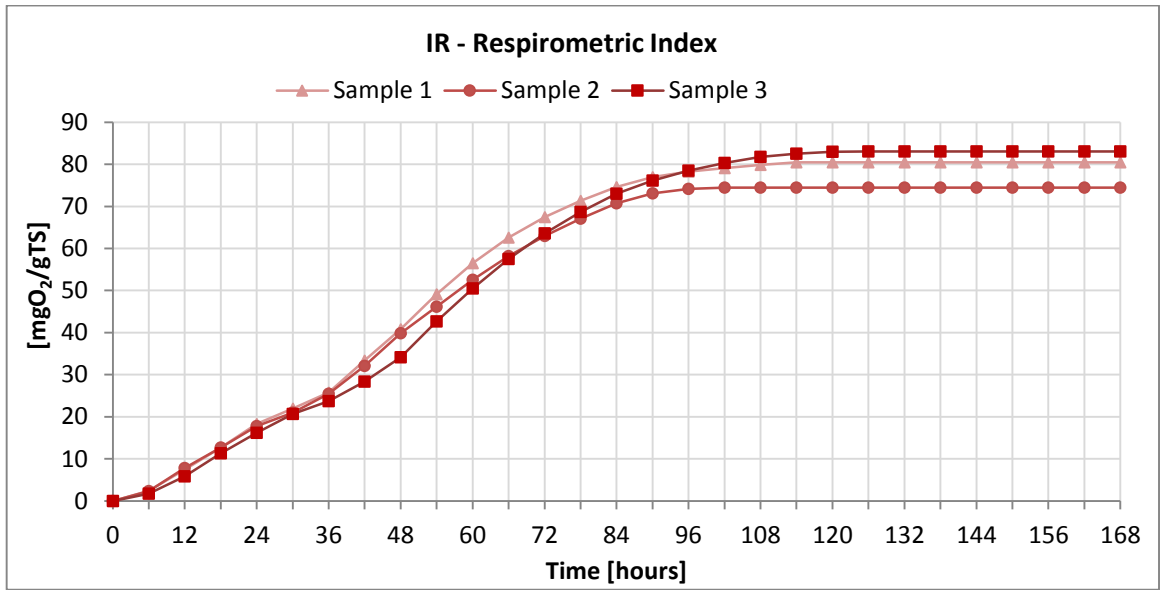
Figure A.9 – Metal content of solid waste material



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## Respirometric Index IR

	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>
<b>Time [hours]</b>	<b>IR-Sample 1 [mgO<sub>2</sub>/gTS]</b>	<b>IR-Sample 2 [mgO<sub>2</sub>/gTS]</b>	<b>IR-Sample 3 [mgO<sub>2</sub>/gTS]</b>
0	0,00	0,00	0,00
6	2,44	2,35	1,74
12	7,47	7,80	5,85
18	12,70	12,67	11,35
24	18,33	17,80	16,21
30	22,00	21,02	20,67
36	25,79	25,47	23,68
42	33,35	32,08	28,35
48	40,86	39,86	34,17
54	49,11	46,18	42,64
60	56,47	52,52	50,45
66	62,62	58,17	57,48
72	67,47	62,97	63,59
78	71,30	67,08	68,68
84	74,59	70,71	72,97
90	76,94	73,06	76,09
96	78,23	74,14	78,48
102	79,09	74,44	80,33
108	79,88	74,44	81,73
114	80,42	74,44	82,50
120	80,42	74,44	82,98
126	80,42	74,44	83,08
132	80,42	74,44	83,08
138	80,42	74,44	83,08
144	80,42	74,44	83,08
150	80,42	74,44	83,08
156	80,42	74,44	83,08
162	80,42	74,44	83,08
168	80,42	74,44	83,08







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# RINGRAZIAMENTI

Padova, 23/11/2014

*“Eccomi qui, giunta alla fine di un lungo percorso, che sta ora per volgere al termine.*

*Quando sei anni e mezzo fa ho scelto l'ingegneria ambientale, ero spinta da ideali ecologici e ambientalisti, convinta che sarei potuta diventare un fiero combattente per i diritti di questa nostra madre terra.*

*In realtà poi, mi sono via via accorta che non si tratta di combattere da soli un ideale contro tutti, ma essere ingegneri è prima di tutto conoscenza e collaborazione con la società, con i professionisti dei tanti settori che si intrecciano in un modo o nell'altro con il tuo lavoro, quali architetti, economisti, giuristi, sindaci, politici, associazioni.*

*Ho poi appreso che non esistono solamente il bianco ed il nero, ma tante sfumature di grigio che devono essere prese in considerazione nelle nostre decisioni. Non è vero che un inceneritore non debba mai essere costruito né che una discarica inquinii sempre e comunque. Ci sono le scelte che permettono di prevenire e/o ridurre i rischi, tutelando i diritti e la salute delle persone e dell'ambiente. Sicuramente in un mondo perfetto ed utopico i rifiuti e l'inquinamento potrebbero scomparire magicamente, senza alcuno sforzo e collaborazione da parte di nessuno, ma nella realtà dobbiamo farne i conti e riuscire ad arrivare ad un compromesso, che consenta di tener conto delle esigenze di tutti.*

*Detto questo vorrei passare ai ringraziamenti, per dar merito a tutti coloro che in questi anni hanno trascorso una parte della loro vita assieme alla mia, condividendo esperienze, emozioni e sacrifici.*

*Il primo posto è sicuramente riservato a mia madre e mio padre, che amo profondamente, i quali mi hanno costantemente sostenuto nelle scelte portate avanti ed hanno cercato di farmi sentire meno sola in tanti momenti difficili di questo percorso universitario. Pur avendone sostenuti davvero tanti, la mia stabilità emotiva davanti ad un esame è sempre risultata pessima e non ho mai imparato a rafforzarla (nonostante i miei buoni propositi!).*

*La seconda persona che desidero ringraziare è Sara F. perché non posso mai nascondere niente. Lei sa tutto di me e riesce a capirmi sempre, se sono felice o triste, anche se cerco invano di nascondere. Nonostante si trovi ora lontana, tanto lontana, rimane sempre nel mio cuore, occupando un posto che riservo a pochi. E preferisco non dire altro, per non rischiare di finire in lacrime.*

*A questo punto vien naturale pensare alle mie amiche Valentina M., Melissa M., e Valentina G., con le quali ho trascorso tantissime serate di tutti i generi, dal ballo sfrenato presso il Molo5, alle lunghe chiacchierate presso il parchetto di Busa. Grazie per la vostra presenza, la vostra pazienza, per avermi ascoltata, per aver riso insieme, per aver bevuto insieme. ... Grazie per aver passato pezzi di vita insieme.*

*Ed ora rivolgo i miei pensieri alle amicizie più “universitarie” e a tutti coloro che ho avuto modo di conoscere tra una lezione e una giornata trascorsa in Pineca. Un grazie a Veronica Z. e Francesca G., per i momenti passati insieme durante la triennale, conclusasi però felicemente il 27 Settembre 2011. Grazie a Silvia C., compagna insostituibile durante il lavoro di Waste Management, per avermi supportata, aiutata e sopportata! Grazie ai compagni di Pineca e a tutti coloro con cui ho condiviso intere giornate rinchiusa lì sotto, per portare a termine gli innumerevoli lavori di gruppo affrontati in questi due anni di magistrale.*

*Un grazie particolare va ad AJ e a Giorgia V., per la loro trascendente simpatia e per le serate passate assieme. Grazie ad Anna V. per l'amicizia nata silenziosamente tra i banchi universitari, per il sostegno reciproco durante i momenti più difficili, per le ore di Pineca trascorse in compagnia, per i fatti e misfatti compiuti al Sardinia, per la enorme lentezza nel fare molte (troppe!!) cose.*

*Finalmente, a Febbraio 2014, giunge il momento di pensare alla tesi. Durante una lezione di Project Work vengono presentati gli argomenti di tesi disponibili e rimango particolarmente colpita dalla discarica S.An.A.*

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*Mando una mail al Professor Raga ed il gioco è fatto. Ad Aprile inizio a frequentare il laboratorio di Voltabarozzo e qui inizia un periodo che non potrò mai più dimenticare.*

*La prima persona che sento di dover ringraziare è Annalisa S., colonna portante di VB. Con la sua presenza costante, disponibilità, pazienza ed affabilità è stata un po' la mamma di noi tutti. Quando non c'è, il vuoto è davvero grande!*

*Un sentito grazie va a Luca M., che nonostante i suoi molteplici impegni, si è sempre dimostrato presente e disponibile per seguirmi durante questo lavoro di tesi. Grazie anche a Luca A., per la sua presenza, professionalità, precisione e disponibilità nell'elargire le sue profonde conoscenze a noi tesisti, e nel rispondere ai nostri tanti e assidui perché.*

*Grazie al mio compare di colonne, Matteo C., per aver ricircolato ogni giorno il percolato.*

*Grazie ai fantastici amici scoperti tra uno spritz alle chiuse e una titolazione in laboratorio: Francesca A., Nicoletta B., Enrico S., Francesco G. Abbiamo condiviso davvero tante cose insieme, passato tanti bei momenti e altrettanti più faticosi. Ma almeno la mattina, quando alzavo la testa dal cuscino, sapevo che durante quella giornata che stava per iniziare, avrei avuto almeno un'occasione per ridere insieme a voi.*

*Un sincero grazie va infine al Professor Raga ed al Professor Cossu per i loro suggerimenti, consigli e per ciò che hanno saputo darmi in questi anni.*

*Concludo qui queste righe, augurandomi di non aver dimenticato nessuno, e scusandomi qualora lo abbia fatto.”*

*Giulia*

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